

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

**NOVEL APPROACHES FOR PROTECTION OF LIGHT METALS UNDER
VARIOUS WEAR CONDITIONS VIA MICRO ARC OXIDATION PROCESS**



Ph.D. THESIS

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Department of Materials Science and Engineering

Materials Science and Engineering Programme

APRIL 2021

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

**HAFİF METALLERİN MİKRO ARK OKSİDASYON YÖNTEMİYLE
FARKLI AŞINMA ŞARTLARINDA KORUNMASINA YÖNELİK YENİLİKÇİ
YAKLAŞIMLAR**

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To Atlas,



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NOVEL APPROACHES FOR PROTECTION OF LIGHT METALS UNDER VARIOUS WEAR CONDITIONS VIA MICRO ARC OXIDATION PROCESS

SUMMARY

Light metals such as magnesium, aluminium and titanium have recently developed great attention for automotive, aerospace, transportation and many other industries. Their low densities make them more favourable than heavier steel and cast iron alloys. In particular, they offer weight reduction and cost-efficient performance and therefore, they bring a subsequent revolutionary change in the design and manufacturing of metallic components. Despite their beneficial specific strength, light metals mostly exhibit low hardness and insufficient wear resistance. Although they pose a native oxide protective layer on their surface after exposure to air, this layer only provides minimal protection to wear- and corrosion-related damages. Thus, surface engineering technologies become necessary to satisfy the specific properties and long service life of fabricated engineering components. Compared to other surface modification processes, micro arc oxidation (MAO) is distinguished by providing a thick, hard and well-adhered oxide coating on the magnesium, aluminium and titanium alloys without jeopardizing the mechanical properties of the substrate because of negligible heat input. Moreover, the MAO technique has advantages like processing materials with complex geometries, no need for extensive preparations of the surface of the substrate and applying in environmentally friendly electrolytes. In the scope of these drawbacks of light metallic alloys, wear performance was aimed to be enhanced against various service conditions such as high contact pressures, corrosive environment, high temperatures, etc.

In the first chapter of the thesis, a study was initiated to extend the usage of magnesium alloys, especially in corrosion and wear-related engineering applications, by coating their surfaces via MAO. Considering the individual influence of phosphate- and aluminate-based electrolytes on the corrosion and wear performances of the synthesized MAO coatings, AZ91 magnesium alloy has been subjected to MAO in aluminate-based reference electrolyte with and without additions of Na_3PO_4 at concentrations of 5 and 10 g/l. Unlike dry sliding conditions, MAO coatings synthesized in the aluminate-based reference electrolyte did not provide reasonable protection of AZ91 magnesium alloy against wear in corrosive media (0.9 wt% NaCl solution). This study revealed that the addition of 5 g/l Na_3PO_4 into this reference electrolyte was sufficient for enhanced resistance of MAO coating against chemical and mechanical degradations (i.e. corrosion-wear) without altering its features in terms of surface roughness and thickness.

In the second chapter of the thesis, a study has been initiated to increase the success of MAO coatings fabricated on aluminium alloys against degradation under sliding contact conditions at high temperatures. For this purpose, the 7075 Al alloy has been micro-arc oxidised in an aluminate-based electrolyte with or without the adding monoclinic zirconia (ZrO_2) particles. Microstructural analyses revealed that the

coating synthesised in a ZrO_2 -added electrolyte consisted of a ZrO_2 particles participated alumina (Al_2O_3) based outer layer and a monolithic Al_2O_3 -based inner layer, which exhibited similar features with that of the synthesised in the ZrO_2 -free aluminate-based electrolyte. Moreover, the coating fabricated in the ZrO_2 -added electrolyte exhibited enhanced wear resistance during the dry sliding wear tests conducted at room temperature and had higher durability during the tests done at 300 °C. Since the examined coatings were worn by the fatigue wear mechanism, their durability during high temperature wear tests was analysed using the conventional stress-based fatigue approach. From the derived equations, the maximum contact pressures at which coatings can endure 10^6 contact cycles at 300 °C were estimated as 851 and 331 MPa for the coatings fabricated in the ZrO_2 -added and ZrO_2 -free aluminate-based electrolytes, respectively.

In the third chapter of the thesis, the influence of Al_2O_3 and ZrO_2 incorporation on the structural properties and wear resistance of titania (TiO_2) based MAO coatings fabricated on Ti6Al4V alloy was studied. For this purpose, MAO was employed in a silicate-based electrolyte with and without additions of Al_2O_3 and ZrO_2 particles. The structural properties were determined via X-ray diffraction (XRD) and X-ray photoelectron (XPS) spectroscopy analysis and an energy dispersive spectrometer (EDS) equipped scanning electron microscope (SEM). Furthermore, thermochemical simulations were made by using FactSage 7.3. Mechanical properties of the MAO coatings were determined by hardness measurements and dry sliding reciprocating wear tests. Structural examinations revealed that the MAO coatings fabricated in Al_2O_3 and ZrO_2 added electrolytes comprised of these oxides and their complex forms (Al_2TiO_5 and ZrTiO_4 , respectively) along with TiO_2 and amorphous silica (SiO_2). Although incorporations of Al_2O_3 and ZrO_2 did not remarkably improve the hardness of the MAO coatings, the highest wear resistance was obtained from the one formed in the ZrO_2 added electrolyte. On the other hand, the MAO coating fabricated in the Al_2O_3 added electrolyte exhibited lower wear resistance than that fabricated in the particle-free silicate-based electrolyte.

In the fourth chapter of the thesis, the structural features, biocompatibility, and mechanical performance of a TiO_2 layer with incorporated ZrO_2 formed by micro arc oxidation on commercially pure titanium have been examined. In comparison to the ZrO_2 -free TiO_2 layer, the ZrO_2 -incorporated oxide layer was dense and contained ZrTiO_4 as a new oxide as well as ZrO_2 particles. Associated changes in the microstructure enhanced the mechanical durability of the TiO_2 layer. Owing to the incorporation of identical biocompatible compounds and almost similar surface roughness, no remarkable difference in bioactivities of the ZrO_2 -free and ZrO_2 -incorporated oxide layers was detected after simulated body fluid tests.

In the fifth chapter of the thesis, a work was initiated to examine the role of counterface materials on the tribological behaviour of Mg alloys subjected to the MAO process and focus on reducing the sliding coefficient of friction (COF) values of MAO treated surfaces. Surfaces of AZ31 grade Mg alloy were subjected to an MAO treatment in a sodium metasilicate and potassium hydroxide containing electrolyte. Unlubricated sliding wear tests were conducted using counterfaces made of nitride-based (N-based), TiN, TiCN, CrN, and hydrogenated diamond-like carbon (HDLC) coated as well as uncoated SAE 52100 grade bearing steel balls. MgO based coatings formed on the surfaces of samples during the MAO process increased the wear resistance of AZ31, regardless of the type of counterface material used. Sliding the MAO treated surfaces against counterfaces made of uncoated steel and N-based coatings yielded high COF

values of 0.6–0.8 that exceeded those of the uncoated AZ31 against the same counterfaces. During dry sliding of the H-DLC counterface on the MgO coating, smooth and stable friction curves with a low steady-state COF value of 0.13 were recorded. Therefore, a significant drawback of MAO treatment that gives rise to surfaces with high COF could be addressed by running them against H-DLC coated counterfaces, a method that could be applied to the development of lightweight tribological components that are both sliding wear-resistant and have low COF.

In the sixth chapter of the thesis, the wear and corrosion performances of AZ91D magnesium alloy have been examined after MgO- and Al₂O₃-based coatings fabricated. While the MAO process was applied to generate a magnesia layer, cold spraying (CS) and MAO processes were combined to obtain a novel alumina layer. CS was conducted to cover the substrate by depositing an aluminium layer (monolithic or composite). Afterwards, application of the MAO process produced an alumina layer on the deposited aluminium layer (monolithic or composite), forming a multilayered coating on the examined magnesium alloy. The experiments revealed that the alumina layer formed on the alumina reinforced aluminium matrix composite layer ensured superior protection for AZ91D alloy against mechanical and chemical degradations compared to the magnesia layer.

In brief, within the scope of the thesis, it has been shown that MAO coatings can be modified especially for wear-related applications to work efficiently at high temperatures, at high contact pressures, in corrosive environments and even in environments with biological fluids. Generally, the primary method in improving the properties of MAO coatings is to generate a composite oxide coating that forms on the base metal substrate by various ions or particles as the additives introduced into the electrolyte. Our studies have shown that when the MAO process is combined with another surface modification process, it can produce only oxides with better properties without forming its oxides of the base metal, which exhibits low hardness and wear resistance. With the combination of CS and MAO methods, magnesium alloys widely used today have gained a much higher wear resistance than the magnesium alloys coated by the MAO process. These coating methods, which are applied at low temperatures, also do not alter the microstructure and mechanical properties of the magnesium alloys having a low melting temperature. However, the general feature of MAO coatings is their high COF values. Therefore, within the scope of the thesis, it has been revealed that it is beneficial to modify contact surface to be used in applications where a low friction coefficient is required, and thus, H-DLC coating was applied on the steel balls, which were the counterfaces of MAO coating. In future works, it is planned to reduce the COF of MAO coatings to improve the wear properties of MAO coatings by adding lubricant additives into the electrolyte.



HAFİF METALLERİN MİKRO ARK OKSİDASYON YÖNTEMİYLE FARKLI AŞINMA ŞARTLARINDA KORUNMASINA YÖNELİK YENİLİKÇİ YAKLAŞIMLAR

ÖZET

Günümüzde magnezyum, alüminyum ve titanyum gibi hafif metaller otomotiv, havacılık, ulaşım ve diğer birçok endüstri için alternatif bir malzeme grubu olmuşlardır. Düşük özgül yoğunluğa sahip olmaları, bu metal ve alaşımlarını daha ağır mühendislik malzemeleri olan çelik ve dökme demir alaşımlarına göre daha avantajlı kılar. Özellikle, araçların ve taşıtların ağırlıklarının azaltılmasında önemli rol alırlar. Bu olumlu özelliklerine rağmen, hafif metaller çoğunlukla düşük sertlik ve yetersiz aşınma direnci sergiler. Her ne kadar havaya maruz kaldıktan sonra yüzeylerinde doğal oksit koruyucu tabaka oluştursalar da bu ince oksit tabaka aşınma ve korozyonla ilgili hasarlara karşı çok sınırlı koruma sağlar. Bundan dolayı, hafif metalik alaşımların yüzey özelliklerinin iyileştirilmesi yaygın kullanımlarını sağlaması yönünden önemlidir. Diğer yüzey modifikasyon işlemleriyle karşılaştırıldığında, mikro ark oksidasyon (MAO) yöntemi, altlık malzemesinin sıcaklığının oda sıcaklığı dolaylarında kalmasını sağlayarak mekanik özelliklerine zarar vermeden magnezyum, alüminyum ve titanyum alaşımları üzerinde kalın, sert ve kuvvetli bir şekilde bağlanmış bir oksit kaplama sağlaması ile ön plana çıkar. Dahası, MAO tekniği, karmaşık geometrilere sahip malzemelerin kaplanması, altlık yüzeyinin kapsamlı bir şekilde hazırlanmasına gerek olmaması ve çevreye zararı olmayan elektrolitlerde uygulanması gibi avantajlara sahiptir. Bu çalışma kapsamında, hafif metal alaşımlarının yüksek yükler altında, korozif ortamda ve yüksek sıcaklıklara maruz kalma gibi çeşitli zorlu hizmet koşullarına karşı aşınma performansının artırılması amaçlanmıştır.

Tez kapsamında yürütülen deneysel çalışmaların birinci bölümünde, magnezyum alaşımlarının yüzeylerini MAO yöntemi ile kaplayarak özellikle korozyon ve aşınma ile ilgili mühendislik uygulamalarında kullanımlarını yaygınlaştırmak amacıyla bir çalışma başlatılmıştır. AZ91 magnezyum alaşımının korozyon ve aşınma direncinin artırılması amacıyla bu alaşım alüminat esaslı referans elektrolit içinde ve 5 ile 10 g/l sodyum fosfat (Na_3PO_4) katkılı alüminat esaslı elektrolitler içinde MAO işlemine tabi tutulmuştur. Kuru kayma koşullarının aksine, alüminat esaslı referans elektrolit içinde sentezlenen MAO kaplaması, AZ91 magnezyum alaşımını ağırlıkça %0,9 NaCl içeren çözelti bulunan korozif test ortamında aşınmaya karşı iyi bir şekilde koruyamamıştır. Bu çalışma sonucunda, bu referans elektrolite olarak belirlenen alüminat esaslı elektrolite 5 g/l Na_3PO_4 eklenmesinin, MAO kaplamanın yüzey pürüzlülüğü ve kalınlığı açısından özelliklerini değiştirmeden kimyasal ve mekanik bozulmalara (yani tribokorozyona) karşı arttırılmış direnci için yeterli olduğunu ortaya koyulmuştur.

Tez kapsamında yürütülen deneysel çalışmaların ikinci bölümünde, alüminyum esaslı alaşımlar üzerinde sentezlenen MAO kaplamaların yüksek sıcaklıklarda aşınma koşullarına karşı direncini artırmak amacıyla bir çalışma başlatılmıştır. Bu amaçla, 7075 alüminyum alaşımı, monoklinik zirkonya (ZrO_2) partikülleri eklenmiş ve eklenmemiş alüminat esaslı referans elektrolit içinde mikro ark oksidasyon işlemine tabi tutulmuştur. Mikroyapısal analizler, ZrO_2 katkılı referans elektrolitte sentezlenen kaplamanın, ZrO_2 partikülleri içeren alümina (Al_2O_3) esaslı üst katman ve ZrO_2 içermeyen alüminat esaslı elektrolitte sentezlenen numunelere benzer özellikler sergileyen monolitik Al_2O_3 esaslı bir alt katmandan oluştuğunu ortaya çıkarmıştır. Ayrıca, ZrO_2 eklenmiş elektrolitte üretilen kaplamanın, oda sıcaklığında gerçekleştirilen aşınma testleri sonucunda iyi aşınma direnci sergilediği belirlenmiş ve aynı zamanda 300 °C'de yapılan testlerde de referans elektrolitte kaplanmış numunelere göre daha yüksek aşınma direnci göstermiştir. İncelenen kaplamalar yorulmalı aşınma mekanizması ile zarar gördüğünden, yüksek sıcaklık aşınma testleri sırasındaki aşınma dirençleri, geleneksel gerilmeye dayalı yorulma yaklaşımı kullanılarak analiz edilmiştir. Bu analiz sonucu elde edilen denklemlerden, kaplamaların 300 °C'de 10^6 çevrim sayısında kadar dayanabildiği maksimum kontak basınçları, sırasıyla, ZrO_2 eklenmiş ve ZrO_2 eklenmemiş alüminat esaslı elektrolitlerde işleme tabi tutulan kaplamalar için 851 ve 331 MPa olarak tahmin edilmiştir.

Tez kapsamında yürütülen deneysel çalışmaların üçüncü bölümünde, Ti6Al4V titanyum alaşımı üzerinde üretilen Al_2O_3 ve ZrO_2 katkılı titanya (TiO_2) esaslı MAO kaplamaların yapısal özellikleri ve aşınma performansları incelenmiştir. Bu amaçla silikat esaslı referans ve Al_2O_3 ile ZrO_2 partikülleri eklenmiş silikat esaslı elektrolitler içinde MAO işlemi uygulanmıştır. Yapısal incelemeler sonucunda, Al_2O_3 ve ZrO_2 katkılı elektrolit içinde sentezlenen MAO kaplamalarının, ortak olarak TiO_2 ve amorf silika (SiO_2) içerdiği, elektrolite Al_2O_3 ilavesinin bir kompleks oksit olan Al_2TiO_5 oluşumuna sebep olurken ZrO_2 ilavesi ise MAO kaplama içinde kompleks $ZrTiO_4$ fazının oluşmasını sağlamıştır. Elektrolit içine Al_2O_3 ve ZrO_2 'nin eklenmesi, MAO kaplamalarının sertliğini dikkate değer ölçüde iyileştirmese de en yüksek aşınma direnci ZrO_2 eklenen elektrolitte sentezlenen kaplamada elde edilmiştir. Öte yandan, Al_2O_3 eklenmiş elektrolit içinde sentezlenen MAO kaplaması, partikül içermeyen silikat esaslı elektrolit içinde sentezlenen kaplamadan daha düşük aşınma direnci sergilemiştir.

Tez kapsamında yürütülen deneysel çalışmaların dördüncü bölümünde, ticari saflıkta saf titanyum üzerinde ZrO_2 partikülleri eklenmiş bir elektrolit içinde MAO yöntemiyle ile oluşturulan bir TiO_2 tabakasının yapısal özellikleri, biyouyumluluğu ve mekanik özellikleri incelenmiştir. ZrO_2 partikülleri içermeyen TiO_2 tabakasına kıyasla, ZrO_2 ile katkılanmış oksit tabakası daha az poroziteli bir yapıya sahip olmuştur ve mikroyapısında ZrO_2 partikülleri ile birlikte $ZrTiO_4$ fazının da oluştuğu gözlenmiştir. Mikroyapıda gözlemlenen az poroziteli ve $ZrTiO_4$ içeren yapı, var olan TiO_2 tabakasının mekanik dayanıklılığını artırmıştır. Her iki kaplamada da özdeş biyouyumlu bileşiklerin varlığı ve benzer yüzey pürüzlülüklerinden dolayı, yapay vücut sıvısı içinde gerçekleştirilen biyoaktivite testleri sonucunda ZrO_2 içermeyen ve ZrO_2 içeren oksit tabakalarının biyoaktivitelerinde kayda değer bir fark tespit edilememiştir.

Tez kapsamında yürütülen deneysel çalışmaların beşinci bölümünde, MAO işlemine tabi tutulan magnezyum alaşımının tribolojik davranışında karşıt yüzey malzemelerinin rolünü incelemek ve MAO işlemi ile kaplanmış yüzeylerin sürtünme katsayısı (COF) değerlerini düşürmeye yönelik bir çalışma başlatılmıştır. Kuru

ortamda yapılan aşınma testleri, nitrür esaslı TiN, TiCN, CrN ve hidrojenize elmas benzeri karbon (H-DLC) kaplamalı ve işlemsiz SAE 52100 kalite rulman çeliği bilyelerinden yapılmış karşıt yüzeyler kullanılarak gerçekleştirilmiştir. MAO işlemi sırasında numunelerin yüzeylerinde oluşan MgO esaslı kaplamalar, kullanılan karşıt yüzey kaplamaları ne olursa olsun AZ31 magnezyum alaşımının aşınma direncini artırmıştır. MAO işlemi ile kaplanmış yüzeyleri, kaplamasız çelik ve N esaslı kaplamalara sahip karşıt yüzeylerle aşınma testine maruz bırakmak 0,6 ile 0,8 değerlerinde sürtünme katsayısı elde edilmesine sebep olmuştur. Ancak MgO ile kaplanmış AZ91 üzerinde H-DLC karşıt malzemesinin kuru ortam aşınma testi sırasında, 0,13 değerinde görece çok daha düşük bir sürtünme katsayısı değerine ulaşılmış ve aynı değerde kararlı bir sürtünme katsayısı eğrisi elde edilmiştir. Bu sonuçlarla, MAO işlemi sonucunda elde edilen kaplamaların kuru ortam aşınmalarında gözlenen yüksek sürtünme katsayısı değerlerini düşürmek amacıyla H-DLC kaplı karşıt yüzeylerin tribo çift olarak kullanılmasının başarılı sonuçlar verebileceği gösterilmiştir.

Tez kapsamında yürütülen deneysel çalışmaların altıncı bölümünde, AZ91D magnezyum alaşımının aşınma ve korozyon performansları, MgO ve Al₂O₃ esaslı kaplamalar elde edildikten sonra karşılaştırmalı olarak incelenmiştir. MgO esaslı bir oksit tabakası oluşturmak amacıyla direkt magnezyum alaşımı üzerine MAO işlemi uygulanırken, Al₂O₃ tabakası elde etmek amacıyla önce soğuk püskürtme uygulanmış ve ardından MAO işlemi gerçekleştirilmiştir. Soğuk püskürtme işlemi ile altlık AZ91D alaşımı üzerinde alüminyum esaslı (monolitik veya kompozit) bir tabaka oluşturulmuştur. Daha sonra, MAO işleminin uygulanması, magnezyum alaşımı üzerinde Al₂O₃ esaslı bir yüzeye sahip çok katmanlı bir kaplama oluşumunu sağlamıştır. Çalışma sonuçlarına göre, Al₂O₃ takviyeli alüminyum matriks kompozit tabaka üzerinde oluşan Al₂O₃ tabakasının, MgO tabakasına göre mekanik ve kimyasal bozunmalara karşı AZ91D alaşımı için üstün koruma sağladığını ortaya koymuştur.

Sonuç olarak, bu tez kapsamında üretilen MAO tabakalarının özellikle aşınma çalışmalarına yönelik olarak modifiye edilebileceği ve yüksek sıcaklıklarda, yüksek kontak basınçlarında, koroziv ortamlarda ve hatta biyolojik sıvıların bulunduğu ortamlarda bile yüksek aşınma direnci gösterebilecekleri ortaya konmuştur. Geleneksel olarak MAO tabakalarının özelliklerinin geliştirilmesinde ön plana çıkan yöntem elektrolit içerisine yapılacak iyonik veya partikül formunda katkılar ile oluşan altlık metali üzerinde büyüyen kompozit bir oksit kaplama oluşturulmasıdır. Tez kapsamında yapılan çalışmalar göstermiştir ki MAO prosesi başka bir yüzey kaplama prosesi ile birleştirildiği takdirde altlık metalinin kendi oksitleri oluşmadan sadece daha iyi özelliklere sahip oksitlerin oluşması sağlanabilmektedir. Bu şekilde kombine edilen CS ve MAO yöntemleri ile birlikte günümüzde kullanımı yaygınlaşan magnezyum alaşımlarının sadece MAO yöntemi uygulanmasına göre çok daha fazla bir aşınma direnci kazanması sağlanmıştır. Düşük sıcaklıklarda uygulanan bu kaplama yöntemleri aynı zamanda düşük ergime sıcaklığına sahip magnezyum alaşımının mikroyapısını ve mekanik özellikleri bozmamaktadır. Ancak MAO kaplamaların genel özelliği sürtünme katsayılarının yüksek olmasıdır. Ondan dolayı tez kapsamında MAO kaplamaların düşük sürtünme katsayısı gereken uygulamalarda kullanılabilmesi için karşıt yüzeyinde özelliklerinin değiştirilmesinin yararlı olduğu düşünülmüş ve böyle karşıt yüzey olan çelik bilya üzerine H-DLC kaplama uygulanmıştır. İleriki çalışmalarda MAO kaplamaların sürtünme katsayılarının düşürülmesi, elektrolit içerisine yağlayıcı özelliği olan katkılar eklenerek MAO kaplamaların aşınma özelliklerinin geliştirilmesi planlanmaktadır.



1. INTRODUCTION

1.1 Light Metals and Alloys

The word light metal is often used for metals of significant industrial value, such as magnesium, aluminium and titanium, which have comparatively lower density than ferrous alloys [1]. Their extensive use emerged towards the end of the nineteenth century, while they were isolated from their ores on a substantial scale. Light metals and alloys have high strength-to-weight ratios and low density and are commonly characterized as low toxicity relative to heavy metals, except beryllium [2]. Lightweight cars designed for customers and the military industries use less fuel and achieve substantial energy savings. In comparison, lighter cars can drive the same distance at a lower cost and emit lower carbon emissions relative to vehicles mainly made from ferrous alloys [3]. Commercial light alloys are compared with few examples of the most available steel and cast iron grades in Table 1.1.

Table 1.1 : Main properties of AZ91 magnesium alloy, 7075 aluminium alloy, Ti6Al4V titanium alloy, ST52-2 steel and 60-40-18 cast iron [2,4–9].

Property	AZ91	7075	Ti6Al4V	ST52-2	60-40-18
Density (g/cm ³)	1.79	2.80	4.43	7.85	7.15
Tensile strength (MPa)	235	565	860	570	414
Yield strength (MPa)	92.8	515	795	355	276
Elastic modulus (GPa)	42.6	72	110	210	164
Hardness (Vickers)	66	175	349	170	173
Elongation (%)	7	18	10	21	18
Poisson's ratio	0.35	0.33	0.34	0.30	0.26

1.2 Magnesium Alloys

Metallic magnesium having a density of 1.74 g/cm³, is one of the most commonly used structural metals, even exhibits a lower density than aluminium alloys [10]. Whereas at least one of the titanium, copper, manganese, zirconium, rare earth metals, etc., is

added to form a magnesium alloy, since its low strength, pure magnesium cannot be used as a building element [10]. Magnesium alloys are distinguished into two different main groups, which are cast and wrought alloys. Generally, magnesium alloys are used as cast alloys in the industries; although, commercial wrought alloys have seen remarkable development over the last decade. The most popular magnesium alloys produced by casting are AZ63, AZ81, AZ91, AM50, ZK51, ZK61, ZE41, ZC63, HK31, HZ32, QE22, QH21, WE54, WE43, and Elektron 21 [11,12] and the most common wrought magnesium alloys can be listed as AZ31, AZ61, AZ80, Elektron 675, ZK60, M1A, HK31, HM21, ZE41, and ZC71 quality alloys [11,12]. Magnesium alloys have drawn growing interest as light alloys for their high strength-to-weight ratios, substituting traditional structural components for weight reduction in vehicles such as automobiles, trucks, trains and aircraft. New light materials are presently being incorporated into the automotive industry's global policies, as the climate demands emissions and a decrease in fuel consumption [13]. Besides, high strength-to-weight ratio, good castability, and exceptional damping behaviour are attractive properties of magnesium alloys which are a variable in the material selection process [14].

The structural uses of magnesium alloys comprise automobile, industrial, material processing, commercial and aviation machinery. Automobile applications of magnesium alloys are ranging from clutch components, brackets, steering wheels to housings. In the manufacturing industry, there are potential uses of magnesium alloys such as sewing and printing equipments. Moreover, dock boards, grain shovels and gravitational conveyors are some other examples of wide-range usage of magnesium alloys [15]. Magnesium alloys developed for aerospace applications are useful since they exhibit high stiffness and high strength-to-weight ratio. Cast magnesium alloys, commonly used in indoor and power-train materials, compensate for more than 90% of the magnesium alloys used today, although only a limited number of wrought items are used. That is because magnesium alloys lack the formability of wrought applications, and their high cost prohibits the use of magnesium alloys for vehicle industries.

Magnesium alloys are typically vulnerable to corrosion, particularly in environments containing chloride ions [11,16]. The potential pH magnesium diagram examines the possible preservation of magnesium at high pH levels that may result from the

formation of Mg(OH)_2 during the corrosion reaction, which yields to failure of the component [11].

1.3 Aluminium Alloys

Aluminium alloys require the utmost attention of non-ferrous materials from the point of view of both production and use. Among the most significant features of aluminium, the largest area of use of the transport business (28%) is the manufacture of a Boeing 747 using more than 66 tons of aluminium [17]. A further 23% is used for the manufacture of cans, tubing and assorted containers; about 14% is used in the building and construction industry (from windows to mobile home construction); while the remaining 35% is used in a wide variety of items, such as electrical cables, parts, specialized machinery, etc. These alloys also involve various amounts of copper, zinc, magnesium and other elements to obtain the required mechanical strength [18]. Aluminium alloys possess many significant advantages when compared to steels, mainly for the automotive industry [19]:

- Having about 2.7 g/cm^3 density (7.8 g/cm^3 for steels),
- Higher specific energy absorption,
- Higher thermal conductivity, which is beneficial for heat exchanger applications,
- Higher formability;
- Greater tolerance to environmental corrosion,

To improve their mechanical properties, the heat treatment methods applied to aluminium alloys are homogenization, nitriding, and precipitation hardening and including solvent treatment, tempering and ageing, either at room temperature (natural ageing) or at high temperature (artificial ageing) [6,20].

1.4 Titanium Alloys

After aluminium, iron and magnesium, titanium is the fourth most common commercial metal and the ninth most abundant material on earth [21]. Titanium exhibits a unique range of mechanical, physical and chemical properties due to its combination of high strength, high hardness, low density and strong corrosion

resistance [22]. With the help of these properties, titanium alloys are used in a wide range temperatures. Low density of titanium also allows weight reductions in several primary aerospace applications and other high-performance applications in the medical, pharmaceutical and automotive industries. Moreover, titanium is elastically rigid (approximately 115 GPa Young's modulus), lightweight and corrosive resistant [7]. Titanium and its alloys have tensile strengths ranging from 240 to 1310 MPa, close to the strengths found in commercial steels [23].

Titanium is a low-density material (nearly 60% of the density of iron) that can be reinforced by solvent alloy, second phase hardening, and plastic deformation. Titanium is non-magnetic and has strong heat transfer properties. Its thermal expansion coefficient is marginally smaller than that of steel and less than half that of aluminium. One of its significant characteristics is its high melting point of 1725 °C, almost 200 °C above that of steel and more than 1000 °C above that of aluminium [23].

Titanium can be passivated, and thus titanium alloys have a good level of resistance to many chemical compounds and chlorine ions [24]. Titanium is well-known for non-toxicity and usually biologically consistent with human tissues and bones. Therefore, the combination of high corrosion resistance and biocompatibility with exceptional hardness features, titanium alloys become very suitable for biomedical applications.

1.5 Micro Arc Oxidation (MAO) Process

Micro arc oxidation (MAO), also called plasma electrolytic oxidation (PEO) or micro spark anodization (MSA), is a theoretically similar process with anodic oxidation technique applied on light metals but differs with used high voltage and current to generate controlled plasma on the exposed surface [25]. Micro-discharges caused by plasma during the MAO process yield partial melting of the produced oxide layer on the surface of the metal and enable the formation of a highly adherent ceramic-based coating. MAO coating has high longevity, good wear and corrosion resistances, along with high thermal stability [25]. Also, MAO coatings act as a suitable sub-layer for organic or polymeric topcoats.

Summarily, major advances and changes in the MAO process were made in the Soviet Union in about the 1970s and 1980s [26]. Researchers were primarily concerned about the possible advantages of micro-discharges during the MAO process as a way of

improving commercially used aluminium anodizing. They stated that, under some process conditions, micro-discharges ensured the rapid growth of oxides, and thus, the fabricated oxide coatings were very hard and well adhered to the base metal. The first U.S. patent was published in 1974 and called as "method of coating metals using anodic discharges" by Gradovsky and Bayles [27]. In the meantime, Van et al., from the University of Illinois, conducted a study and filed a patent named "Anodic Spark Deposition Mechanism" [27]. Markov et al. published a patent in 1982 with the title of "AC and pulsed bipolar processes for the production of hard oxide ceramic coatings on Al" announced the launch of Russian progress into the technology as a rival of hard anodising of aluminium alloys [27]. It was a important step in the growth of this technique, so its future advantages were eventually understood and the market interest grew dramatically.

The formulation of the MAO oxide coatings is complex as it includes many chemical and electrochemical reactions [25]. The development of MAO coating consists of many stages such as dielectric breakdown, breakdown of anodic film and micro-discharges of arcs. The predominance of each of these stages is determined by the elemental composition of the metal, the species of the electrolyte, and the applied voltage or current density. However, heavy dissolution of the anodized metal and the chemical dissolution of the previously formed oxide layer during the MAO process, along with the intense evolution of oxygen, reduces the efficiency of the process and increases energy consumption [25].

A descriptive schematic of the MAO process for a magnesium alloy is represented in Figure 1.1 [28]. Sufficient electrical potential for the MAO process is applied to the valve metal, which acts as the anode, to increase the oxide layer thickness (Figure 1.1a) [29]. While the surface of the metal is passivated by a newly formed thin oxide layer, the generated voltage due to the applied current between the metal and the surrounding electrolyte increases quickly along with thickening the native oxide (Figure 1.1b) and subsequently, the voltage approaches over 200 V [29]. It grows until the dielectric layer is too strong, and the micro-discharges alter the oxide layer and produce a vast amount of rapid and very small micro-arcs (Figure 1.1c) [29]. Such micro-arcs yield localized plasma-assisted reactions at elevated temperatures and pressures that influence the growth of the oxide. This degradation causes the generation of a relatively thicker oxide coating and which will then be dissolved during the next step

under a marginally greater potential gap [29]. In summary, stages such as heating, melting, re-solidification, diffusion, sintering and densification of the formed oxide are combined in the MAO process.

There are three simultaneous processes for coating development, comprising electrochemical reactions, plasma chemical reactions and thermal diffusion [29]. The major electrochemical reactions occur on the coating/electrolyte interface. Plasma chemistry of surface discharges is very complicated, requiring, on the one hand, a transfer of ions to the metal/electrolyte interface and, on the other hand, a heavy ionization results between the substrate surface and the electrolyte via the oxide coating with the help of plasma [30]. Molten oxide is expelled from the coating/substrate interface to the coating surface, in which it is quickly crystallized and re-crystallized by the electrolyte, as seen in Figure 1.1d [29]. Consequently, the degradation of metal hydroxide to oxide and the development of complex phases can occur (Figure 1.1e) [29]. The direction and strength of these stages depend on the density and intensity of the micro-arcs, which are revealed to be dictated by the thickness of the oxide layer. As a result, the thicker the coating with less regularity is formed, but the discharges become more efficient and prolonged.

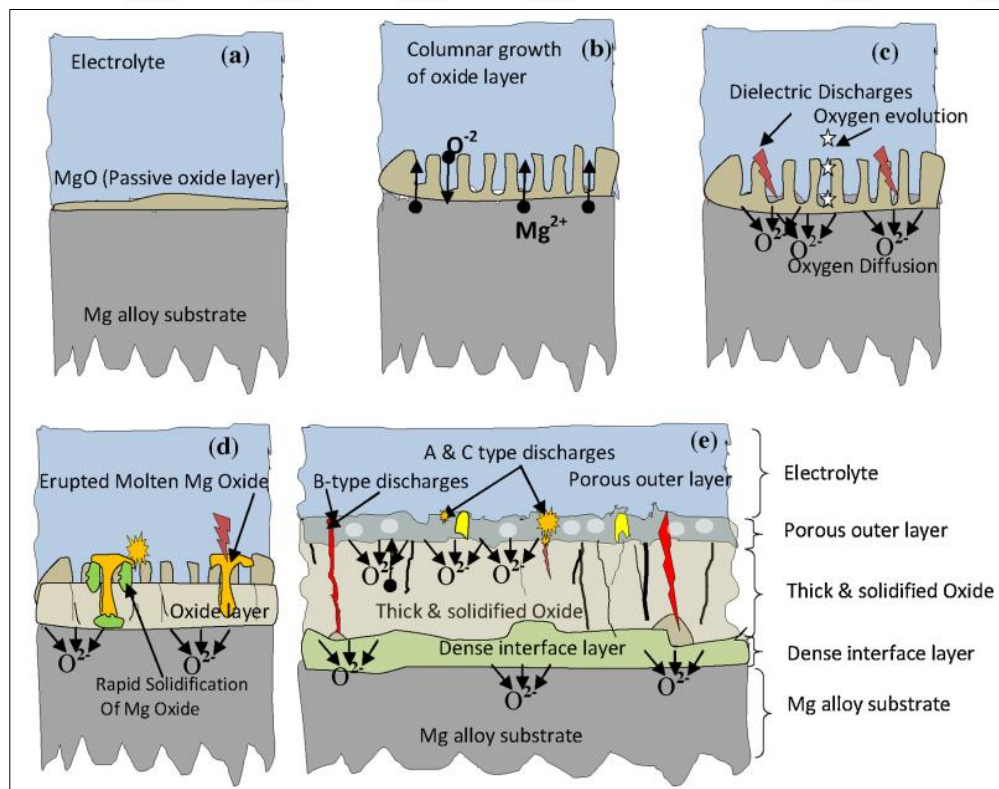


Figure 1.1 : Schematic of the coating process during MAO treatment [28].

1.6 Modifications of MAO Coatings for Tribological Applications

Science of interacting surfaces in sliding relative motion is called tribology, which originates from the Greek term "tribos", meaning friction [31]. Tribology is a discipline that includes friction, wear, contact mechanics and lubrication phenomena and is known to be one of the most crucial engineering details in many daily circumstances. Many various research fields, including physics and chemistry, mechanical engineering and materials science, study the principles of tribology, ranging from microscopic to macroscopic. While this scientific concept was first adopted in 1966 by a public study from the Department of Education and Science of Great Britain, it has always been a human engineering concern since the early civilizations were founded in the archaic lands of Egypt, Mesopotamia and Anatolia, where primitive technology was built to construct their communities [32].

The tribological structure consists of four fundamental elements: the two contacting partners, the interface, the medium and the environment. Friction emerges if two rigid bodies move against one another due to the tangential resistance of the sliding interface in a dynamic environment. The tangential friction force is equivalent to the normal load by the coefficient of friction and explained by Amontom as the "first law of friction" [33]. The coefficient of friction depends on the rigid body in contact and changes over time as the properties of the surface alter. In general terms, the softer material will deform at the point of impact, and the material with weaker shear strength will be damaged during sliding action. Concerning external variables such as lubrication, ambient temperature and humidity, geometry, and so forth, the friction dynamics and the friction coefficient can change and respond to present circumstances [33].

Almost every engineering system has contact points between moving parts (e.g. car engines, train axles, wind turbine gearboxes, etc.) and are subjected to intense friction and thus wear failures that reduce service life and performance. These conditions typically lead to increased maintenance and can cause major failure if the consideration needed is overlooked. Besides, friction and wear also play a significant role in global energy use, economic investment and CO₂ emissions. During one of the early studies released by Peter Jost in 1966, he reported that Britain had suffered substantial financial losses of more than 1% of GDP that year due to early system breakdown due

to friction and wear [32]. The reason of the International Energy Agency (IEA) to minimize CO₂ emissions is to reduce global warming to 2 °C over pre-industrial levels by 2050 [3]. The word 'green tribology' is then introduced and described as tribological aspects of ecological equilibrium and environmental and biological impacts [3]. To compensate for losses due to friction and wear, the main components of the tribocontact system must be built to be robust and sustainable. Figure 1.2 shows the schematic diagram for calculating energy savings in terms of reducing fuel usage in the short and long term by minimizing friction-related and wear-related energy losses.

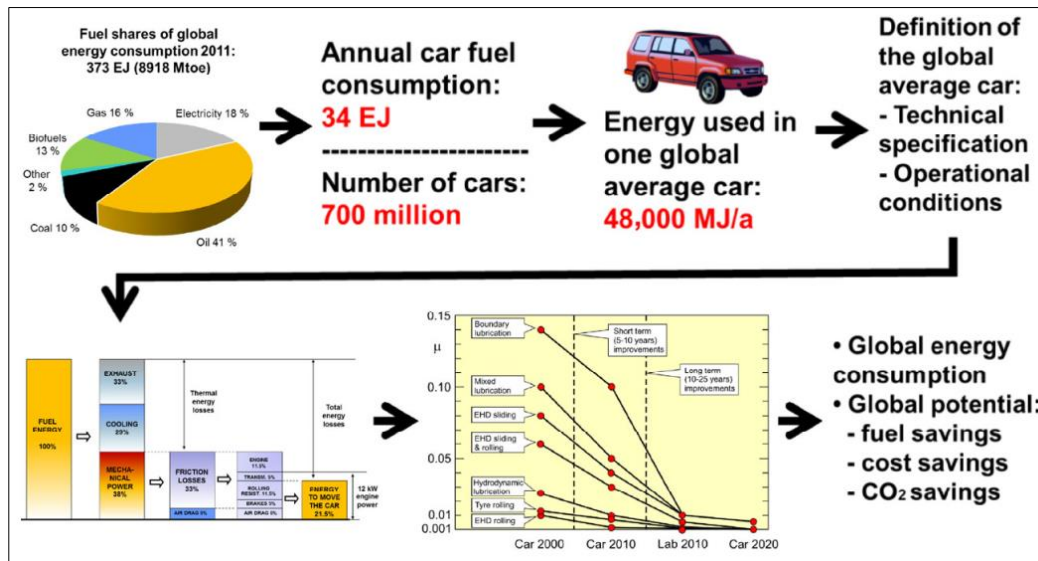


Figure 1.2 : Sematic illustration presenting the global influence of friction on fuel consumption for passenger automobiles and potential savings [3].

1.6.1 Effect of process parameters for MAO coatings

In the MAO method, the effect of the discharge waveform and its related power parameters on the test is comparatively high. In particular, the applied high voltage causes a higher coating thickness of the MAO coating; however, the smooth surface and density of the coating will be reduced; if low voltage is applied, it could be challenging to create the oxide coating, so the selection of the required voltage is very critical for the efficiency of the coating and is also the most significant factor influencing the required energy [34]. On the other hand, with the rise in pulse frequency, the thickness of the coating decreases steadily and is like a linear reduction as the hardness of the dense material declines gradually. However, with the rise of the pulse rate, the percentage of the thick layer is steadily increased during MAO process [34].

1.6.2 Electrolyte composition

The concentration and formulation of the electrolytes utilized directly affect the morphological properties, porosity, thickness, and resistance to wear and corrosion of the MAO coatings [25]. Therefore, the appropriate selection of electrolyte composition and concentration is important for the rapid passivation of metals and the early achievement of sparking voltage. The alkaline electrolytes are widely used for the deposition of MAO coatings to resist the unnecessary metal dissolution of the anode. The rate of deposition in alkaline electrolytes is comparatively lower relative to neutral electrolytes [25].

To satisfy the criteria for dielectric breakdown, solid metal passivation additives (such as silicates, aluminates and phosphates) are commonly used as basic electrolyte constituents [35]. The three classes have the following advantages: they allow the sparking voltage to be quickly achieved, thereby saving time; the components present in the electrolyte are easily integrated into the coatings by poly-reaction and deposition, therefore improving the growth rate of the coating; the use of environmentally safe and low-cost electrolytes provides strong wear and corrosion-resistant coatings that are to be used.

1.6.3 Particle reinforcement

The presence of particles influences the microstructure and morphology of MAO coatings, e.g. pore properties, thickness and compactness of the substrate [36,37]. The addition of oxide particles to the electrolytes can reduce the amount and size of the pores on the coating surface. Typically, sealing is more efficient when applying sols to the electrolyte and in the case of reactive incorporation. Similarly, this was also asserted that the surface of the coating did not have too much impact or become more brittle as oxide particles were applied to the electrolytes [37]. In the presence of oxide ions, the stability and thickness of the coating may be changed or improved. It has been stated that the outer layer of the coating has been more robust and uniform relative to the coatings produced in particle-free electrolytes [37]. There is no strong pattern for the effect of the particles on the thickness of the coating. It has been observed that oxide particles have not been effective in increasing the thickness of the coating, as the coatings have usually seen comparable thickness or have also been thinner with the incorporation of the particles [37].

1.7 Research objectives of the thesis

The motivation of this study was to examine the possibility of enhancing tribological properties of light metals including titanium, aluminium and magnesium alloys under various testing conditions such as at high loads, in a corrosive environment, at high temperatures etc. For this purpose, these alloys were MAO'ed in electrolytes having different compositions, and ceramic particle added electrolytes. In the case of magnesium alloys, the addition of sodium phosphate was studied to increase the corrosion resistance of the MAO coating, which is beneficial for wear performance in corrosive environments. Another approach for enhancing wear resistance magnesium alloys is to provide an intermediate aluminium layer for the MAO process by utilising the cold spraying technique. This study showed that fabricating an aluminium layer on a magnesium alloy before the MAO process yields increased wear performance compared to MAO'ed magnesium alloy. Different from those approaches, modifying the counterface sliding against MAO coating is also shown as a promising solution. Sliding against H-DLC coated steel counterface demonstrated its good effectiveness by reducing the coefficient of friction significantly. Aluminium alloys suffer from low hardness and high wear rates; therefore, the MAO process was applied to 7075 aluminium alloy to increase its wear performance, especially at high temperatures. Studies showed that zirconia addition into the electrolyte generated a favourable zirconia embedded alumina coating, which provided better wear performance than zirconia-free alumina coating. A considerable part of titanium alloys are used in biomedical fields; therefore, their surface properties are important, as well as their tribological performance in the body. In this respect, an MAO coating was fabricated on CP-Ti with the addition of zirconia particles, and the resultant coating showed higher wear resistance with the help of synthesised zirconia titanate, which exhibits higher fracture toughness than titania. Similarly, Ti6Al4V alloy was MAO'ed in the electrolytes composed of zirconia and alumina particles to enhance the wear performance of titania coating formed in the particle-free electrolyte. The results showed that the zirconia titanate phase generated in the MAO coating was beneficial for wear resistance due to its high fracture toughness.

2. DEVELOPMENT OF CORROSION AND WEAR RESISTANT MICRO ARC OXIDATION COATING ON A MAGNESIUM ALLOY ¹

2.1 Introduction

Magnesium alloys, which are gaining increasing attention for many industries day by day, have a potential to substitute for aluminium alloys because of their comparative mechanical properties with about 35% lower density. However, their inherent poor corrosion and wear related surface degradation resistances are the main shortcomings limiting their wide spread commercial usage. In this respect, protection of the surfaces by surface modification/coating techniques appears as the most attractive technical solution for enhancing the service performance and lifetime of magnesium alloys. Among the surface modification/coating techniques, micro arc oxidation (MAO), which is an environmentally friendly electrochemical technique conducted at voltages higher than 200 V, is one of the most effective and economical method forming magnesium oxide (MgO) based coating having thickness ranging from 5 to 200 μm , depending on the process parameters and type of the electrolyte used [10,30,38–40].

The electrolytes used in MAO processes are mainly alkaline based solutions containing silicate, phosphate or aluminate compounds. In general, aluminate-based (i.e. NaAlO_2) electrolytes are very attractive for improving dry sliding wear resistance of Mg alloys after MAO process as they lead to formation of very hard (about 16 GPa) MgAl_2O_4 spinel phase within the coating. In this respect, increasing concentration of aluminate in the electrolyte increases the thickness and surface roughness of the MAO coatings, while providing enhanced tribological properties [41–43]. However, MAO coatings synthesized in aluminate-based electrolytes show fairly less corrosion resistance as compared to coatings formed in silicate- or phosphate-based electrolytes [44].

¹ This chapter is based on the paper “F. Muhaffel and H. Cimenoglu, Development of corrosion and wear resistant micro arc oxidation coating on a magnesium alloy, *Surf. Coatings Technol.* 357 (2019) 822-832”

Thus, silicate- and phosphate-based electrolytes favour Mg_2SiO_4 and $\text{Mg}_3(\text{PO}_4)_2$ phases, respectively, within the MAO coating and provide better corrosion resistance as they form passive layer inhibiting the corrosion attack [45,46]. Different from individual utilization of above mentioned electrolytes, Sheng et al. [47] employed MAO in the mixture of aluminate- and phosphate-based electrolytes (i.e. a dual electrolyte) with some additives and determined the optimum composition of this dual electrolyte for formation of a compact, smooth and corrosion-resistant coating on ZK60 Mg alloy. Liang et al. [48] revealed that utilizing dual electrolyte, consisting of phosphate and aluminate species for MAO of AM60B magnesium alloy, improved corrosion resistance along with a rough and coarse surface morphology. Likewise, Li et al. [49] reported that MAO coating produced in a dual electrolyte, which contained species of alumina and phosphate, exhibited high hardness and low friction coefficient sliding against 2GCr13 steel disk as compared to AZ31 magnesium alloy. In a recent study, Yang et al. [50] have reported promising tribo-corrosion performance for AZ31B magnesium alloy for biomedical applications upon combination of ultrasonic cold forging technology and MAO process employed in a dual electrolyte prepared by a mixture of aluminate- and phosphate-based electrolytes with some additives.

As an alternative to sole protection against corrosion or wear, the authors of this study employed MAO in dual electrolytes for the possibility of optimizing the combination of corrosion and wear resistances benefitting from the respective positive contributions of phosphate- and aluminate-based electrolytes on the fabricated coating. This complementary approach (i.e. enhancing the corrosion-wear resistance of MAO coating), which is scarce in open literature to the best of author's knowledge, has potential to provide better and long-term performance under sliding contact conditions in environments accelerating degradation of magnesium alloys i.e. moist conditions. Considering acceleration of corrosion attack by chlorides due easy breaking down of the protective layer formed on the surface of magnesium alloys [30], 0.9 wt.% NaCl solution was chosen as the corrosive media in this study. Briefly, structural examinations, corrosion and corrosive-wear tests were done on the MAO coatings synthesized in dual electrolytes over AZ91 Mg alloy, which is a low cost and widely used one.

2.2 Experimental Procedures

Samples of AZ91 magnesium alloy (Al 9.6 wt.%, Zn 0.7 wt.%, Si 0.5 wt.%, others $\leq$ 0.3 wt.%, Mg balance) composed of α -Mg and β -Mg₁₇Al₁₂ phases, having diameter of 34 mm and height of 3.7 mm were used in this study after cutting them in half along the diameter (i.e. semi-circular geometry). Then they were ground up to grit of 2500 by SiC abrasive papers, then rinsed with ethanol and dried in warm air prior to MAO process.

2.2.1 MAO process

The equipment for MAO process consisted of a DC bi-pulsed power supply, a stainless steel container, a stirring system and external cooling device that maintained the solution temperature below 25 °C. The MAO process was employed for 5 min under a constant voltage regime at a positive voltage of 450 and a negative voltage of 80 V. The frequency and duty cycle ratio during MAO process was kept at 500 Hz and 40%, respectively. During MAO treatment, variation of current densities was continuously recorded with a sampling time of 750 ms by using a memory recorder system (Hioki, Memory Hicorder 8808).

In this study, aluminate-based electrolyte consisting of 10 g/l NaAlO₂ and 2 g/l KOH has been used as the reference electrolyte. Dual electrolytes have been prepared with the addition of phosphate in the form of Na₃PO₄ into the reference electrolyte at concentrations of 5 and 10 g/l. The codes, compositions, conductivities and pH values of electrolytes are listed in Table 2.1.

Table 2.1 : Description of the electrolytes used in this study.

Code	Components	Concentration (g/l)	pH	Conductivity (mS/cm)
Al	NaAlO ₂	10	12.48	16.55
	KOH	2		
AlP5	NaAlO ₂	10	12.47	20.92
	KOH	2		
	Na ₃ PO ₄	5		
AlP10	NaAlO ₂	10	12.47	25.43
	KOH	2		
	Na ₃ PO ₄	10		

Appearance of the samples before and after MAO process along with their average surface roughness (Ra) and average thickness values of the coatings determined by a

2-D surface profilometer (Veeco Dektak 6M) and an eddy current thickness gauge (Fischer Dualscope), respectively, are displayed in Fig. 2.1. Application of MAO process in Na_3PO_4 containing electrolyte changed the colour of the samples from bluish to dark grey along with an increment in the surface roughness. As compared to sample MAO'ed in ALP5 electrolyte, the sample MAO'ed in ALP10 electrolyte covered with much thicker and rougher coating. Hence, Na_3PO_4 concentration in the electrolyte was limited to maximum 10 g/l in the present study. Hereafter, original Mg alloy and samples MAO'ed in Al electrolyte, 5 and 10 g/l Na_3PO_4 containing electrolytes are referred to as AZ91, Al, ALP5 and ALP10 samples, respectively.

(a) 	(b) 	(c) 	(d) 
Ra: $0.14 \pm 0.02 \mu\text{m}$	$0.51 \pm 0.05 \mu\text{m}$	$0.54 \pm 0.06 \mu\text{m}$	$1.46 \pm 0.11 \mu\text{m}$
Coating thickness: $10.3 \pm 0.6 \mu\text{m}$		$13.2 \pm 1.6 \mu\text{m}$	$33.5 \pm 3.5 \mu\text{m}$

Figure 2.1 : Surface appearances, average surface roughness (Ra) and average MAO coating thickness values of the (a) AZ91, (b) Al, (c) ALP5 and (d) ALP10 samples.

2.2.2 Microstructural characterization

Phase composition of the MAO'ed samples was investigated by X-ray diffraction technique (XRD, GBC MMA 027) using $\text{Cu-K}\alpha$ radiation at 35 kV and 28.5 mA with a scan range between $15-75^\circ$ at a step of 0.020° and a scanning speed of $1^\circ/\text{min}$. Functional group analyses on MAO'ed samples were carried out by using a Fourier transform infrared spectroscope (FTIR, Bruker Alpha-T) at ATR mode. Background was calibrated by a reference sample coated with Au. Spectra were recorded in between $4000-500 \text{ cm}^{-1}$ at 4 cm^{-1} with a scanning time of 24 scan/min. Surface and cross-sectional morphologies of the samples were investigated by a SEM (Hitachi TM-1000). High magnification surface SEM examination and elemental composition analysis were conducted by a field emission SEM (Philips SFEG XL30) equipped with energy dispersive X-ray (EDX) spectrometer.

2.2.3 Corrosion tests

Corrosion performance of the three identical samples (of each state) were evaluated by immersing in 40 ml of 0.9 wt.% NaCl solution at ambient temperature up to 7 days. Each day of the immersion period, the samples were ultrasonically cleaned in distilled

water, dried in oven and then, the mass loss of the samples were measured by an electronic balance having accuracy of 0.1 mg. The surface appearance of the samples was observed by a camera for 3, 5 and 7 days of immersion period. Additionally SEM examinations, EDS and XRD analyses have been conducted on the samples corroded for 7 days.

2.2.4 Wear test

Wear tests were performed using a ball-on-flat reciprocating tribometer (Tribotech Oscillating Tribotester) and an alumina ball (purity 99.80%, Ra: 0.02, 1900 HV) with a diameter of 6 mm used as counterface. The wear tests were performed at ambient temperature under dry and wet (in 0.9 wt.% NaCl solution) sliding condition. Wet sliding wear tests were run in 15 ml of 0.9 wt.% NaCl solution, while the humidity was kept at 40% during dry sliding wear tests. The sliding speed, sliding distance, length of the wear track were 4 mm/s, 100 m and 2 mm, respectively. Wear testing loads were 1 and 3 N. The friction coefficients were obtained directly from the software of the tribometer. Following the wear tests, width and depth of the wear tracks were measured by a 2-D surface profilometer (Veeco Dektak 6M). Surface and cross section examinations were conducted on the wear tracks by an EDX equipped SEM.

2.3 Results and Discussion

2.3.1 Current density response

The variations of the current density during MAO process employed in different electrolytes (Al, AlP5 and AlP10) are illustrated in Fig. 2.2. MAO started with a sharp increase in current density at a rate of $0.05 \text{ A/cm}^2\text{s}$ and reached to maximum current density values of about 0.6 A/cm^2 for the AlP5 sample and about 0.9 A/cm^2 for Al and AlP10 samples after about 15 s from the start-up. Later current density decreased to the values of about 0.4, 0.55 and 0.75 A/cm^2 for Al, AlP5 and AlP10, respectively, till about 60 s of processing time. Following this, the current densities decreased rather gradually so that by the end of the MAO process (i.e. 300 s from the start up) the current densities of 0.25, 0.45 and 0.65 A/cm^2 , were recorded for Al, AlP5 and AlP10, respectively.

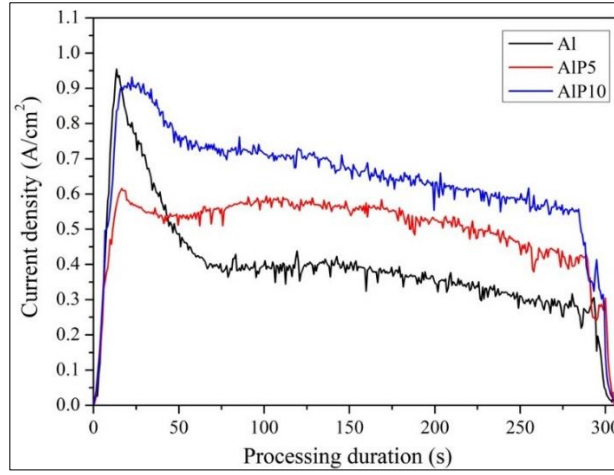


Figure 2.2 : Variation of current density during MAO processing of the examined samples.

It is well documented that formation of MAO coating [10,38,51–53] starts with covering of the substrate with a thin passive oxide layer (i.e. MgO for Mg alloys) similar to conventional anodization, which corresponds to the sharp current density increase region in Fig. 2.2. Upon breakdown of thin oxide layer, current density tends to decrease, while white coloured small sparks appear all over surface of the substrate. Afterwards, current density gradually decrease (after remaining stable for a certain duration in some cases) due to the increasing intensity and life span of the white colored sparks during growth of the oxide layer. Later, white colored sparks are replaced by orange colored ones having much larger size, much longer life span and ability for deeper penetration into the growing oxide layer. Sparking during MAO is the result of discharge channel formation within the oxide layer so that some substances from the inner regions of the oxide layer can migrate outwards through these discharge channels if they are big enough. Therefore, the surface of the MAO coatings can be characterized by its porous and relatively rough nature. Since their sizes are in μm range these pores will be referred to as micro-pores, hereafter. Although the main constituent of MAO coatings developed over Mg alloys is MgO, some other phases can also be present in it, as the result of the incorporation of species of the electrolyte [38,44,54,55]. When the main constituents of the electrolyte used in this study (NaAlO_2 and Na_3PO_4) are of concern, incorporation of aluminate (AlO_2^-) and phosphate (PO_4^{3-}) into the growing MgO oxide layer to form aluminate and phosphate based compounds are favourable [47,52].

As can be seen in Table 2.1, addition of Na_3PO_4 increased electrical conductivity of the electrolyte and caused progress of MAO process at higher current density levels

(Fig. 2.2), where intense sparking is visible. It is suggested that mobility of AlO_2^- and PO_4^{3-} ions (formed by decomposition of NaAlO_2 and Na_3PO_4) towards AZ91 substrate were accelerated in the electrolyte having higher electrical conductivity. Rapid incorporation of these ionic species into the growing MgO can accelerate growth of the oxide layer. When the average thickness values of the fabricated coatings (Fig. 2.1) and the conductivity of the relevant electrolyte used in the MAO process (Table 2.1) are considered it can apparently be seen that electrical conductivity of electrolyte has significant influence on the thickness of the MAO coating, whereby the thickness increases with the increasing conductivity of the electrolyte. In association with its highest thickness, roughest coating formed over the AlP10 sample (Fig. 2.1).

2.3.2 Structural features of the coatings

The XRD and FTIR spectra given in Fig. 2.3a and b, respectively. XRD studies demonstrate that the MAO coatings fabricated in the examined electrolytes composed mainly of MgO and spinel MgAl_2O_4 phases. Additionally, peaks related to the AZ91 alloy (α -Mg and β - $\text{Mg}_{17}\text{Al}_{12}$ phases) are also present in all XRD spectra due to penetration of X-ray through MAO coatings. Unlike Al and AlP5 samples, on the XRD spectrum of AlP10 sample, weak peaks of AlPO_4 phase have also been detected within 2θ range of 16 and 32° , where the highest intensity peaks of AlPO_4 phase lie [56,57]. Intensity of peaks corresponding to MgO phase increased with increasing concentration of Na_3PO_4 in the reference electrolyte (thus, in the order of Al, AlP5 and AlP10 coded electrolytes), while peak intensities of MgAl_2O_4 , α -Mg and β - $\text{Mg}_{17}\text{Al}_{12}$ phases decreased conversely.

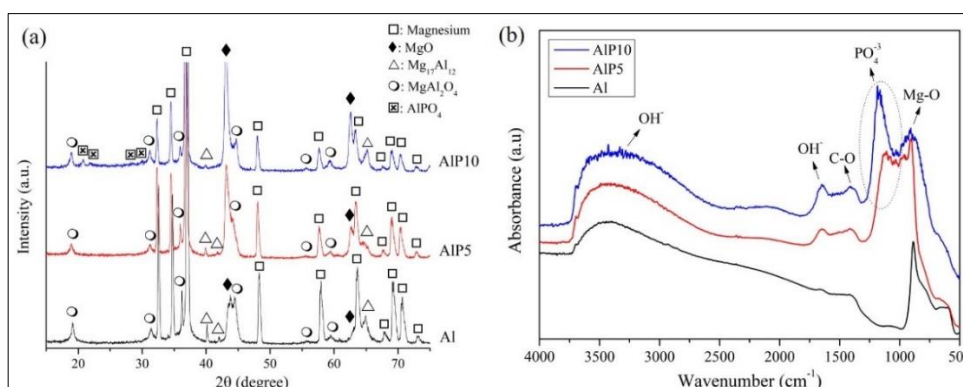


Figure 2.3 : (a) XRD and (b) FTIR spectra of Al, AlP5 and AlP10 samples.

On the FTIR spectra of MAO'ed samples (Fig. 2.3b), the broad absorption band between 3200 and 3700 cm^{-1} is a characteristic that can be assigned to the free OH^-

stretch of the water molecules absorbed on the sample surface. The peaks at about 880 cm^{-1} and about 694 cm^{-1} can be assigned to metal-oxygen stretching vibration of Mg-O [58,59]. Two adsorption peaks appeared at 1424 and 1464 cm^{-1} on the FTIR spectra of the examined samples can be attributed to the carboxyl group symmetric stretching vibrations [60]. Presence of bending and stretching modes of PO_4^{3-} bands at $900\text{-}1200\text{ cm}^{-1}$ [61] on the FTIR spectra of the AlP5 and AlP10 samples is clearly identified as the indication of incorporation of PO_4^{3-} ions from the electrolyte into the MAO coating. Hence, darkening of the MAO coatings fabricated in Na_3PO_4 containing electrolytes (Fig. 2.1) is suggested to be the result of presence of phosphate containing phase (i.e. AlPO_4) in the MAO coatings. It should be noted that, absence of AlPO_4 peaks on the XRD spectra of the AlP5 sample (Fig. 2.3a) can be attributed to its low fraction beyond the detectable range of XRD.

Surface SEM micrographs and relevant elemental compositions of the MAO coatings fabricated on AZ91 substrate are shown in Fig. 2.4. Surfaces of the coatings contained micro-pores and micro-cracks. Increase of Na_3PO_4 concentration in the reference electrolyte caused a reduction in the number of micro-pores and an increase in their size, while making micro-cracks more visible. In association with enlargement of the sparks at higher current densities (Fig. 2.2) larger discharge channels formation in AlP10 electrolyte imposed bigger micro-pores on the surface of the relevant MAO coating (Fig. 2.4). In addition to the larger pores, existence of deeper cracks on the surface of AlP10 sample can be attributed to high energy input arising from high current density generating higher thermal gradient/stress during MAO process [62]. Moreover, nano-scale deposits in whisker morphology were also detected on the surfaces of MAO coatings at higher magnifications with increasing Na_3PO_4 concentration of the reference electrolyte i.e. more apparent for AlP10 samples.

EDS analyses conducted on the surfaces revealed that all three MAO coatings consisted of Mg, Al, and O as the main elements along with Na and small amounts of K. Addition of Na_3PO_4 at concentrations of 5 and 10 g/l into the reference electrolyte resulted in incorporation of P into the MAO coatings of AlP5 and AlP10 samples as 2.94 and 7.41 wt.%, respectively. Increased Na_3PO_4 concentration in reference electrolyte also caused corresponding decrease in proportion of Al content (from 32.92 wt.% to 16.81 wt.%), while leading to an increase in Na content (from 0.20 to 3.43 wt.%) in the coating. It should be mentioned that many attempts to determine the sole

composition of whisker like deposits, detected on the surface of AlP10 samples, were unsuccessful owing to their nano-size nature.

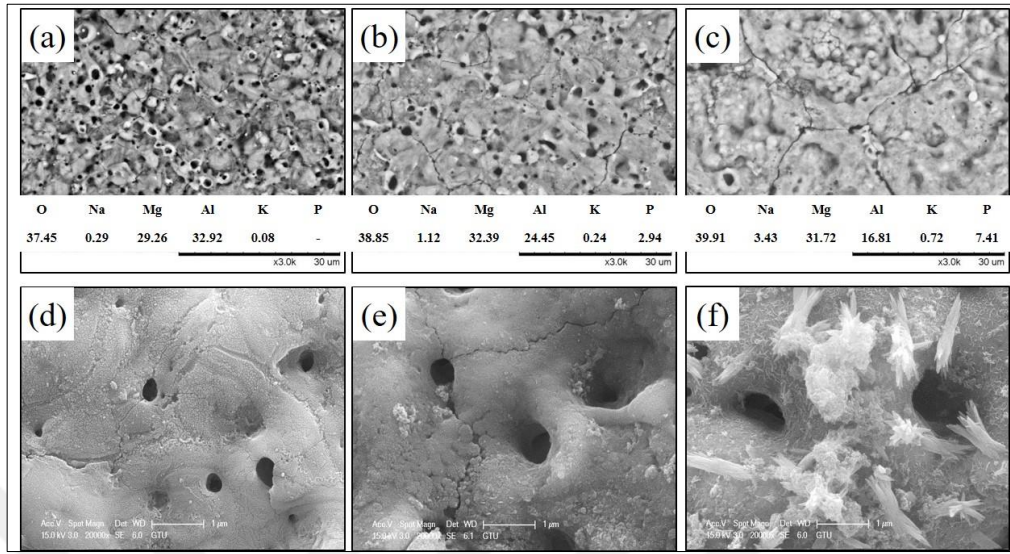


Figure 2.4 : Surface SEM micrographs of (a, d) Al, (b, e) AlP5 and (c, f) AlP10 samples along with the results of EDX analysis.

Cross-sectional SEM micrographs of the examined MAO coatings along with EDS elemental mapping of the main elements are shown in Fig. 2.5. Along with increment of coating thickness by increasing concentration of Na_3PO_4 in the reference electrolyte, the uniformity and regularity of the interface between coating and substrate is deteriorated, which can be associated with an increase in standard deviation of coating thickness values (Fig. 2.1). Independently of Na_3PO_4 concentration in the electrolyte, inner layers of the MAO coatings were relatively compact, when compared to the outer layers. Discharge channels elongated towards the surface are more visible within the outer layer of the AlP10 sample.

Elemental mapping revealed that outer and inner layers of the MAO coatings have different compositions, mainly in terms of enrichment of Al and Mg, respectively. According to the results of the XRD analyses (Fig. 2.3a), Al enriched outer layers of the MAO coatings are rich in spinel MgAl_2O_4 , while its Mg enriched inner layer is dominated by MgO. In case of the coating fabricated in the Al coded electrolyte as seen in Fig. 2.5a, Al enriched outer layer was nearly half of the thickness of the MAO coating, however the coatings fabricated in AlP5 and AlP10 coded electrolytes consisted of relatively thicker Mg enriched inner layers as compared to Al enriched outer layers. For this reason, more intense MgO peaks appeared on the XRD spectra (while intensity of MgAl_2O_4 peaks were decreasing) of the MAO coating fabricated in

Na_3PO_4 containing electrolytes (Fig. 2.3a). Moreover, P was distributed throughout the thickness of the coatings fabricated in the ALP5 electrolytes, while it was mostly segregated in the outer layer of the coating fabricated in the ALP10 electrolyte (Figs. 2.5b and c).

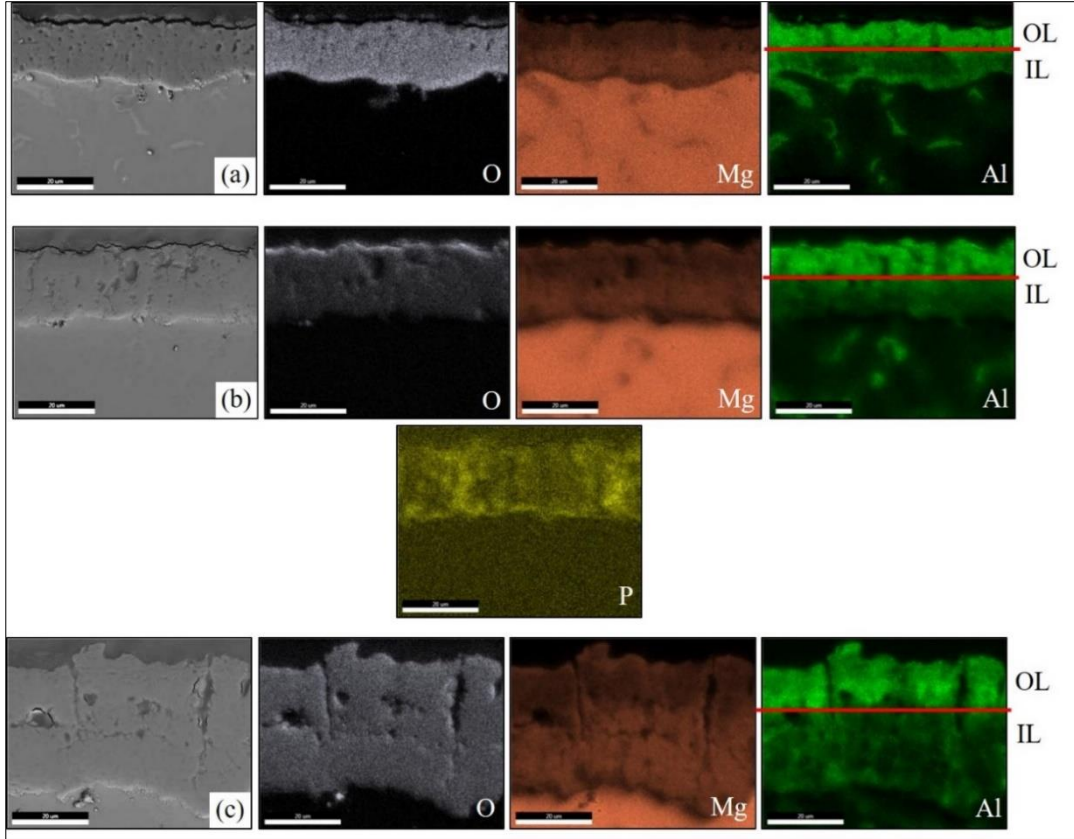


Figure 2.5 : Cross-section elemental mapping of (a) Al, (b) ALP5 and (c) ALP10 samples (OL and IL are showing outer Al rich and inner Mg rich layers, respectively).

It is well established that MAO of Mg alloys starts with the formation of MgO because of outward migration of Mg^{2+} ions from the substrate (i.e. AZ91 Mg alloy in this study), which then react with OH^- ions at the metal/electrolyte interface. Owing to the unstable nature of $\text{Mg}(\text{OH})_2$ formed on the metal surface, it simultaneously tends to dehydrate to MgO under high heat input imposed during the MAO process [30,38,45]. Formation of spinel MgAl_2O_4 containing Al enriched outer layer within MAO coating can be explained by transfer of AlO_2^- ions, which were generated by dissolution of NaAlO_2 in the electrolyte, towards the growing MgO layer. Thus the reaction between Mg^{2+} ions released from the substrate and these AlO_2^- ions [30,40] favors MgAl_2O_4 containing outermost surface layer within the MAO coating.

On the other hand, Dong et al. [63], who studied MAO of AM60 grade Mg alloy in aluminate free phosphate-based electrolyte, explained AlPO_4 formation within the MAO coating by the reaction of PO_4^{3-} ions with Al^{3+} ions released from the substrate (at a higher migration rate than Mg^{2+} ions). The presence of P even at the deeper regions of the MAO coating of the ALP5 sample (Fig. 2.5b) indicates that incorporation of PO_4^{3-} ions into the growing MgO layer has started at the early stages of the MAO process and formed homogeneously distributed fine AlPO_4 phase within the coating by following the mechanism proposed by Dong et al. [63]. Detection of P mostly at the outer layer of MAO coating of ALP10 sample (with P deficient inner layer) can be associated with the excess incorporation of PO_4^{3-} ions assisting formation of larger discharge channels within the MgO layer. During rapid growth of the MgO layer at higher current density levels (Fig. 2.2), AlPO_4 formed in the inner regions of the MAO coating were easily transferred outwards through these discharge channels and accumulate mostly at the surroundings of the micro-pores (volcano effect). As the result of this, not only P enriched outer layer (Fig. 2.5c) but also the highest surface roughness have been obtained from the ALP10 sample (Fig. 2.1). Moreover, Na enrichment at the outermost surface of ALP10 samples can be attributed to the incorporation of Na^+ ions formed upon the dissolution of Na_3PO_4 in the electrolyte in the MAO coating simultaneously with the PO_4^{3-} ions favouring the formation of nano-whiskers on the surface as can be seen in Fig. 2.5c.

2.3.3 Corrosion behaviour

General surface appearances of AZ91 and MAO'ed samples after corrosion tests conducted by immersing in 0.9 wt.% NaCl up to 7 days are presented in Fig. 2.6. As a result of corrosion attack, surface of the AZ91 sample heavily deteriorated even after 3 days of immersion. Longer immersion times imposed rough and hollow pit containing surface topography. Surface degradation of the Al sample was almost negligible as compared to the AZ91 sample, if the corrosion pathways appeared on the surface were ignored. It is clearly evident that corrosion pathways tended to progress and cover wider surface area at longer immersion durations. On the surfaces of the ALP5 and ALP10 samples, indications of corrosion attack were not clearly identified with the exceptions of very fine pits detected mostly at the edges of the samples immersed for 7 days.

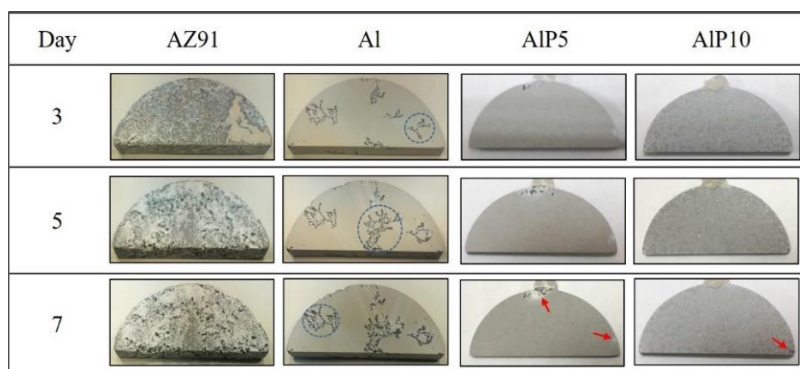


Figure 2.6 : Surface appearances of samples after immersion in NaCl solution up to 7 days (Circles show corrosion pathways and arrows show localized corrosion attacks).

Surface SEM micrographs and XRD spectra of MAO samples immersed in 0.9 wt.% NaCl solution for 7 days are presented in Fig. 2.7. The surface of the Al sample exhibited completely different characteristics than its uncorroded state (Fig. 2.6a and d) so that holding in 0.9 wt.% NaCl solution for 7 days caused complete covering of the surface with deposits identified as $\text{Mg}(\text{OH})_2$ by XRD analysis. Other peaks on the relevant XRD spectrum were identical with the spectrum of uncorroded state of the Al sample (Fig. 2.3a). When the morphology of the corrosion pathways is of concern, corrosion attack proceeded through the coating towards the substrate. Unlike Al sample, no deposits were observed on the surfaces of the AIP5 and AIP10 samples immersed for 7 days. Hence, no additional peaks different from XRD spectra of the uncorroded state of AIP5 and AIP10 samples (Fig. 2.3a) have been identified on the relevant XRD spectra.

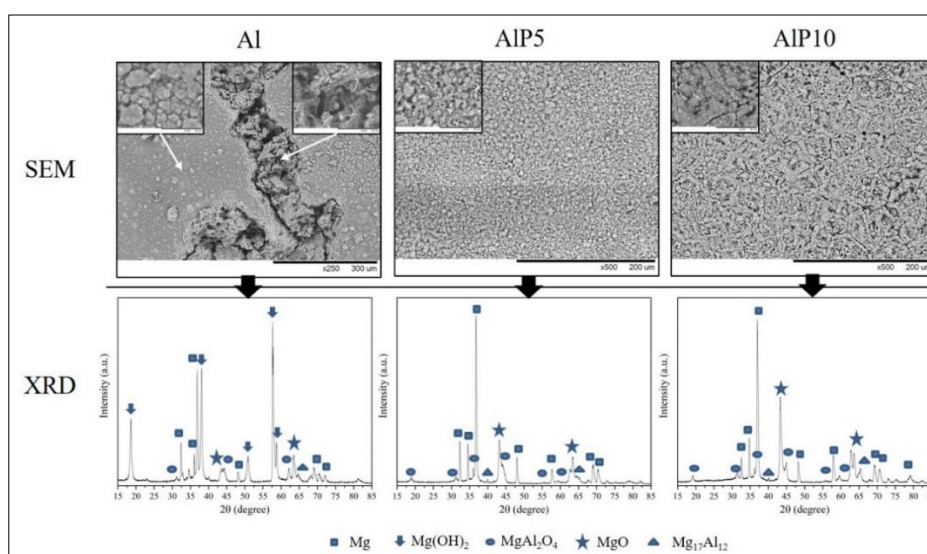


Figure 2.7 : Surface SEM micrographs and XRD spectra of MAO'ed samples held in 0.9 wt.% NaCl solution for 7 days.

The cross-sectional SEM micrographs of the MAO samples following immersion in 0.9 wt.% NaCl solution for 7 days are presented in Fig. 2.8. As also confirmed by EDS analyses, Mg(OH)_2 covered the surface of the Al sample with enrichment of Cl as a thick layer (Point 1 in Fig. 2.8a) at a thickness of about 15 μm . High magnification SEM examinations showed that micro-pore channels (noted with arrows in Fig. 2.8b) of the coating were also filled with Mg(OH)_2 indicating penetration of corrosive solution through coating towards the AZ91 substrate. EDS analyses conducted along the depth of corrosion pathway revealed that corrosion products mostly consisted of Mg and O, which hinted towards the presence of Mg(OH)_2 right underneath the corrosion pathway (Point 2 in Fig. 2.8a). No evidence of corrosion product have been observed on the cross-sections of the AlP5 and AlP10 samples (Fig. 2.8c and d, respectively) in accordance with their surface SEM examinations and XRD analyses (Fig. 2.7).

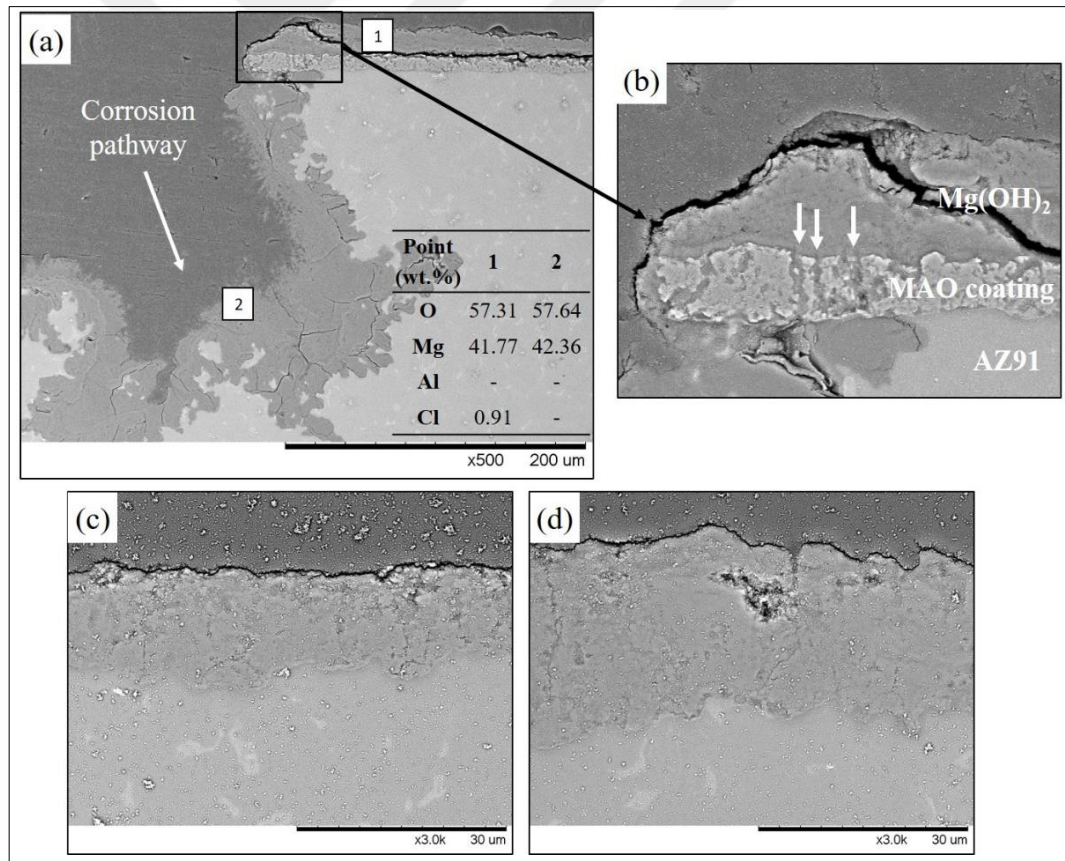


Figure 2.8 : Cross-sectional SEM micrographs of (a,b) Al, (c) AlP5 and (d) AlP10 samples after immersion in 0.9 wt.% NaCl solution for 7 days (arrows are showing penetration of the solution into the discharge channels).

The specific mass losses of the AZ91 and MAO'ed samples during corrosion tests are presented in Fig. 2.9 as a function of immersion time. Specific mass loss values were

calculated by dividing the mass loss values of the samples to their total surface areas in the unit of mg/cm^2 . Longer immersion durations in the solution yielded linearly higher mass losses for all the examined samples due to increasing severity of the corrosion attack. When AZ91 sample is taken as a reference, application of MAO process provided a resistance against corrosion attack. Indeed, ALP5 and ALP10 samples exhibited better corrosion resistance than the Al samples. However there was no distinguishable difference between ALP5 and ALP10 samples in terms of corrosion mass loss.

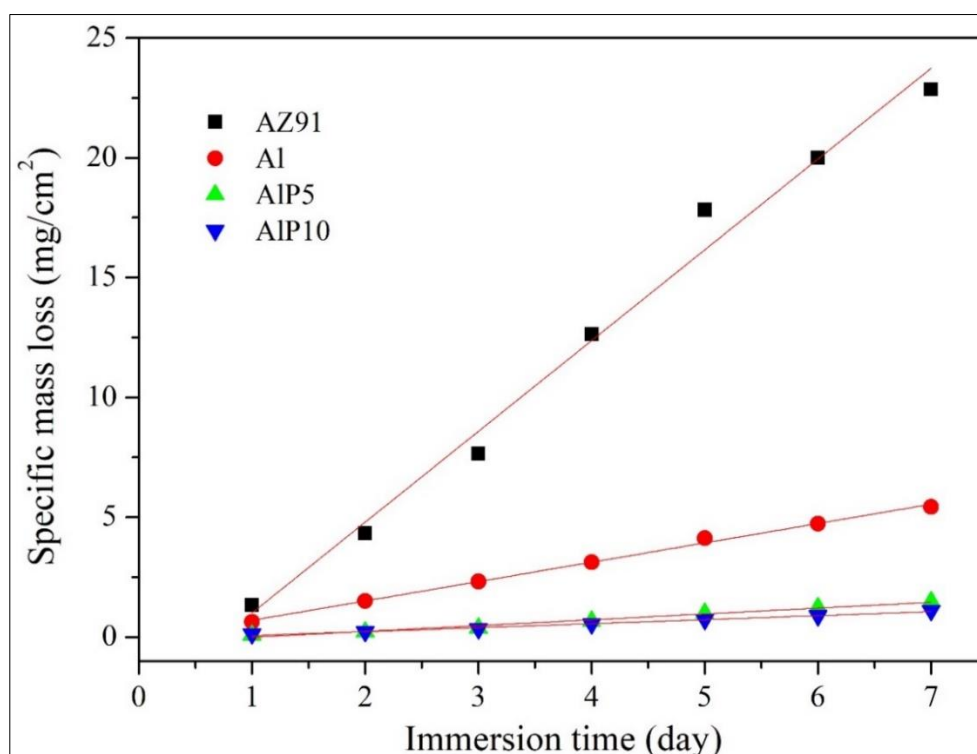


Figure 2.9 : Specific mass loss of the examined samples against immersion time in 0.9 wt.% NaCl solution.

The mechanism for the rapid progress of corrosion in Mg and its alloys is well known i.e. the corrosion starts with formation of MgO on the surface which tends to react with water (even with moisture in air) to form $\text{Mg}(\text{OH})_2$. Owing to slight solubility of $\text{Mg}(\text{OH})_2$ in water, this layer does not provide long term protection. Moreover, the presence of corrosive ions (such as chloride, bromide, sulfate, and chlorate) in the media breaks down this $\text{Mg}(\text{OH})_2$ layer and thereby accelerates the progress of corrosion [64]. While the enhancement in the corrosion resistance of the examined AZ91 alloy by MAO process can be explained in terms of the shielding characteristics of the fabricated coating preventing the direct contact between AZ91 substrate and the

corrosive media. However, the nature of the MAO coatings (phase structure and morphology etc.) played a crucial role in the effectiveness of their shielding behaviour. In case of the Al sample having a MAO coating consisting of MgO and stable spinal MgAl_2O_4 , the progress of corrosion is suggested to be controlled by MgO component of the coating, which is more susceptible to react with water to form $\text{Mg}(\text{OH})_2$. Later, this $\text{Mg}(\text{OH})_2$ layer reacts with the Cl^- ions in the corrosive media (as discussed above) to form highly soluble MgCl_2 [65]. This mechanism is expected to result in homogenous corrosion on the MAO coating, however in Al samples corrosion was not homogenous rather it appeared to have preferred pathways (Figs. 2.6-2.8). The formation of these pathways can be explained in terms of penetration of the Cl^- ions into the coating along the favourable discharge channels (i.e. through thickness micro-pores, as shown by the arrows in Fig. 2.8b) forming soluble MgCl_2 . This explains localized degradation rather than homogenous corrosion attack over the surface.

In case of ALP5 and ALP10 samples, their better corrosion resistance than Al sample can be attributed to the presence of AlPO_4 in their coating. Owing to the lower solubility product constant (k_{sp}) of AlPO_4 in aqueous solution ($k_{sp} \sim 10^{-20}$), dissolution of slightly soluble MgO was retarded as it is shielded by AlPO_4 [66]. Thus, despite the presence of larger micro pores and cracks, phosphate containing compounds enhance the chemical stability of MAO coating by inhibiting sequential formation of MgOH_2 and MgCl_2 .

2.3.4 Wear behaviour

Representative 2-D profiles of the wear tracks formed on the surfaces of the samples tested in dry and wet (0.9 wt.% NaCl solution) sliding conditions under test load of 3 N are presented in Fig. 2.10 along with the average wear track areas. Under dry sliding conditions wear loss of MAO'ed samples were almost negligible as compared to the AZ91 alloy so that depths of the wear tracks are in the range of surface roughness of the MAO coatings. However, remarkable different wear loss values has been measured for the MAO'ed samples tested in wet sliding condition. While wear track depths of ALP5 and ALP10 samples were within the thicknesses of their MAO coatings (about 13 and 33 μm , respectively), wear track depth of Al sample (about 25 μm) was well beyond the coating thickness (about 10 μm).

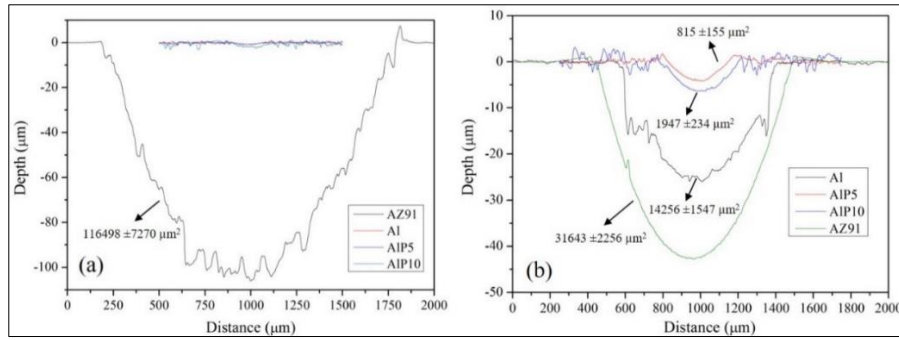


Figure 2.10 : Representative 2-D profiles of the wear tracks developed during (a) dry and (b) wet sliding conditions under test load of 3 N.

The worn surface appearances of the examined samples are presented in Fig. 2.11. For AZ91 alloy tested under dry sliding conditions the worn surface consisted of grooves aligned in the sliding direction indicating the dominant wear mechanism as micro-abrasion. On the worn surface of the MAO samples, no evidence of scratching and deformation have been identified as the rubbing action of the counterface eliminated the asperities and smoothed the contact surfaces. The worn surfaces of the AZ91 and Al samples tested in wet sliding conditions exhibited similar topography in terms of accumulation of deposits. Unlike AZ91 and Al samples, worn surfaces of AlP5 and AlP10 samples are very smooth without any evidence of accumulated deposits on the worn surfaces.

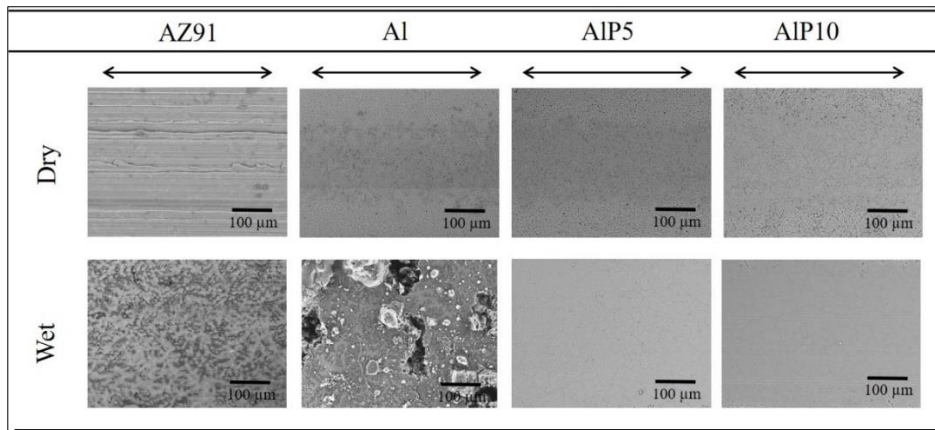


Figure 2.11 : SEM micrographs of wear tracks during dry and wet sliding conditions under test load of 3 N.

Additional SEM examinations have been conducted on the transverse section of the wear track of Al and AlP5 samples worn under wet sliding conditions (Fig. 2.12). The transverse section SEM appearance is completely different for Al and AlP5 samples in terms of presence of deposits in accordance with their worn surface SEM appearances (Fig. 2.11). The EDS analyses conducted (from the worn surface) on the

piles of corrosion products revealed that they are rich in Cl indicating formation of $MgCl_2$ similar to corrosion mechanism explained above. While the smooth regions of the wear tracks of Al (other than piles) sample and worn surface of the AlP5 are Cl deficient. Surface and transverse section analysis of the wear tracks confirmed that on the Al samples the wear progressed by corrosive wear mechanism in wet sliding conditions unlike AlP5 and AlP10 samples.

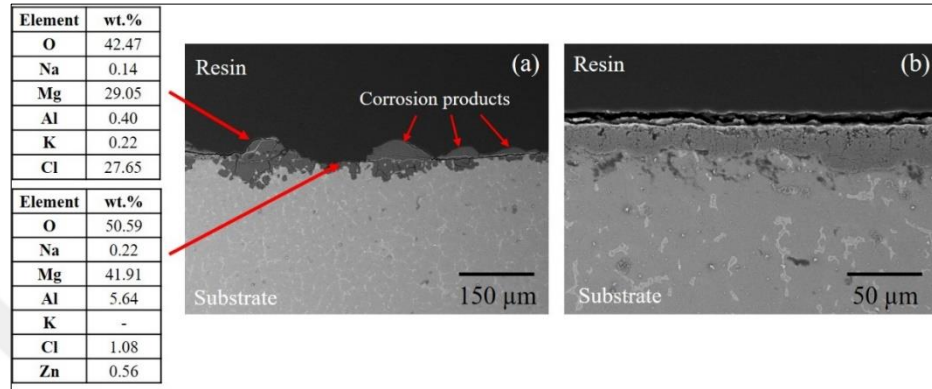


Figure 2.12 : Cross-sectional SEM micrographs of the wear tracks developed on the surfaces of the (a) Al, with EDS elemental analyses of corrosion products and (b) AlP5 samples under wet sliding conditions at test load of 3 N.

The friction curves of the examined samples tested under dry and wet sliding conditions, at 3 N testing load, are shown in Fig. 13a and b, respectively. In dry sliding condition, coefficient of friction (CoF) of AZ91, Al and AlP5 samples remained almost stable in the range of 0.25-0.35. While, CoF of AlP10 continuously increased and reached a value of 0.5 by the end of the wear test. In case of wet sliding conditions, CoF steadied at lower values (i.e. 0.05 to 0.35). Whereas reduction in CoF is much more notable for AZ91 and Al samples (whereby it reduced from 0.3 to 0.05 from dry to wet sliding conditions).

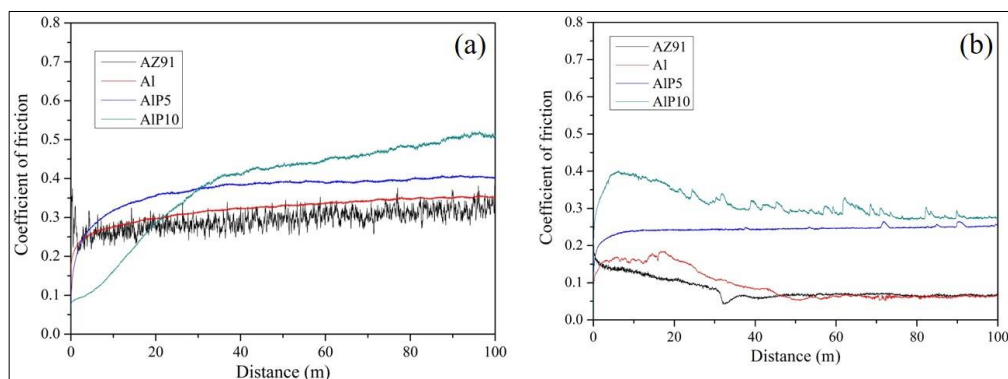


Figure 2.13 : Friction curves of the examined samples tested under 3 N in (a) dry and (b) wet sliding conditions.

Since the wear track depth of the Al sample tested under 3 N testing load (Fig. 2.10b) in wet sliding condition is beyond the thickness of the coating so it was decided to conduct wet sliding wear tests at the lowest capacity of the wear tester i.e. 1 N. The results of these tests are presented in Fig. 2.14 as 2-D profiles of the wear tracks, friction curves and worn surface SEM appearances. As can be seen from Fig. 14a, the depth of the wear tracks of Al samples is still bigger than other samples but it is almost within MAO coating thickness. When the wear track areas are considered, AZ91 has the largest wear track area while for Al sample it is one third of it. AlP5 and Al10 samples have the lowest wear track areas. The friction curves obtained under 1 N testing load (Fig. 2.14b) exhibited almost similar characteristics to those of obtained under 3 N testing load (Fig. 2.13b) and minimum CoF values were again obtained for AZ91 and Al samples. As far as the worn surface SEM micrographs (Fig. 2.14c) are concern, worn surfaces showed identical appearance to that of worn surfaces obtained from 3 N testing load (Fig. 2.11). On the worn surface of the Al sample, some local delamination was detected is in accordance with the contoured appearance of their 2-D profile (Fig. 2.14a). This observation indicates the contribution of adhesive wear as an additional mechanism for Al sample.

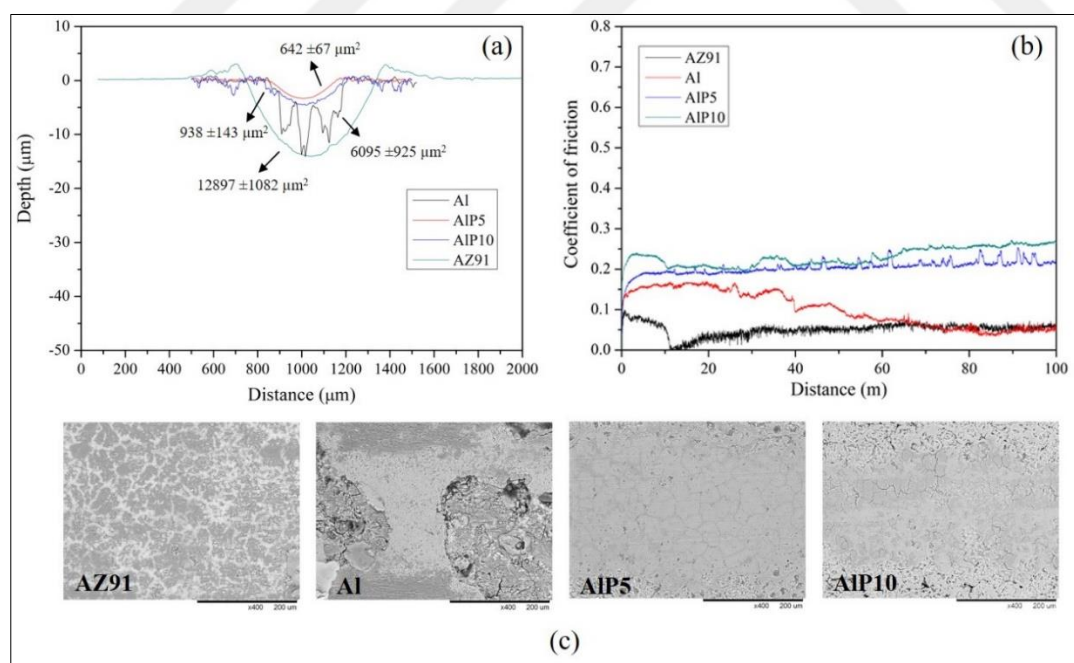


Figure 2.14 : (a) Representative wear track 2-D profiles, (b) friction curves and (c) worn surface SEM micrographs of the examined samples tested under test load of 1 N in wet sliding conditions.

Regardless from the wear test load, MAO'ed samples can be rank as AlP5, AlP10 and Al with respect to the increase in wear loss (i.e. wear track areas of calculated from the 2-D profiles presented in Figs. 2.10b and 2.14a) under wet sliding conditions. Higher wear loss of AlP10 sample than that of AlP5 sample can be associated with its higher surface roughness (Fig. 2.1) and/or progress of wear on the P deficient inner layer of the coating after removal of P rich outermost layer (Fig. 2.5c), which in turn tend to increase the contribution of corrosion towards wear mechanism.

On the basis of above explanations, poor wear resistance and lower CoF of Al sample is due to the acceleration of corrosion under sliding contact so that the rubbing action removes the corrosion products ($\text{Mg}(\text{OH})_2$ and MgCl_2), leading to perpetual exposure of the fresh surface to the corrosive action of the media. In this respect, remarkable reduction in CoF during wet sliding conditions can be associated to the lubricious nature of these corrosion products [67,68]. The discrepancy between CoF and wear loss for Al sample can be explained by the penetration of corrosion attack through the micro-pores (beneath the contact surface) causing material removal by adhesion. Such discrepancy between CoF and wear loss is not observed for AZ91 sample due to the absence of adhesive wear mechanism as there are no pores for the penetration of corrosive media beneath the contact surface. For AlP5 and AlP10 samples, there is negligible contribution of corrosion to the progress of wear as they exhibited much better wear resistance than Al sample in wet conditions thanks to their enhanced corrosion resistance.

A mutual comparison for AlP5 and AlP10 samples in wet sliding condition showed that the AlP5 having lower surface roughness and uniform distribution of P within the coating exhibited better wear performance. Thus, surface roughness and chemical homogeneity (i.e. P distribution throughout the thickness) of the MAO coatings synthesized in phosphate based chemicals added electrolytes are much more critical than the structural defects (such as micro-pores and cracks) for enhanced wear performance in moist environments.

2.4 Conclusion

In the present study, characteristics of the MAO coatings synthesized on AZ91 Mg alloy in a reference aluminate based (NaAlO_2) and, 5 and 10 g/l phosphate (Na_3PO_4)

added electrolytes were examined. Findings of the present study can be summarized as follows:

1. The MAO coating synthesized in the reference electrolyte was composed of MgO and MgAl_2O_4 phases. Na_3PO_4 addition into the reference electrolyte led to AlPO_4 presence within the coating as a new phase and caused fabrication of remarkably thicker and rougher MAO coating especially at concentration of 10 g/l.
2. MAO coatings fabricated in all electrolytes consisted of two layers in terms of enrichment of Al and Mg, indicating the outer layers are rich in spinel MgAl_2O_4 , while inner layers are dominated by MgO. However, higher concentration of Na_3PO_4 in the reference electrolyte (i.e. 10 g/l) deteriorated the homogenous distribution AlPO_4 and favoured its segregation mostly at the outer layer of the MAO coating.
3. MAO coating fabricated in all electrolytes enhanced the corrosion and wear resistances of the AZ91 alloy. When compared to the reference electrolyte, Na_3PO_4 added electrolytes caused fabrication of MAO coatings exhibiting much better corrosion and corrosion-wear resistances in 0.9 wt.% NaCl solution due to the inhibition of formation of corrosion products ($\text{Mg}(\text{OH})_2$ and MgCl_2) by AlPO_4 . Increase of Na_3PO_4 concentration of the electrolyte from 5 g/l to 10 g/l slightly deteriorated the corrosion-wear performance of the fabricated MAO coating in association with its higher surface roughness.

2.5 Acknowledgement

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3. A STUDY TO ENHANCE THE MECHANICAL DURABILITY OF THE MAO COATING FABRICATED ON THE 7075 AL ALLOY FOR WEAR-RELATED HIGH TEMPERATURE APPLICATIONS ²

3.1 Introduction

Continuous growth of transportation sector is causing significant increase of greenhouse gas emissions. In this respect, Corporate Average Fuel Economy (CAFE) standards, which was designed to improve vehicle transportation efficiency, aim for an average fuel economy of 40.3 – 41.0 miles per gallon by 2021, and 48.7 – 49.7 miles per gallon by 2025 [69]. For this reason, the substitution of iron-based alloys by light metals became extremely demanding for vehicles to reduce the weight for providing fuel efficiency and limiting the harmful emissions. Among the light metals, aluminium alloys have received the most attention owing to their confirmed properties, such as the high strength-to-weight ratio, good corrosion resistance and excellent formability [6,20,70]. On the other hand, aluminium alloys exhibit low hardness, a high and unstable friction coefficient and poor wear resistance, which seriously restrict their extensive usage. As a technical solution to these drawbacks, the micro-arc oxidation (MAO) process, which forms hard and firmly adhered thick alumina (Al_2O_3)-based coating, has appeared as the most efficient and cost-effective electrochemical surface modification technique for aluminium alloys. In this respect, a vast number of studies reported remarkable enhancement in room temperature (RT) wear resistance of aluminium-based materials after the MAO process [71–77].

However, limited studies are available in the open literature about the high temperature (HT) performance of MAO coatings applied to critical components used at temperatures higher than 250 °C, such as cylinder heads, engine blocks, manifolds and pistons [78–83]. In one of the earliest studies, Lee et al. [84] employed the MAO process in an electrolyte containing NaAlO_2 and Na_2SiO_3 to coat A356/20 vol.% SiCp

² This chapter is based on the paper “F. Muhaffel, M. Baydogan and H. Cimenoglu, A study to enhance the mechanical durability of the MAO coating fabricated on the 7075 Al alloy for wear-related high temperature applications, *Surf. Coatings Technol.* (2020) Article in Press”

composites and studied the wear behaviour using pin-on-disc configuration at RT, 100, and 180 °C with an applied load between 50-400 N against a hardened AISI D2 tool steel disc. They reported that the MAO coating containing Al_2O_3 and $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ (mullite) had a significantly lower wear rate at high temperatures (i.e. 100 and 180 °C) in the severe wear regions for A356/20 vol.% SiCp composites. In another study [85], MAO'ed 2014 Al alloy in a KOH, Na_2HPO_4 , and Na_2SiO_3 containing electrolyte have been subjected to pin-on-disc type wear tests at a load of 2 N against a 6 mm of diameter Al_2O_3 ball at RT, 50, and 200 °C. They observed that the MAO coating that consisted of $\alpha\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$ exhibited a reduction of the wear rate from $4.5 \times 10^{-6} \text{ mm}^3/\text{Nm}$ to $3.5 \times 10^{-6} \text{ mm}^3/\text{Nm}$ with increasing testing temperature from RT to 200 °C. Liu et al. [86], who formed an $\alpha\text{-Al}_2\text{O}_3$ and $\beta\text{-Al}_2\text{O}_3$ containing MAO coating on 2219 Al alloy in an electrolyte consisted of Na_2SiO_3 and KOH, reported a reduction in the wear rate of about 60% against a 4 mm of diameter agate ball as compared to the uncoated alloy tested at 160 °C under the load of 0.5 N. After conducting ball-on-disc wear tests on the MAO coatings, which were fabricated on a 2618 Al alloy in an electrolyte containing Na_2SiO_3 and KOH and were subsequently exposed to ultrasonic cold forging technology, Yi et al. [87] observed about 71% reduction in wear rate compared to the uncoated substrate at RT, 80, 160, and 200 °C against a 4 mm of diameter Al_2O_3 ball under 0.5 N test load. Yang et al. [88], who synthesised an MAO coating composed of $\alpha\text{-Al}_2\text{O}_3$, $\gamma\text{-Al}_2\text{O}_3$ and $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ phases on a 7075 Al alloy in an electrolyte containing Na_2SiO_3 and KOH, found a remarkable enhancement on the wear resistance (about 11 times higher than the uncoated alloy) after the wear tests employed at 300 °C under 5.5 N test load against a 6 mm diameter of ZrO_2 ball. Most recently, Shirani et al. [89] produced an MAO/Chameleon hybrid coating on A356 cast Al alloy via burnishing $\text{MoS}_2/\text{Sb}_2\text{O}_3/\text{graphite}$ layer over the $\gamma\text{-Al}_2\text{O}_3$ -based MAO coating fabricated in an electrolyte containing Na_2SiO_3 and KOH for high temperature applications. The wear tests carried out using pin-on-disc tribometer at temperatures from 25 to 300 °C against 6 mm Si_3N_4 ball at test loads in between 2 and 10 N revealed a reduction in the coefficient of friction (COF) and enhancement in the wear performance when compared to uncoated alloy. However, the wear resistance tended to deteriorate significantly with increasing testing temperature. In these studies, MAO coated aluminium alloys demonstrated much better wear resistance than uncoated alloys at high temperatures (up to 300 °C) while the wear rate of the MAO coatings tended to increase with increasing test temperature.

The enhanced properties of zirconia toughened alumina (ZTA), including high strength, high hardness, high thermal shock resistance, high wear resistance, and the most importantly, higher fracture toughness than monolithic Al_2O_3 [90–94], motivated the authors to tailor the structure of Al_2O_3 -based MAO coatings via participation of zirconia (ZrO_2) particles. This approach came into consideration to benefit of the incorporation of the ceramic particles from the electrolyte into the growing oxide layer during the MAO process [76,95–98]. It is stated in the previous studies that appropriate addition of ZrO_2 into the electrolyte enhanced wear resistance of MAO coating fabricated on Ti6Al4V alloy [99,100]. Furthermore, beneficial effect of ZrO_2 incorporation into the MAO coatings has been reported for biomedical-related applications [101], thermal shock resistance [102], and corrosion protection [103–105]. Different from these works, we aimed to examine the high temperature wear performance of ZrO_2 participated MAO coatings fabricated on Al alloys.

The major concern of this study was weight critical industrial applications needing to use light alloys extensively. In this respect, possibility of extending the service life of Al alloys used in wear-related applications via MAO process to meet the demands of the automotive industry has been focused more specifically. For this purpose, we have fabricated MAO coatings on an extensively used aluminium alloy (with and without participation of ZrO_2) by considering the results of the above mentioned previous works and examined their wear behaviour at room and high temperatures under different maximum contact pressures for various sliding distances. The ultimate goal was estimating the maximum contact pressure that MAO coatings can endure 10^6 contact cycles at 300 °C by using a pin-on-disc wear tester.

3.2 Experimental Procedures

3.2.1 MAO process

In the present study, the MAO process was employed to 7075 Al alloy disc samples having a diameter of 12 mm and a thickness of 3.7 mm. Before the MAO process, samples were grounded using SiC abrasive grinding papers up to a grit size of P2500, then cleaned ultrasonically in ethanol and distilled water, and later dried in the air at RT.

The MAO equipment used in this study consisted of a 30-kW bipolar pulsed DC power supply unit, a stainless steel electrolyte bath, an air pump for stirring the electrolyte and an external cooling system. The sample was connected to the electrochemical cell as the anode, and the stainless steel container served as the cathode. MAO coatings were prepared in an aluminate-based basic electrolyte containing 10 g/l sodium aluminate (NaAlO_2 , Alfa Aesar), 2 g/l sodium phosphate tribasic anhydrous (Na_3PO_4 , Alfa Aesar) and 2 g/l potassium hydroxide (KOH, Alfa Aesar), and this electrolyte was coded as the reference electrolyte.

Afterwards, monoclinic ZrO_2 (m- ZrO_2) particles that had a mean particle size of 1.2 μm (determined by the X-Ray diffraction (XRD) and laser particle size analyses, Fig. 3.1a and 1b, respectively), were added into the reference electrolyte, which was then stirred for 1 h on a magnetic stirrer to disperse ZrO_2 particles in the reference electrolyte homogenously. The dispersibility of m- ZrO_2 particles in the reference electrolyte was determined by a zeta potential analyser (Stabino Zetasizer) at 25 °C after a homogenization time of 1 h. Zeta potential of the m- ZrO_2 particles was found to be -53.5 ± 0.9 mV as an indication of a good dispersibility.

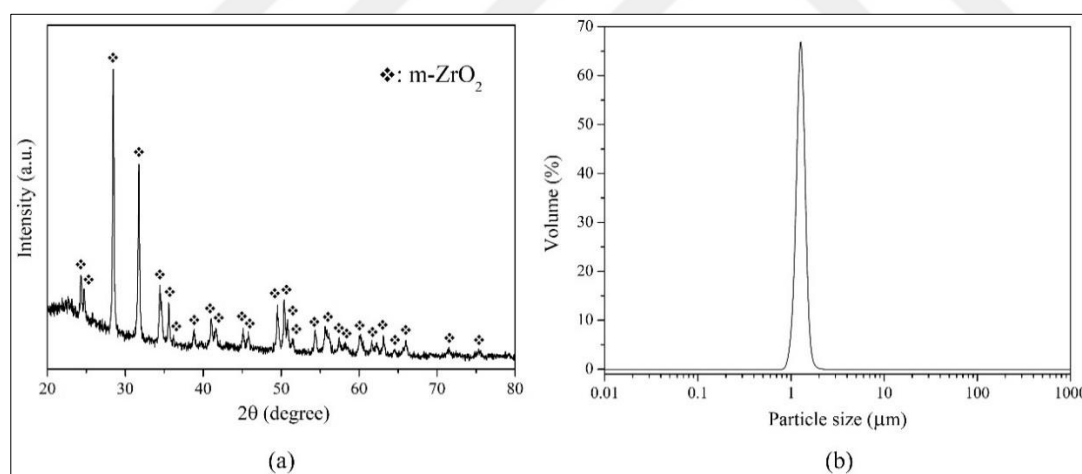


Figure 3.1 : (a) XRD spectrum and (b) particle size distribution of ZrO_2 particles used in the present study.

The MAO coatings were synthesised using a constant voltage of 520 V applied in the positive half cycle and 80 V applied in the negative half cycle. The pulse frequency, positive and negative voltage pulse ratio and duty cycle were 500 Hz, 1:1 and 40%, respectively. Each sample was treated for 5 min and then cleaned ultrasonically in ethanol and distilled water, then dried in the air at RT. The temperature of the electrolyte was maintained below 25 °C using an external cooling system during the

MAO process to prevent evaporation of the solution and to regulate the chemical reaction rate in the electrolyte/sample interface. During coatings synthesis in the reference electrolyte, the maximum and mean current densities were measured as 1.99 and 1.18 A/cm², while they were measured as 2.25 and 1.27 A/cm² for the coatings formed in the ZrO₂-added electrolyte. Hereafter, the coating fabricated in the reference electrolyte will be referred to as MAO, while the coating produced in the ZrO₂-added electrolyte will be referred to as MAO-Zr.

3.2.2 Microstructural characterisation

Structures of the fabricated coatings were analysed using a field emission scanning electron microscope (SEM, FEI XL30 SFEG) equipped with an energy dispersive X-ray spectrometer (EDX) and a conventional Θ -2 Θ geometry utilised XRD (GBC MMA 028) using Cu-K α radiation at 35 kV and 28.5 mA with a scan range between 15-75° at a step of 0.020° and a scanning speed of 1 °/min. XRD analyses have been also employed on the MAO-Zr coating having different thicknesses. For this purpose, MAO-Zr coating was gently grounded with P2500 grade SiC abrasive papers up to 14, 10, and 6 μ m of thickness, which were determined by utilising an Eddy current thickness gauge. The mean surface roughness (Ra) values of the fabricated coatings were measured by a 2-D contact surface profilometer (Veeco Dektak 6M). The hardness of MAO and MAO-Zr coatings was measured from cross-sections of the polished samples using a Vickers micro-hardness tester (Wilson Tukon 1102) at a load of 25 g.

3.2.3 Wear tests

HT wear characteristics of the fabricated MAO coatings were investigated at 300 °C using a ball-on-disk type tribo-tester (CSM Instruments). The counterface, which followed a circular path having 6 mm diameter on the sample surfaces at a sliding speed of 5 cm/s, was a 6 mm diameter WC ball. The friction curve was continuously recorded during the wear tests. High temperature wear tests were employed to determine the wear performance and more importantly, the durability of the coatings under dry sliding contact conditions. For the tests employed to determine the wear performance of the coatings, test load and total sliding distance were chosen as 1 N and 100 m, respectively. The durability of the coatings was determined using test loads between 1 and 10 N, and the strategy applied was finding out the sliding distance at

which the coating was completely removed from the contact surfaces. In order to compare HT wear characteristics with RT characteristics, MAO and MAO-Zr coatings were also tested at RT under identical parameters at test loads of 1 and 10 N for a total sliding distance of 100 m.

Wear tests were conducted on the gently ground surfaces of the coatings with SiC abrasive papers to reduce the average surface roughness (R_a) below $0.25\text{ }\mu\text{m}$. Following the wear tests, wear tracks formed on the samples were examined using a 2-D contact surface profilometer (Veeco Dektak 6M), a stereo microscope (Leica) and a tabletop back-scattered SEM (Hitachi TM-1000).

3.3 Results

3.3.1 Microstructural examinations

Surface and cross-section SEM images of the MAO and MAO-Zr coatings are depicted in Fig. 3.2. In general, surfaces of the coatings consisted of pancakes and micro-pores, where the discharging electric sparks evolved. Although the size of the pancakes was larger for the MAO-Zr coating, R_a values were measured as; $2.18 \pm 0.11\text{ }\mu\text{m}$ for the MAO coating and $2.05 \pm 0.21\text{ }\mu\text{m}$ for the MAO-Zr coating. Cross-section SEM examinations showed that the thicknesses of the MAO and MAO-Zr coatings were both about $25\text{ }\mu\text{m}$, but they exhibited different structural features. The porosity distribution and composition were homogenous for the MAO coating. The detection of a high amount of Al and O (50 and 47 wt.%, respectively, on average) during EDX analysis indicated that MAO coating was monolithic and mainly consisted of Al_2O_3 . On the other hand, MAO-Zr coating consisted of two distinctive oxide layers. The outer layer had a compact (i.e. remarkably less porous) and dense nature and contained a high amount of Zr (about 13 wt.% on average) at the expense of Al, whose amount was measured about 42 wt.%. On the other hand, the inner layer, which had a porous structure similar to the MAO coating but contained less Zr (about 1.5 wt.%) along with 48.7 wt.% of Al and 46.9 wt.% of O. Furthermore, accumulation of bright coloured ZrO_2 particles around the micro-pores was observed in the structure of the MAO-Zr coating. It should be noticed that in the composition of the MAO and MAO-Zr coatings, other than Al, O and Zr, elements such as Mg, Zn, Na, K and P, were detected at minor amounts ($< 3\text{ wt.}\%$ in total) as presented by ME on Fig. 3.2.

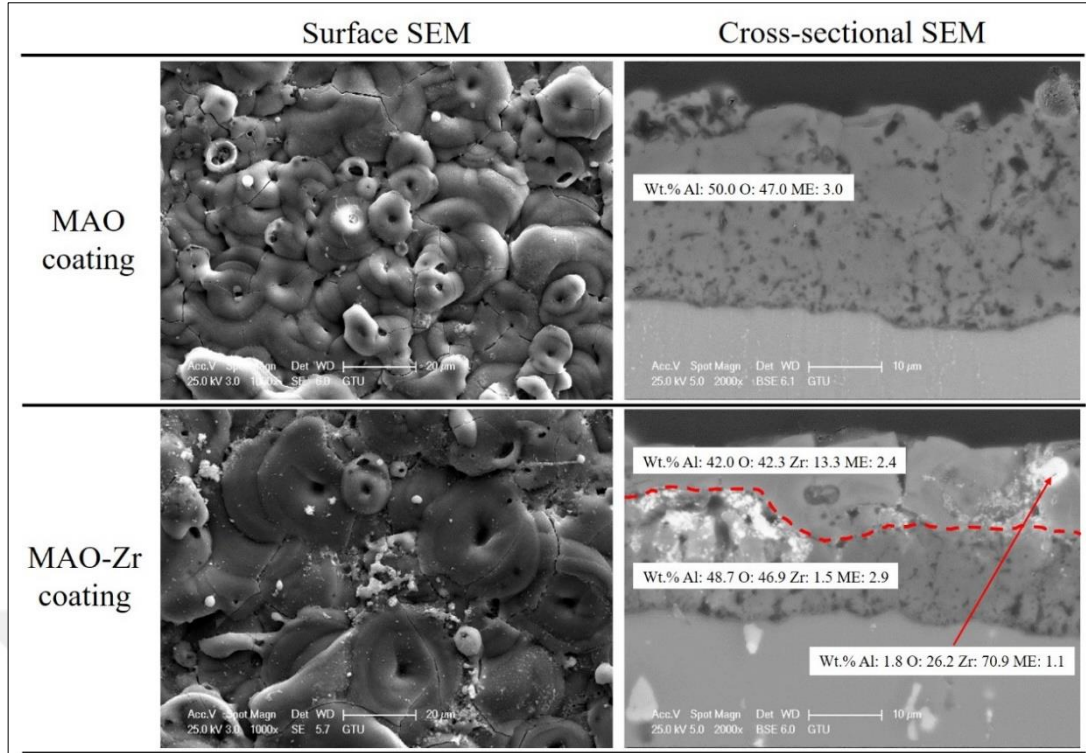


Figure 3.2 : Surface and cross-sectional SEM images of MAO and MAO-Zr coatings with the results of EDX analyses. (ME is representing elements such as Mg, Zn, Na, K and P detected at minor amounts).

According to the micro-hardness measurement conducted on the cross-sections of the examined coatings, the average hardness of the MAO coating was determined as $1468 \pm 182 \text{ HV}_{0.025}$. For the MAO-Zr coating, the average hardness of outer and inner layers was measured as 1822 ± 110 and $1435 \pm 154 \text{ HV}_{0.025}$, respectively. It is interesting to note that hardness of the inner oxide layer of the MAO-Zr coating and the MAO coating was in the same range, while the higher hardness of the outer oxide layer of the MAO-Zr coating can be associated with its less porous and denser microstructure. The positive effect of reducing porosities on the hardness of MAO coatings has been well documented previously [106–108].

The XRD spectra of MAO and MAO-Zr coatings are shown in Fig. 3.3, and XRD analyses demonstrated that the MAO coating was mainly Al_2O_3 in forms of $\alpha\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$. Additionally, the XRD spectra of the MAO-Zr coating contained the characteristic peaks of the m- ZrO_2 and tetragonal ZrO_2 (t- ZrO_2), besides the peaks of Al_2O_3 . Moreover, for the XRD spectrum taken from the MAO-Zr coating in the as-coated state, it is worth to remark that the height of the most substantial peak of t- ZrO_2 appeared at 30.48° for the (111) plane was more than 3 times of that of m- ZrO_2 appeared at 28.24 for the ($\bar{1}\bar{1}1$) plane. This indicated that the content of t- ZrO_2 at the

outermost surface of the MAO-Zr coating was higher than the content of m-ZrO₂. On the XRD spectra taken after successive grinding the MAO-Zr coating to thicknesses of 14, 10, and 6 μm implied that t-ZrO₂ was gradually reduced and lastly peaks of t-ZrO₂ and m-ZrO₂ almost disappeared at the coating thickness of 6 μm. The absence of the complex oxide peaks in the XRD spectra of the MAO-Zr coating indicated that no reactions between Al₂O₃ and ZrO₂ took place during the MAO process. The peaks of phases favoured by the Mg, Zn, Na, K, and P elements introduced into the coating either from the electrolyte or substrate were not identified in the XRD spectra because of their low amount. On the XRD spectra of the examined coatings, some diffraction peaks of the substrate (7075 Al alloy) appeared due to the penetration of X-rays beyond the coatings.

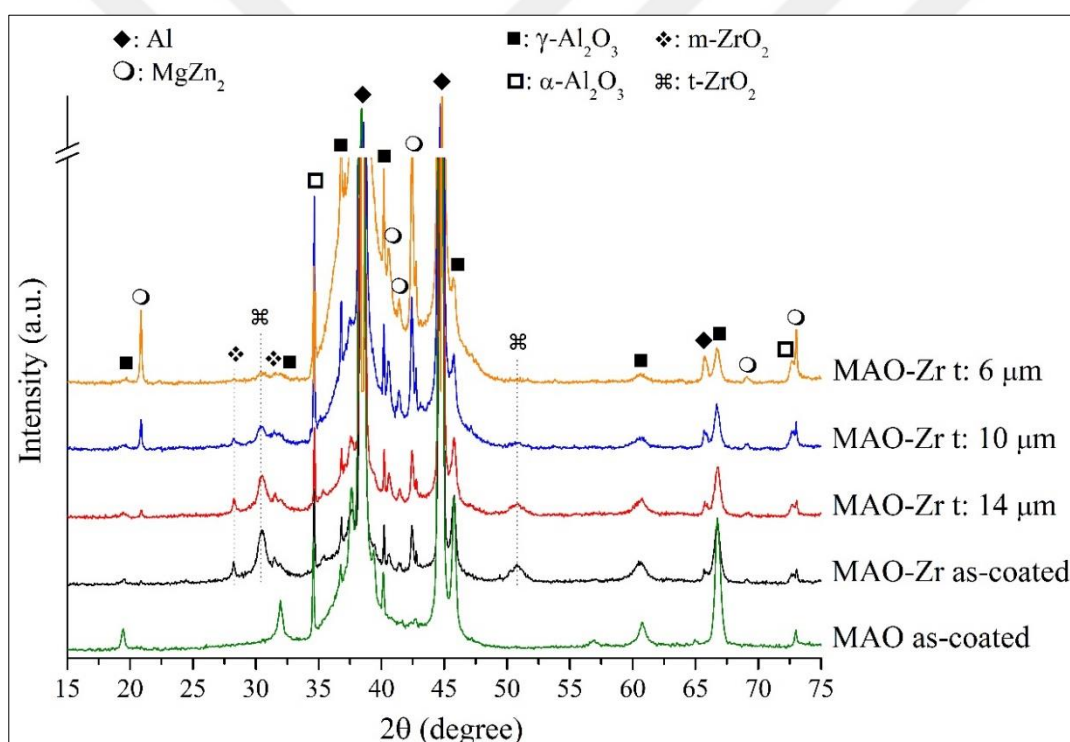


Figure 3.3 : XRD spectra of (a) MAO and (b) MAO-Zr coatings (“t” is the coating thickness).

3.3.2 HT wear tests

Findings of the wear test conducted on the 7075 Al alloy, MAO and MAO-Zr coated samples at 300 °C under the load of 1 N for a total sliding distance of 100 m are presented in Fig. 3.4. As can be seen in Fig. 3.4a, the friction curve of the 7075 Al alloy exhibited a heavy fluctuation throughout the wear test and had an average COF value of about 1.8. Such type of friction behaviour (i.e. heavy fluctuations) has been

attributed to the stick-slip phenomenon developed at the contact surfaces [31]. Unlike the friction curve of the 7075 Al alloy, the friction curve of the MAO-Zr coated sample was smooth and after the running-in corresponding to about 0.7, COF continuously increased until the sliding distance of about 30 m and then reached the steady-state value at about 1.4. This smooth friction curve is the characteristics of mild wear for ceramic-ceramic tribo-contacts, where remarkable wear loss and severe surface degradation were not likely [109]. Besides, the friction curve of the MAO coated sample exhibited the characteristics of MAO-Zr sample at the early stage of the wear test as the COF increased smoothly to the peak value of about 1.8 at a sliding distance of about 40 m. Then the COF tended to decrease and fluctuate similarly with that of the 7075 Al alloy and remained at about 1.2 in average after the sliding distance of about 60 m as emphasised by an arrow in Fig. 3.4a. Hence, heavy fluctuations similar to friction curve of 7075 Al alloy indicated the removal of the MAO coating imposing the shifting ceramic-ceramic contact to metal-ceramic contact after sliding distance of 60 m. The stereo microscope examinations conducted after the wear tests (Fig. 3.4b) showed that the MAO coating was completely removed from the contact surface during the wear tests, so that the wear track appeared as a dark coloured circular path. When compared with the appearance of the wear track formed on the 7075 Al alloy, it is obvious that MAO coating protected the substrate from the destructive action of the counterface to some extent (until removal from the contact surface). Unlike the MAO coating, the MAO-Zr coating remained on the contact surface throughout the testing duration, and the wear track was hard to be distinguished unless its trace was emphasised by a red coloured dashed line. When the 2-D profiles of the wear track formed on the surface of the examined samples are compared (Fig. 3.4c), the deepest wear track has been measured for the 7075 Al alloy, it was around 140 μm , while the depth of the wear track formed on the MAO-Zr coating was not measurable. In the case of the MAO coating, the wear track depth was about 26 μm . Based on these findings, it is concluded that MAO-Zr coating could be promising for wear-related applications at HTs, as long as it can endure sliding distances longer than 100 m.

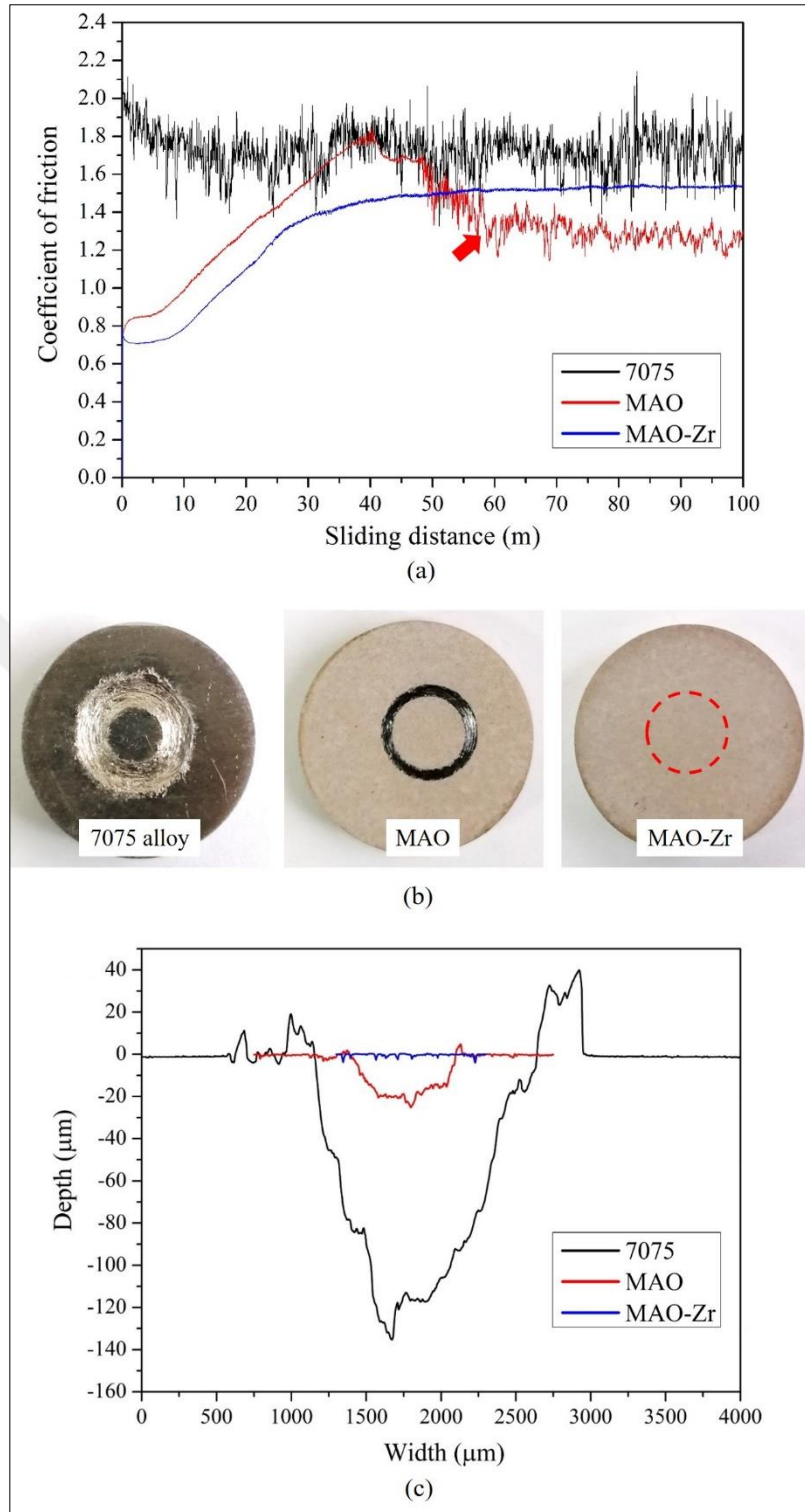


Figure 3.4 : XRD (a) Friction curves of uncoated and coated 7075 alloy samples worn under testing loads of 1 N at 300 °C for total sliding distance of 100 m. The red arrow shows the sliding distance where COF of the MAO coated sample started to fluctuate and remain stable in similar fashion with that of the 7075 alloy. (b) Stereo microscope appearances of the sample surfaces after the wear tests. The wear track on the MAO-Zr sample was presented with an intermittent red circle to make it more visible. (c) Representative 2-D profiles of the wear tracks developed on the surface of examined samples.

The results of HT wear tests employed on MAO and MAO-Zr coated samples under various test loads up to 10 N are presented in Fig. 3.5, and it can be seen the sliding distance at which coatings fail depending on the test load. As the failure criteria, we have assumed that failure is the complete removal of the coating from the contact surface, corresponding to the sliding distance where COF tended to fluctuate and started to remain constant in average (in similar characteristics with that of the 7075 Al alloy) after reaching the peak friction coefficient value on the friction curve (as emphasised by an arrow on the friction curve of the MAO coated sample in Fig. 3.4a). In general, the increase of the test load caused a reduction in coating failure distance, and at all test loads, the MAO coating was completely removed from the contact surface after a certain sliding distance. Nevertheless, the difference between failure distances of MAO and MAO-Zr coatings became more distinguishable at test loads lower than 3 N, so that at the test of 1 N, MAO-Zr coating remained on the contact surface after a sliding distance as high as 1000 m.

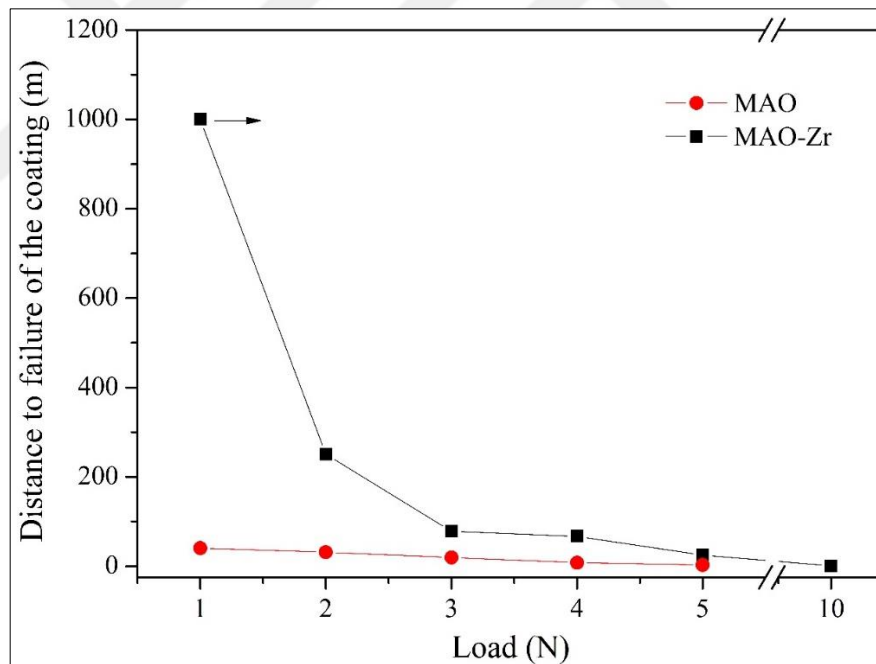


Figure 3.5 : The effect of wear test load on sliding distance to failure of the MAO and MAO-Zr coatings during wear tests employed at 300 °C. The black horizontal arrow represents that MAO-Zr coating did not fail under 1 N for sliding distance of 1000 m.

Moreover, to determine the wear mechanism, MAO and MAO-Zr coated samples were subjected to wear tests at 300 °C under the test load of 3 N for a sliding distance close to the coating failure distance (approximately 20 and 70 m, respectively). For this purpose, the friction curve was carefully followed during tests to stop the wear tester

at a sliding distance at which the friction curve was getting closer to the peak point on the friction curve. Stereo microscope images of these samples and the 2-D profiles of the wear tracks formed on their surfaces are presented in Fig. 3.6. It was evident that the MAO coating has worn homogeneously during the wear tests by yielding a wear track depth of about 14 μm on average. However, the wear track of the MAO-Zr coating was not homogeneous as can be clearly seen from the 2-D profiles taken from X and Y regions of the wear track. While the depth of the wear track at Region X was not measurable, the wear track at Region Y was about 12 μm .

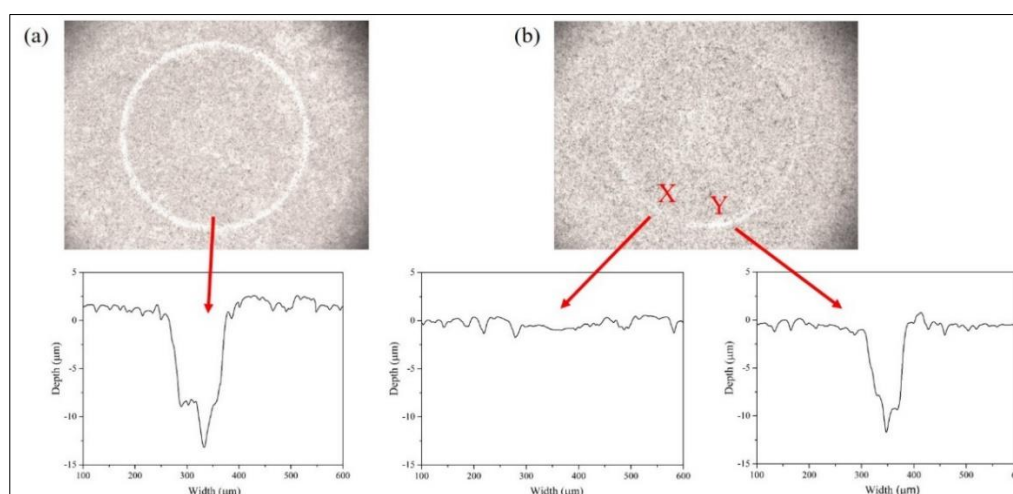


Figure 3.6 : Stereo microscope images and corresponding 2-D profiles of the wear tracks formed the (a) MAO and (b) MAO-Zr coatings after the wear tests run at 300 °C under load of 3 N for sliding distances just before complete removal of the coatings (approximately 20 and 70 m, respectively). Regions X and Y represent two different sections of the wear track formed on the MAO-Zr sample.

The surface and cross-section SEM images of wear tracks formed on MAO and MAO-Zr coatings under test load of 3 N are presented in Fig. 3.7. On the worn surface of the MAO coating, the elevation difference between the coating surface and contact surface of the wear track were noticed. Traces of arc-shaped cracks were also observed on the contact surface of the wear track. While local spallation was evident on the contact surface of MAO-Zr coating at Region X, contact surface at Region Y exhibited similar features to the wear track appearance of the MAO coating. Cross-section SEM examinations revealed the presence of perpendicular and parallel cracks beneath the worn surfaces. For the MAO coating, perpendicular cracks were very intense, and some of them extended to the coating/substrate interface, whereas parallel cracks connected them at a certain depth from the worn surface. Shorter perpendicular cracks were visible beneath the Region Y of the MAO-Zr coating at a lower intensity, while

parallel cracks tended to propagate along with the interface of the inner and outer oxide layers. However, cracks were hardly observed beneath the Region X of the MAO-Zr sample.

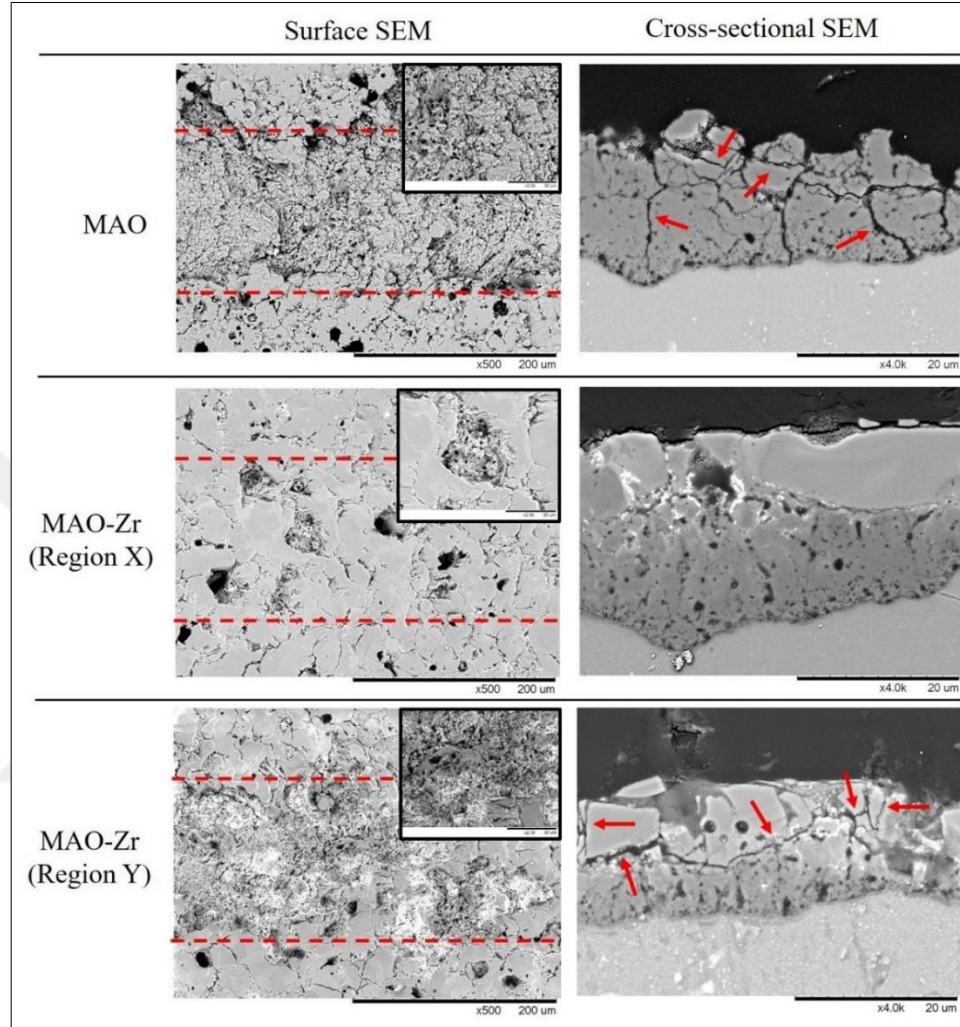


Figure 3.7 : Surface and cross section SEM images of wear tracks formed on MAO and MAO-Zr coatings after the wear test run at 300 °C under load of 3 N for sliding distances just before complete removal of the coatings (approximately 20 and 70 m, respectively). The intermittent red lines represent the edges of the wear tracks and red arrows show cracks under the worn surfaces.

3.3.3 RT wear tests

Results of the dry sliding wear tests conducted on MAO and MAO-Zr coated samples at RT under test loads of 1, and 10 N for a total sliding distance of 100 m are displayed in Fig. 3.8. At both test loads, friction curves of the samples were fluctuation free, indicating that the coatings on the surfaces throughout the testing period were not worn out (Fig. 3.8a). It should be noted that the MAO-Zr coating exhibited a lower friction coefficient compared to the MAO coating. When the 2-D profiles of the wear tracks

are observed (Fig. 3.8b), it can be seen that no measurable wear track was formed on the MAO and MAO-Zr coatings after testing under the load of 1 N. Nevertheless, increasing the test load to 10 N, generated wear tracks with depths of 6 and 3 μm on the MAO and MAO-Zr coatings, respectively, which were far lower than the thicknesses of the coatings. This observation implied that the MAO-Zr sample has a better wear resistance than the MAO coating at RT. Moreover, SEM examinations conducted on MAO and MAO-Zr coated samples after the wear tests employed under the test load of 10 N (Fig. 3.8c and 8d, respectively) revealed that there is a significant difference between the worn surfaces visible in the surface cracks. Furthermore, the worn surface of the MAO sample had an intensive crack network, while on the worn surface of MAO-Zr sample, cracks were less intense and without any evidence of a crack network.

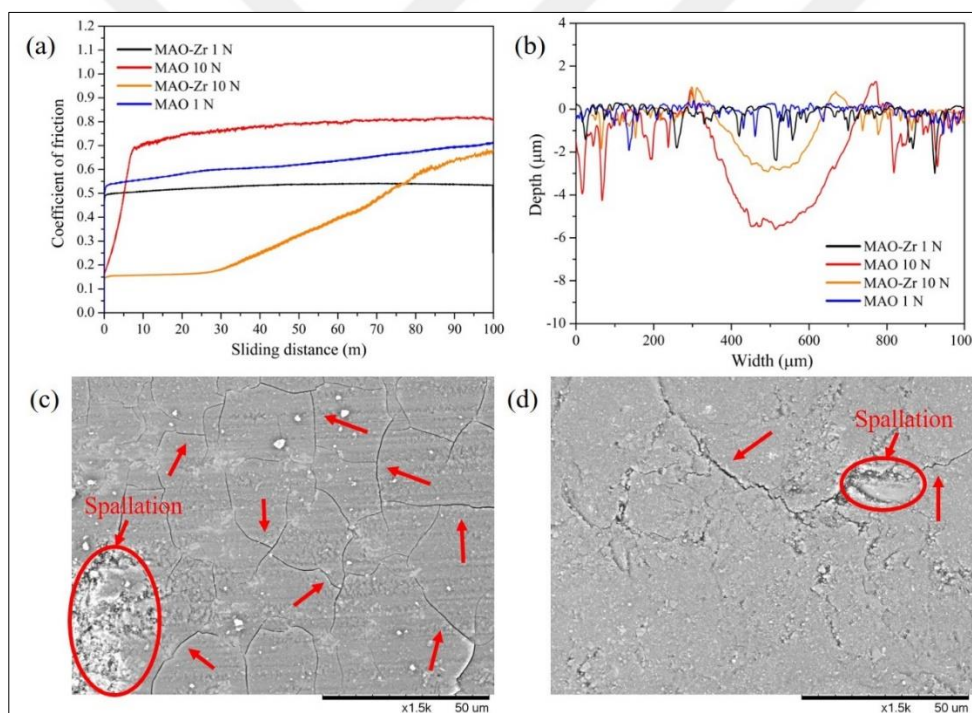


Figure 3.8 : (a) Friction curves and (b) 2-D profile of the wear tracks formed on the MAO and MAO-Zr coatings worn under tests loads of 1 and 10 N at RT for sliding distance of 100 m. (c, d) Surface SEM images of wear tracks formed on the MAO and MAO-Zr coatings, respectively, after the wear tests employed under 10 N. Spallations and cracks were shown by red circles and arrows, respectively.

3.4 Discussion

In accordance with the previous works conducted on Al alloys [110–113], MAO of the 7075 Al alloy in the aluminate-based electrolyte produced a monolithic Al_2O_3 -

based coating with a thickness of about 25 μm , which was referred as MAO coating in this study. The addition of m-ZrO₂ particle into this aluminate-based electrolyte disturbed the monolithic nature of the coating and instead generated a coating with the same thickness, having two distinct oxide layers, which was referred as MAO-Zr coating in this study. While the outer oxide layer of the MAO-Zr coating was the mixture of Al₂O₃ and ZrO₂, the inner oxide layer was Al₂O₃-based, exhibiting similar characteristics to the monolithic MAO coating. The transfer of ZrO₂ particles into the developing Al₂O₃-based MAO coating from the reference electrolyte during MAO process, has been maintained by the electrophoretic effect [103,114] arising from attraction of negatively charged m-ZrO₂ particles by the 7075 Al alloy acting as anode. Even though m-ZrO₂ particles were added into the reference electrolyte, ZrO₂ particles incorporated into the outer layer of the MAO-Zr coating were in monoclinic and tetragonal forms of ZrO₂.

Thermochemical modelling of binary Al₂O₃ - ZrO₂ phase diagrams employed by using FactSage 7.3 software confirmed that t-ZrO₂ is stable over 1170 °C and transforms into m-ZrO₂ when cooled slowly, as can be seen in the equilibrium diagram (Fig. 3.9a). On the other hand, according to the Scheil-Gulliver diagram (Fig. 3.9b) representing rapid cooling conditions, t-ZrO₂ can be retained in the microstructure at temperatures lower than 1170 °C for the Al₂O₃ and ZrO₂ mixture having a ZrO₂ mole ratio higher than 0.2. It is suggested that during processing of the MAO-Zr coatings upon formation of plasma, surfaces were exposed to high temperatures (over 2500 K), which let physical mixing of incorporated ZrO₂ with the molten Al₂O₃. Subsequent rapid cooling due to the quenching effect of the electrolyte favoured remaining of t-ZrO₂ in the structure of the MAO-Zr coating even at room temperature. Moreover, reduction of melting temperature on the binary Al₂O₃ - ZrO₂ phase diagram with increasing ZrO₂ up to 0.6 mole ratio (Fig. 3.9) could be contributed development of less porous and compact ZrO₂ enriched outer layer in the MAO-Zr coating as compared to the monolithic Al₂O₃-based MAO coating. In accordance with our observations, suppression of m-ZrO₂ formation in the MAO coating synthesized in ZrO₂ added electrolyte has also been reported previously in the absence of stabiliser such as Y₂O₃, CaO or MgO [115]. In this context, exposure of the deeper regions of MAO-Zr coating exposed to relatively low temperatures and/or cooling rates could have encouraged transformation of t-ZrO₂ to m-ZrO₂ during cooling. As the consequence of this, it is

more likely that the deeper regions of the outer oxide layer closer to the inner oxide layer of the MAO-Zr coating had a higher content of m-ZrO₂ at the expense of t-ZrO₂.

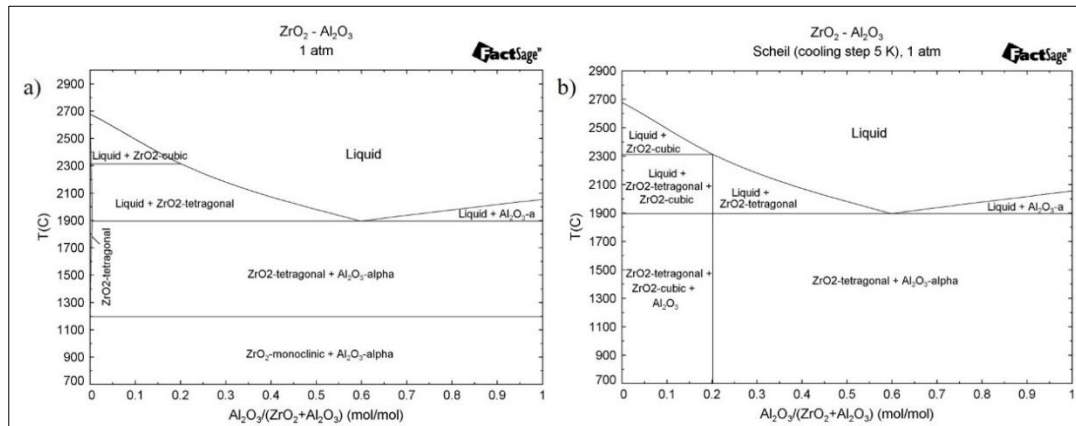


Figure 3.9 : (a) Equilibrium and (b) Scheil-Gulliver diagrams of Al₂O₃ - ZrO₂ system plotted by using FactSage 7.3 software.

During the sliding wear tests, the initiation and propagation of subsurface cracks are in perpendicular and parallel directions to the contact surface, which is characteristic of fatigue wear [116–118] and played a crucial role on the wear of the examined coatings. Thus, after repeated contacts, the combination of the contact-stress that induced perpendicular cracks together with the shear-stress that induced parallel cracks at a certain depth from the contact surface promoted the detachment of fragments from the contact surface (spallation). As compared to the RT wear tests, the spallation was accelerated during HT wear tests, leading to coatings being completely removed from the contact surface after a certain testing duration, which was dependant on the test load. Moreover, it is suggested that softening of the substrate at HTs caused deeper penetration of the counterface ball and therefore generated higher bending stresses within the coatings, facilitating the cracking of the coating as well as rapid crack propagation.

As a general trend, the MAO-Zr coating exhibited enhanced wear resistance and better durability compared to the MAO coating, and this result can be associated with the presence of t-ZrO₂ particles in the outer compact oxide layer of the MAO-Zr coating, in addition to the reduction in porosity that could have accelerated crack initiation by acting as stress concentration sites. It is well documented that the transformation of t-ZrO₂ into m-ZrO₂ under stress causes the volume expansion of ZrO₂ particles, providing an enhancement in fracture toughness (K_c) due to the retardation of the crack propagation by the compressive stress generated in the Al₂O₃ matrix in ZTA

[119–121]. In this respect, K_{IC} values were over $12 \text{ MPam}^{1/2}$ and around $3 \text{ MPam}^{1/2}$ for ZTA and commercial Al_2O_3 , respectively [90]. From this perspective, it is suggested that on the MAO-Zr coating, the wear progressed in two stages as schematically modelled in Fig. 3.10. In the first stage, the outer layer (a mixture of Al_2O_3 and ZrO_2) with a relatively high K_{IC} value was in contact with the counterface, and the wear rate was low. Compressive stress generated beneath the contact surface upon transformation t- ZrO_2 into m- ZrO_2 not only restricted the propagation of perpendicular cracks but also favoured the parallel cracks to propagate along with the interface of outer and inner oxide layers instead of propagating at a certain depth from the contact surface. Also, the extension of propagation length of perpendicular cracks that intersected parallel cracks delayed the spallation. In the second stage, which became dominant after the complete removal of the outer oxide layer, the wear rate was increased upon the exposure of Al_2O_3 -based inner layer to rubbing action of the counterface ball, similarly to the MAO coating. Owing to its relatively low K_{IC} value, in the Al_2O_3 -based coatings perpendicular cracks easily penetrated deeper sections, while the maximum shear stress-induced parallel cracks were joining them at a relatively shallow depth from the contact surface. For this reason, material removal by spallation was accelerated in the second stage, which finalised with the complete removal of the MAO-Zr coating from the contact surface.

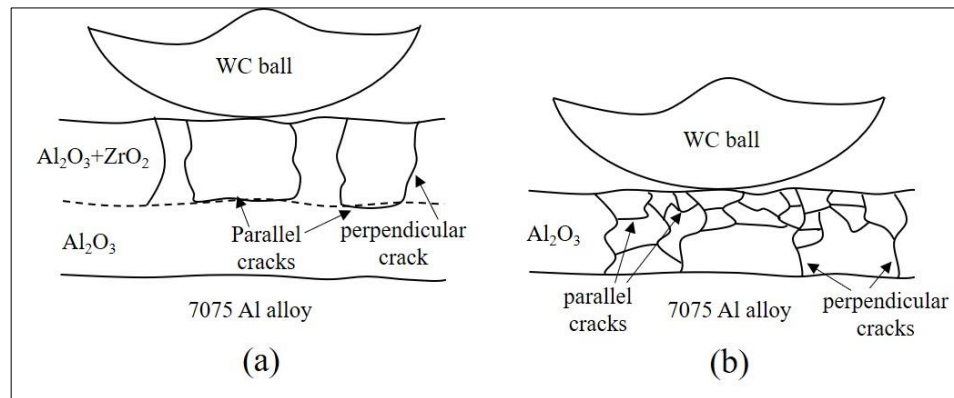


Figure 3.10 : Schematic modelling showing progress of wear on MAO-Zr coating. (a) and (b) are the first and second stages of wear, respectively.

In order to analyse the durability of the examined coating without removal for longer sliding contacts at HTs, results of wear tests employed at 300°C were analysed according to stress-based fatigue approach as explained in the Appendix. For this purpose, Fig. 3.5 was converted into logarithmic “maximum contact stress ($\sigma_{\max}$) - number of cycles to coating failure (N_f)” graph at first, as presented in Fig. 11. A linear

relationship between $\sigma_{\max}$ and N_f in logarithmic scale yielded following power-law mathematical equations:

$$\sigma_{\max} \cdot N_f^{0.11} = 3890 \text{ for the MAO coating and}$$

$$\sigma_{\max} \cdot N_f^{0.21} = 6025 \text{ for the MAO-Zr coating,}$$

Since the engineering components exposed to repeated/cyclic stresses under service conditions are expected to endure typically 10^6 cycles [122], we attempted to determine the maximum contact pressure ($\sigma_{\max}$) values for the examined coatings sustaining 10^6 contact cycles which corresponded to a total sliding distance of about 19 km, at 300 °C for the test configuration of this study. This approach yielded $\sigma_{\max}$ values of 331 and 851 MPa for the MAO and MAO-Zr coatings, respectively. This approach also confirmed the superior durability of the MAO-Zr coating on the surface of an aluminium alloy substrate during the HT wear tests as compared to the MAO coating.

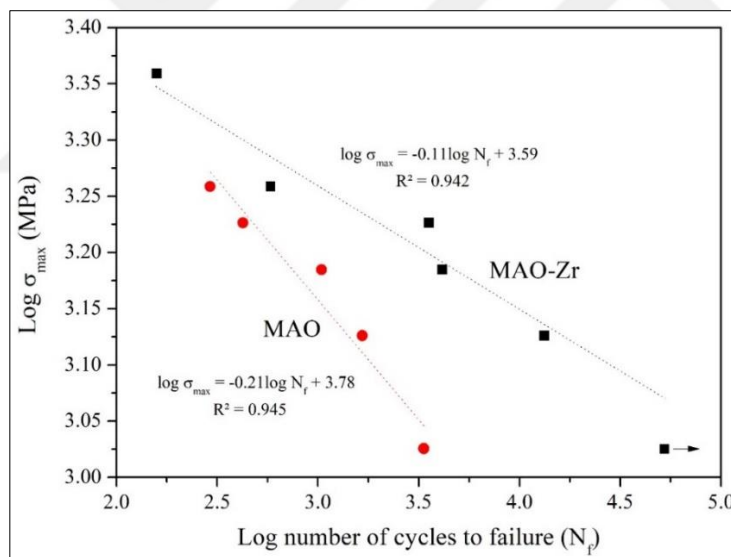


Figure 3.11 : Maximum contact pressure ($\sigma_{\max}$) vs number of cycles to coating failure (N_f) graphs of the MAO and MAO-Zr coatings obtained from Fig. 5. R^2 is the coefficient of determination for the derived equations derived. The black horizontal arrow represents that MAO-Zr coating did not fail under 1 N for sliding distance of 1000 m.

From the technological point of view, the fact that the MAO-Zr coating with the underlying Al alloy substrate kept its integrity at a temperature of 300 °C for 10^6 contact cycles under a maximum contact pressure as high as 850 MPa suggests that it could be attractive for the transportation industry as it can lead to weight reduction in the manufacturing of vehicle components.

3.5 Conclusion

The influence of m-ZrO₂ particles addition into the aluminate-based reference electrolyte on the microstructural features and wear performance coatings synthesised on a 7075 Al alloy by MAO process was investigated. The findings of this study can be summarised as follows:

1. While the MAO coating synthesised in the reference electrolyte was monolithic and Al₂O₃-based, the MAO-Zr coating synthesised in the m-ZrO₂ added reference electrolyte consisted of two distinctive oxide layers, with the first layer having ZrO₂ particles (in the forms of monoclinic and tetragonal) that participated in the Al₂O₃-based outer layer and the second inner layer having a monolithic Al₂O₃-based composition.
2. Dry sliding wear tests employed at RT for a total sliding distance of 100 m reveal that both MAO and MAO-Zr coatings sustain their stability under test loads as high as 10 N, but the wear loss of the MAO-Zr coating was remarkably lower compared to the MAO coating.
3. During sliding wear tests conducted at 300 °C, MAO and MAO-Zr coatings tended to detach from the surface after a certain sliding distance depending on the test load. In general, the MAO-Zr coating had both higher durability and a longer sliding distance compared to the MAO coating. At the lowest wear test load of 1 N employed in this study, the MAO-Zr coating sustained its stability for the total sliding distance of 1000 m, while the MAO coating was removed after sliding distance of about 60 m.
4. From the mathematical equations derived from the results of the wear tests employed at 300 °C, the maximum contact pressures that do not cause coating removal until the contact cycles of 10⁶ were estimated as 851 and 331 MPa for the MAO and MAO-Zr coatings, respectively.

3.6 Appendix

Fatigue fracture is the major issue of engineering components working under cyclic maximum and minimum stresses ($\sigma_{\max}$ and $\sigma_{\min}$, respectively). The increase in the algebraic difference between $\sigma_{\max}$ and $\sigma_{\min}$, which is defined as stress range ($\Delta\sigma$),

leads to early fracture and therefore shorter fatigue life mostly quantified by the number of cycles to failure (N_f). For stress levels in elastic deformation range, the relationship between $\Delta\sigma$ and N_f can be expressed by a mathematical equation known as Basquin's law [122–124];

$$\Delta\sigma \cdot N_f^a = C \quad (3.1)$$

where a and C are material constants. The values of these material constants can be found from the log-log plot of Eq. 1.

It is suggested that Basquin's law can be extended to removal of coatings by fatigue wear from the contact surface during wear tests. Since the stresses acting to the coating during repeated sliding contacts varied in between maximum contact pressure and zero, Basquin's law was simplified as;

$$\sigma_{max} \cdot N_f^a = C \quad (3.2)$$

by taking σ_{max} as the maximum contact pressure calculated via Hertz elastic contact mechanics [125], for each load applied during the wear tests. The σ_{max} values acting on the examined coatings were determined for WC/ Al_2O_3 tribo-couple for ball-on-disc configuration by utilising the elastic constants given in [126,127]. On the other hand, N_f values can be found by dividing the coating failure distance to the periphery of the circular path of the wear track, which corresponds to the sliding distance in one cycle of the wear test. Table 3.1 lists the σ_{max} and corresponding N_f values for MAO and MAO-Zr samples calculated from the results of the wear tests employed at 300 °C (Fig. 3.5).

Table 3.1 : Maximum contact pressure and the number of cycles to failure values of MAO and MAO-Zr coatings tested at 300 °C.

Maximum contact pressure (σ_{max} , MPa)	Number of cycles to failure (N_f , cycles)	
	MAO Coating	MAO-Zr coating
1061	2.15×10^3	53.05×10^3 *
1337	1.66×10^3	24.19×10^3
1530	1.04×10^3	4.14×10^3
1684	0.42×10^3	3.55×10^3
1814	0.29×10^3	0.58×10^3
2286	-	0.16×10^3

*Not failed

3.7 Acknowledgement

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4. INFLUENCE OF ALUMINA AND ZIRCONIA INCORPORATIONS ON THE STRUCTURE AND WEAR RESISTANCE OF TITANIA-BASED MAO COATINGS ³

4.1 Introduction

Titanium and its alloys are attractive engineering metals for chemical, aerospace, marine and biomedical industries owing to their two enhanced characteristics; i.e. corrosion resistance and specific strength. While, commercially pure titanium (Cp-Ti) is mostly preferred for applications where corrosion resistance is a priority, titanium alloys are used in the manufacturing of engineering components requiring high strength. Among the various grades of titanium alloys available in the market, Ti6Al4V alloy is the most popular one because of good balance between chemical, physical and mechanical properties [128]. However, it suffers from poor wear resistance, which is an inherent characteristic of titanium and its alloys [129].

As an electrochemical process MAO has gained special attention for enhancing the surface related properties of titanium base materials, thanks to its applicability to complex geometries in environmental friendly electrolytes, low cost and large-scale production without exposing the work piece to high temperatures. In general, MAO allows formation of thick and adherent oxide based coatings, with porous nature owing to spark discharge and gas bubble formation during processing [130–134].

The structure and properties of MAO coatings can be controlled by altering the electrical parameters and composition of the electrolyte via introducing various soluble chemicals [131,135,136]. Recently, fabrication of composite MAO coatings via employing the process in particle added electrolytes received more attention as it leads to microstructure adjustment, compactness and/or sealing of pores, which in turn provides better corrosion resistance, hardness, wear resistance and bioactivity [10–23].

³ This chapter is based on the paper “F. Muhaffel, M. Kaba, G. Cempura, B. Derin, A. Kruk, E. Atar and H. Cimenoglu, Influence of alumina and zirconia incorporations on the structure and wear resistance of titania-based MAO coatings, *Surf. Coatings Technol.* 377 (2019) 124900”

Since Al_2O_3 and ZrO_2 enjoy wide spread usage in manufacturing of technical ceramics due to enhanced mechanical properties, good chemical stability, high melting point and environmental friendly nature, researchers are motivated to fabricate composite coatings on titanium based materials via employing MAO process in Al_2O_3 and ZrO_2 particle added electrolytes with the focus of wear performance. In this respect, Aliofkhazraei et al. [141], who added Al_2O_3 particles into a silicate-based electrolyte, reported the formation of compact MAO coating on Cp-Ti consisting of TiO_2 (more specifically rutile, a high temperature form of TiO_2), Al_2TiO_5 , $\alpha\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$. Their attempt of introducing Al_2O_3 particles into the electrolyte led to a decrease in wear rate against a steel counterface; as the amount of Al_2O_3 particles in the electrolyte increased. Similarly, the MAO coating fabricated on Cp-Ti in Al_2O_3 added aluminate-based electrolyte by Shokouhfar et al. [148], comprised of Al_2TiO_5 and $\gamma\text{-Al}_2\text{O}_3$ and it exhibited a slightly better wear resistance against an Al_2O_3 counterface compared to particle-free MAO coating. In accordance with previous studies, Li et al. [137] also reported a slight increase in wear resistance of the MAO coating fabricated in Al_2O_3 added silicate-based electrolyte on Ti6Al4V alloy, which consisted of rutile, anatase (low temperature form of TiO_2), Al_2TiO_5 and $\alpha\text{-Al}_2\text{O}_3$, against Si_3N_4 counterface as compared to particle-free MAO coating. In another recent study, Ding et al [140], fabricated rutile, anatase, Al_2TiO_5 , $\alpha\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$ containing MAO coatings on Ti2AlNb alloy by using Al_2O_3 added sodium aluminate based electrolyte, reported an enhancement in wear resistance against Si_3N_4 counterface.

On the other hand, it has been declared by Li et al. [145] that the concentration of ZrO_2 in a phosphate-based electrolyte plays a crucial role in the wear resistance of the MAO coatings fabricated on Ti6Al4V alloy. The presence of ZrO_2 in the electrolyte favoured t- ZrO_2 and ZrTiO_4 along with rutile and anatase in the structure of the MAO coating and provided an enhancement in the wear resistance against a steel counterface. But additions over 6 g/l of ZrO_2 into the electrolyte caused a reduction of wear resistance due to the increment in the surface roughness. Authors of the current study [146] previously synthesized a MAO coating comprised of rutile, dicalcium phosphate dihydrate, ZrTiO_4 , CaTiO_3 , t- ZrO_2 and m- ZrO_2 on Cp-Ti in 10 g/l ZrO_2 added calcium acetate hydrate and sodium phosphate containing electrolyte for biological applications and obtained an improvement in wear resistance against Al_2O_3 counterface in simulated body fluid as compared to particle-free MAO coating.

Since, incorporation of Al_2O_3 and ZrO_2 into the TiO_2 based MAO coatings provided more or less enhancement in wear resistance of titanium and its alloys, this study was initiated with the aim of comparing their effectiveness. Considering the formation of complex oxides (such as Al_2TiO_5 and ZrTiO_4), in the structure of MAO coatings upon incorporation of these ceramic particles [137,140,141,145,146,148], special attention has been paid to thermochemical modelling for formation of these complex oxides. The ultimate goal was to establish a relationship between microstructure and dry sliding wear resistance of fabricated MAO coatings under severe loading conditions (contact pressure > 1 GPa) to evaluate their applicability to wear-related engineering applications.

4.2 Experimental Procedures

Discs with a diameter of 28 mm were cut from Ti6Al4V (Grade 5) titanium alloy rods with a thickness of 3.5 mm and then they were cut in half along the diameter (i.e. semi-circular geometry). Prior to the MAO process samples were ground with SiC abrasive papers till an average surface roughness (R_a) of $0.15 \pm 0.02 \mu\text{m}$, followed by ultrasonic degreasing in ethanol and distilled water.

The MAO device used in this study consists of a bipolar pulsed DC power supply (constant voltage and constant current density modes are provided), a stainless steel electrolyte bath, an air stirring system and a cooling chamber system. In the present study, the constant voltage mode was selected. Ceramic particle-free MAO coatings were synthesized in an aqueous electrolyte containing sodium metasilicate anhydrous (Na_2SiO_3 , Alfa Aesar) and sodium phosphate tribasic anhydrous (Na_3PO_4 , Alfa Aesar) and this electrolyte was named as the reference electrolyte. In order to obtain composite coatings, $\alpha\text{-Al}_2\text{O}_3$ (1.5 μm , Alfa Aesar) and m- ZrO_2 (1.2 μm , Alfa Aesar) particles were added into the reference electrolyte. Concentration of Al_2O_3 and ZrO_2 was chosen as 10 g/l by considering our previous work [146], which yielded promising wear resistance in simulated body fluid. Different from Ref [146], silica based electrolyte has been used in this study to avoid formation of biocompatible compounds (such as dicalcium phosphate dihydrate, CaTiO_3) to clearly detect the influence of incorporated particles (Al_2O_3 and ZrO_2) on the properties of MAO coatings. Prior to MAO process, Al_2O_3 and ZrO_2 added electrolytes were stirred for 1 h on a magnetic stirrer to disperse the particles homogenously. The composition, pH and conductivity

values of the electrolytes used in the present study are listed in Table 4.1. Zeta potentials of the Al_2O_3 and ZrO_2 particles in the electrolyte were measured as about – 19 and – 8 mV, respectively.

MAO treatment was performed with an applied voltage of 500 V in the positive half cycle and 100 V in the negative half cycle. The pulse frequency and duty cycle were 500 Hz and 40%, respectively. Each sample was treated for 8 min and then cleaned ultrasonically in ethanol and distilled water. Samples were used as anodes, while a stainless steel cylinder container was used as the cathode in the electrolyte bath kept at 20 ± 2 °C by a circulating water in the cooling chamber system, both to prevent evaporation and to regulate the possible reactions in the electrolyte. During MAO process, the variation of current density was continuously recorded for each sample, which are referred to as MAO, MAO-Al and MAO-Zr samples depending on the type of particles added in the electrolyte (i.e. reference electrolyte, Al_2O_3 and ZrO_2 added electrolytes, respectively).

Table 4.1 : Description of the electrolytes used in the present study.

Code	Composition	pH	Conductivity (mS/cm)
MAO	10 g/l Na_2SiO_3 5 g/l Na_3PO_4	12.38	23.1
MAO-Al	10 g/l Na_2SiO_3 5 g/l Na_3PO_4 10 g/l $\alpha\text{-Al}_2\text{O}_3$	12.37	22.8
MAO-Zr	10 g/l Na_2SiO_3 5 g/l Na_3PO_4 10 g/l m- ZrO_2	12.38	22.9

After the MAO process, Ra and thickness values of the coatings were measured by a stylus type profilometer (Veeco Dektak 6M) and an eddy current thickness gauge (Fischer Dualscope), respectively. The phase composition of the MAO'ed samples was investigated by XRD technique (GBC MMA 027) using Cu-K α radiation at 35 kV and 28.5 mA with a scan range between 20-80° at a step of 0.020° and a scanning speed of 1 °/min. Surface and cross-sectional morphologies and elemental composition of the MAO coatings were determined by a field emission SEM (Zeiss Merlin Gemini II) equipped with an EDS (Quantax 800). XPS analysis (Thermo Scientific K α) were also conducted on the MAO'ed samples by using an aluminium anode (Al K α = 146.3

eV). Avantage 5.9 data system was used to analyse XPS spectra of samples, which were calibrated by setting binding energy scale of C 1s at 284.6 eV.

In order to describe the formation of phases identified by XRD analyses, in the structure of the MAO coatings, thermochemical modelling studies have also been employed using FactSage 7.3 [149]. The FToxid solution database, which contains oxide solutions evaluated/optimized by the FACT group, was selected in the calculations.

The hardness of Ti6Al4V alloy substrate and MAO coatings were measured (average of 10 measurements) from cross-sections of the polished samples using a Vickers micro-hardness tester (Wilson Tukon 1102) at a load of 25 g.

Wear tests were performed using a ball-on-flat reciprocating tribometer (Tribotech Oscillating Tribotester) at room temperature under dry sliding conditions. As the counterface WC ball with a diameter of 6 mm was used. Prior to wear tests surfaces of the MAO'ed samples were gently ground with SiC sandpapers to reduce the roughness under Ra value of 0.25 μm . The sliding speed, sliding distance and length of the wear track were 10 mm/s, 200 m, and 5 mm, respectively. Wear testing loads were selected as 2, 3 and 4 N, which yielded contact pressures in between 1 and 1.5 GPa for TiO₂/WC tribo-couple. Friction curves were recorded by the software of the tribometer. Following the wear tests, 2-D profiles of the wear tracks developed on the surfaces of the examined samples were determined by using a stylus type profilometer (Veeco Dektak 6M). At least five 2-D profiles were taken from different locations of each wear track. Worn surface examinations were conducted by using a SEM (Hitachi TM-1000). The images of the wear scars on WC balls were obtained by an optical microscope (Leica DM750M) after each wear test.

4.3 Results and Discussion

4.3.1 Formation of MAO coatings

The effect of the electrolyte composition (Table 4.1) on the variation of the current densities during the MAO process and appearances of the fabricated coatings are illustrated in Fig. 1 along with their Ra and thickness values. For the MAO coating, current density raised sharply at a rate of 0.05 A/cm²s within about 20 s from the start-up and then reached an approximate maximum current density value of 1.25 A/cm².

The maximum current density values were about 1.1 A/cm² for MAO-Al coating and about 0.9 A/cm² for MAO-Zr coating. After the sharp linear increase to their maximum current density values, a reduction in current density was observed for all samples. However, the current density values were then distinguished into two groups; while the current densities of the MAO-Al and MAO-Zr samples decreased gradually till the end of the MAO process, the current density of the MAO sample declined to about 0.65 A/cm² after remaining stable for almost 250 s. By the end of the MAO process, the current density values of MAO-Al and MAO-Zr samples diminished nearly to 0.03 and 0.2 A/cm², respectively.

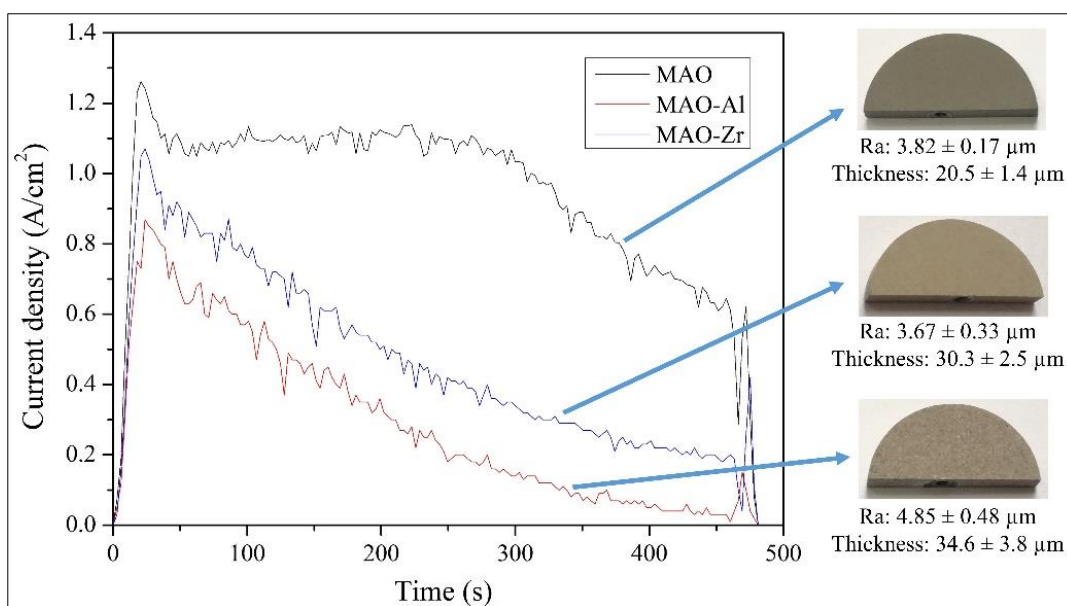


Figure 4.1 : Variations of current density during processing of MAO, MAO-Al and MAO-Zr samples. Appearances of the coatings and their Ra and average thickness values are also presented.

After MAO process, samples displayed different colours (Fig. 4.1). MAO coating formed in the reference electrolyte (processed at the highest current density), exhibited a uniform dark grey surface appearance with Ra and average thickness values of 3.82 and 20.5 µm, respectively. The addition of ceramic particles into the reference electrolyte caused progress of MAO process at lower current density levels and promoted the formation of thicker coatings with light-coloured surface appearances. The MAO-Al coating, having Ra and average thickness values of 4.85 and 34.6 µm, respectively, exhibited a light grey colour and contained dark grey small islands like appearance on its surface. On the other hand, the MAO-Zr coating with Ra and average

thickness values of 3.67 and 30.3 μm , respectively, exhibited a light beige colour and a smoother appearance.

It has been well documented that MAO favours mainly TiO_2 -based coatings on titanium-based materials [131,133]. As depicted in Fig. 4.1, Al_2O_3 and ZrO_2 containing electrolytes enabled thicker coatings as compared to particle free reference electrolyte, which is more dominant for the MAO-Al coating. Higher growth rates of MAO-Al and MAO-Zr coatings than MAO coating can be attributed to the in-situ transfer of Al_2O_3 and ZrO_2 particles from the electrolyte to the growing TiO_2 -layer by electrophoretic effect. Thus, during positive DC pulses of MAO process, negatively charged particles (due to attachment of OH^- ions) tend to move in the electrolyte towards the substrate acting as anode. Further prolonging for processing time causes increased incorporation of these particles in the growing MAO coating [37]. Since high absolute value of zeta potential (measured as 19 and 8 mV for Al_2O_3 and ZrO_2 in the reference electrolyte, respectively) accelerates particle movement in the electrolyte and facilitates faster incorporation of particles into growing coating, the thicker coating was developed in the Al_2O_3 added electrolyte as compared to ZrO_2 added one.

Other than possible changes in the microstructure of MAO coatings (compactness, new phase formation, etc), differences in current densities recorded during MAO process can be associated with the difference in electrical resistivity's of Al_2O_3 and ZrO_2 ($>10^{14}$ and $>10^{13}$ $\Omega\cdot\text{cm}$, respectively, according to [150]). The particle incorporation into growing TiO_2 (having electrical resistivity of $>10^{12}$ $\Omega\cdot\text{cm}$ [151]) tended to increase the electrical resistance of the developing MAO coating, which in turn kept on lowering the current densities as the MAO coating grew in the ceramic particle added electrolytes.

4.3.2 Structural features of MAO coatings

The XRD spectra of the MAO'ed samples are given in Fig. 4.2. MAO coating fabricated in the reference electrolyte mainly constituted of anatase and rutile forms of TiO_2 . In the case of MAO coatings fabricated in Al_2O_3 and ZrO_2 added electrolytes, additional peaks of added ceramic particles and their complex oxide forms (Al_2TiO_5 and ZrTiO_4) appeared on the XRD spectra, in accordance with the relevant literature [137,140,141,145,146,148]. Moreover, halo appeared on the XRD spectra (below 40°) as an indication of amorphous phase in the structure of the coatings. Presence of α -Ti

peaks on the XRD spectra can be attributed to penetration of X-rays beyond the porous MAO coatings [137,141,145,146].

The presence of complex oxides (Al_2TiO_5 and ZrTiO_4) in structure of MAO-Al and MAO-Zr coatings could be the results of following plasma induced reactions between growing TiO_2 and incorporated ceramic particles (Al_2O_3 and ZrO_2) during MAO process [135,147].

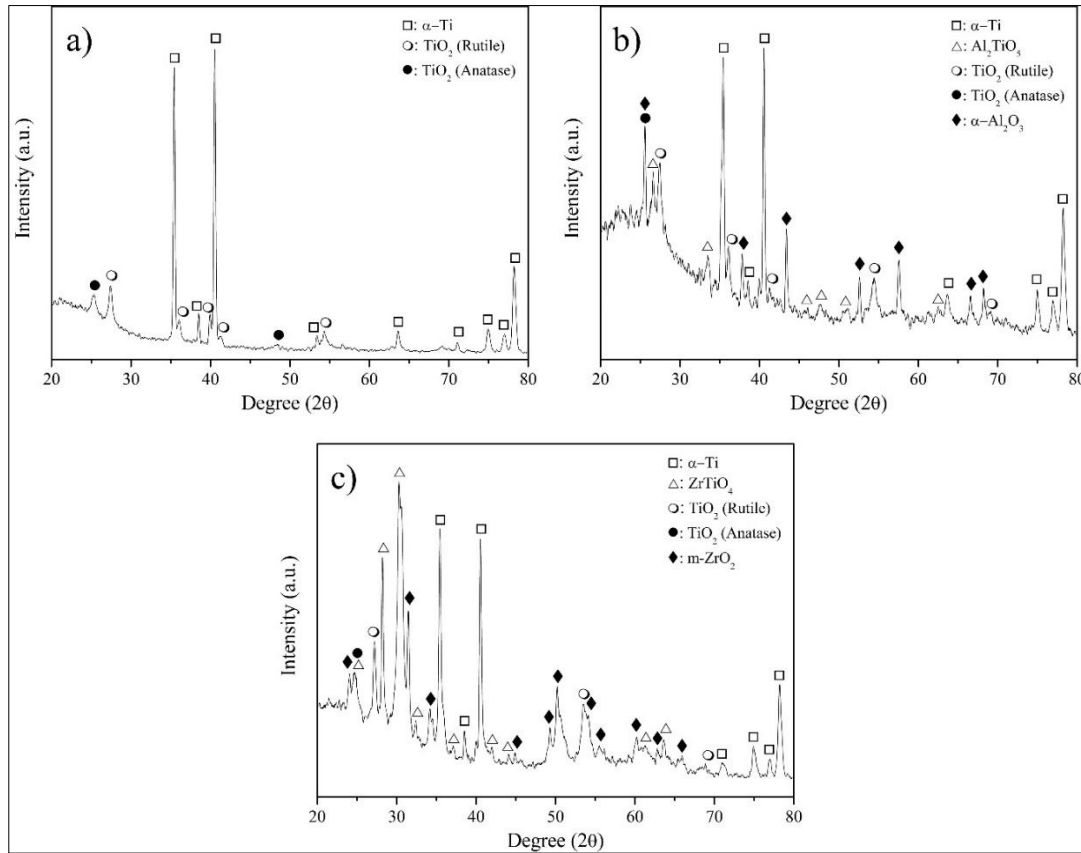
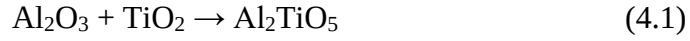


Figure 4.2 : XRD spectra of (a) MAO, (b) MAO-Al and (c) MAO-Zr samples.

In order to evaluate the formation of these complex oxides (Eqs. 1 and 2), thermochemical modelling studies have been employed by using FactSage 7.3 software to calculate binary TiO_2 - Al_2O_3 and TiO_2 - ZrO_2 phase diagrams (in molar fraction) as depicted in Figs. 4.3 and 4.4, respectively.

In equilibrium conditions of the TiO_2 - Al_2O_3 system presented in Fig. 4.3a, Al_2TiO_5 is stable above 1264 °C and below this temperature, it decomposes into a mixture of corundum form of Al_2O_3 and rutile form of TiO_2 throughout the calculated binary

diagram. Since, the presence of Al_2TiO_5 in the structure of the MAO coating at room temperature was previously attributed to suppression of its decomposition into the mixture of TiO_2 and Al_2O_3 because of the rapid cooling of plasma exposed surfaces in the electrolyte [152] therefore, an attempt has been made in this study to plot the TiO_2 - Al_2O_3 system by Scheil-Gulliver approach. This is particularly used when the cooling rate of a homogenous liquid is high, by assuming no diffusion in the solid phases, always a homogeneous liquid phase and a local equilibrium at the solid/liquid interface [149,153,154]. In the process, when the liquid phase disappears, the cooling calculation is terminated, and the precipitates are assumed to be chemically stable. The Scheil-Gulliver solidification diagram for TiO_2 - Al_2O_3 system is shown in Fig. 4.3b. Different from the equilibrium phase diagram (Fig. 4.3a), two types of aluminium titanate phases (Al_2TiO_5 and Al_4TiO_8) were calculated to be stable in the whole solid region. In the TiO_2 -rich zone of the diagram ($0 < X_{\text{Al}_2\text{O}_3} \leq 0.56$), the precipitated phases are rutile and Al_2TiO_5 . As the Al_2O_3 content in the system increases, rutile disappears and Al_4TiO_8 ($0.56 \leq X_{\text{Al}_2\text{O}_3} \leq 0.68$) and corundum (Al_2O_3) phases ($0.68 \leq X_{\text{Al}_2\text{O}_3} < 1$) occur.

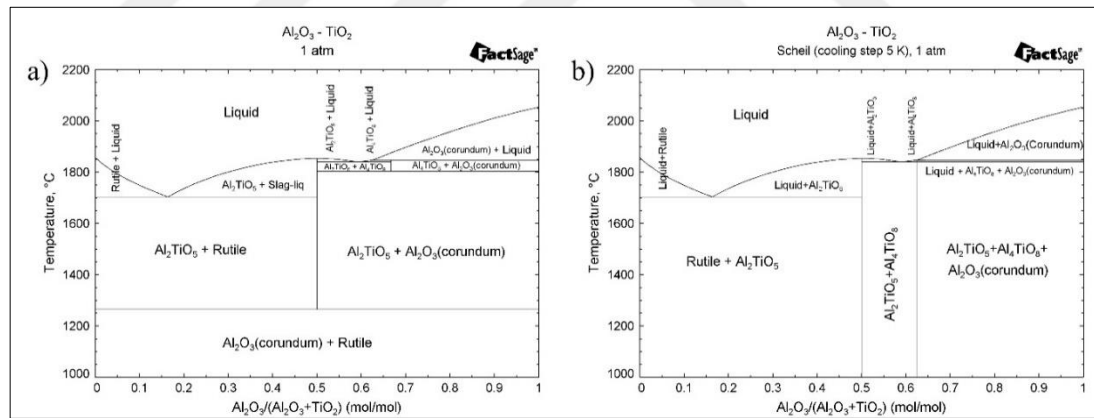


Figure 4.3 : (a) Equilibrium and (b) Scheil-Gulliver cooling diagrams for the binary TiO_2 - Al_2O_3 system.

The equilibrium and Scheil-Gulliver diagrams for the TiO_2 - ZrO_2 system are shown in Figs. 4.4a and b, respectively. In equilibrium conditions, as the system cools down, ZrTiO_4 phase, which occurs between rutile and t- ZrO_2 solid solutions, changes to Ti_2ZrO_6 in the presence of rutile or m- ZrO_2 phases depending on the $\text{ZrO}_2/\text{Al}_2\text{O}_3$ ratio. Finally, t- ZrO_2 solid solution completely transforms into m- ZrO_2 below $\sim 920^\circ\text{C}$. According to the Scheil-Gulliver solidification diagram (Fig. 4.4a), the precipitated phases are rutile and ZrTiO_4 in the TiO_2 -rich zone of the diagram ($0 < X_{\text{ZrO}_2} \leq 0.32$).

As the ZrO_2 content in the melt increases, t- ZrO_2 ($0.32 \leq X_{\text{ZrO}_2} \leq 0.72$) and c- ZrO_2 phases ($0.72 \leq X_{\text{ZrO}_2} < 1$) are added up to the system, respectively. It should be noted that Ti_2ZrO_6 does not occur anywhere in the system. It can be concluded that the presence of the ZrTiO_4 phase observed in the MAO-Zr sample (Fig. 4.2) can be well explained by Scheil-Gulliver solidification, whereas m- ZrO_2 formation in the sample may be explained by a subsequent transformation from the precipitated ZrO_2 (cubic or tetragonal) at lower temperatures.

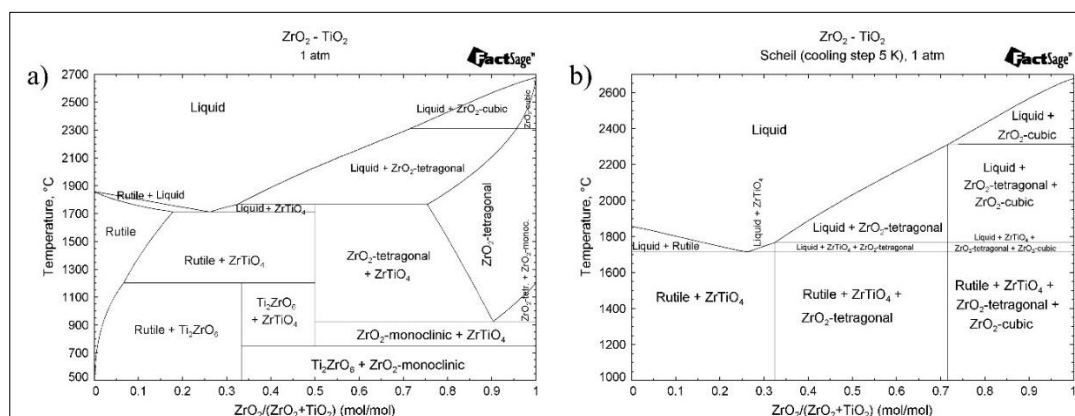


Figure 4.4 : (a) Equilibrium and (b) Scheil-Gulliver cooling diagrams for the binary TiO_2 - ZrO_2 system.

The surface and cross-section SEM micrographs (along with elemental mappings of Al and Zr as the main constituents of the incorporated ceramic particles) of the examined MAO coatings are shown in Figs. 4.5 and 4.6, respectively. In general, surface appearances exhibited microporous characteristics of MAO coatings. Although, the coatings exhibited almost similar surface morphologies, the surface of MAO-Al and MAO-Zr coatings contained larger micro-pores as compared to MAO coating. Furthermore, cross-section examinations revealed that MAO coatings were well integrated to the substrate and MAO-Al coating was less dense than MAO and MAO-Zr coatings. Surface and cross-section elemental mappings of the MAO-Al and MAO-Zr coating showed almost an even distribution of Al and Zr. A closer examination on the elemental mappings revealed the presence of bright areas within the coatings, with the size ranging from submicron to about $5 \mu\text{m}$. Given the average size of the ceramic particles added to the electrolytes (about $1 \mu\text{m}$), it has been suggested that these larger bright areas correspond to precipitates of the relevant ceramic particles formed during solidification.

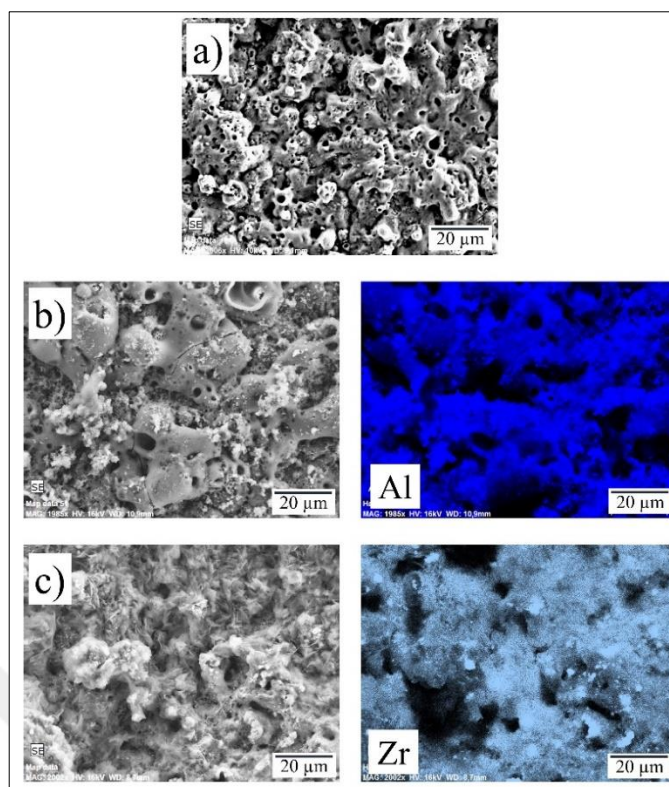


Figure 4.5 : Surface SEM micrographs of (a) MAO, (b) MAO-Al and (c) MAO-Zr samples. Elemental mappings of Al and Zr are also depicted for MAO-Al and MAO-Zr samples, respectively.

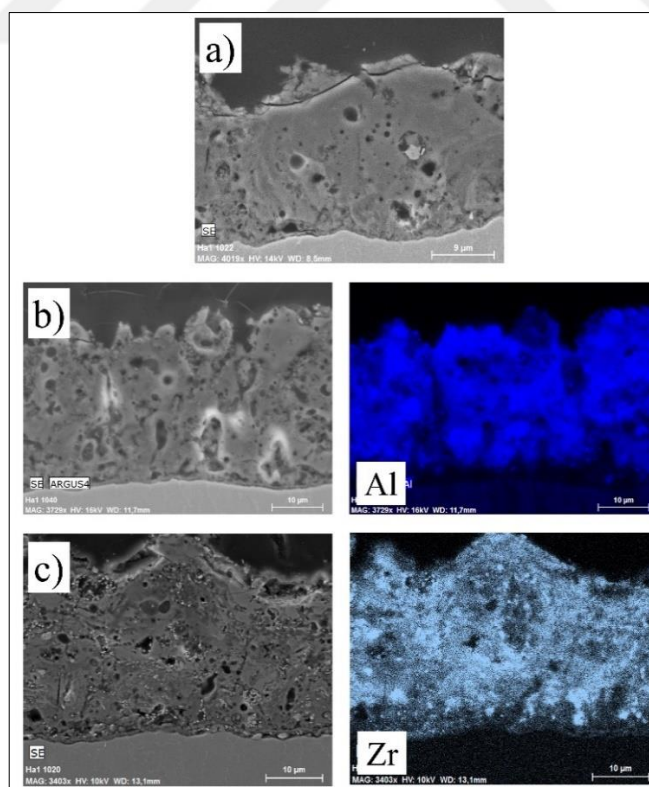


Figure 4.6 : Cross-section SEM micrographs of (a) MAO, (b) MAO-Al and (c) MAO-Zr samples. Elemental mappings of Al and Zr are also depicted for MAO-Al and MAO-Zr samples, respectively.

Although EDS analyses conducted during SEM surveys of MAO coatings revealed the incorporation of Si, P and Na elements in the electrolytes into the MAO coatings as given in Table 4.2, no peaks of Si-, P- and Na- based compounds were identified on the XRD spectra (Fig. 2). Considering the higher amount of Si than P and Na in the coatings (Table 4.2), XPS analyses were carried out for confirmation of presence of SiO₂ in structure. The XPS spectrum of the MAO, MAO-Al and MAO-Zr coatings for Si and O elements are shown in Fig. 4.7. Peaks located at about 533 eV on the O 1s spectrum and the peaks located at about 103 eV on the Si 2p spectrum are characteristics of SiO₂ [155,156].

Table 4.2 : Average surface elemental composition of MAO, MAO-Al and MAO-Zr coatings.

Element (wt. %)	MAO	MAO-Al	MAO-Zr
O	53.7 ± 2.3	42.2 ± 1.8	44.1 ± 1.6
Ti	5.3 ± 0.7	6.9 ± 0.8	3.5 ± 0.4
Si	36.2 ± 1.4	16.5 ± 1.2	19.2 ± 1.1
P	2.2 ± 0.2	1.4 ± 0.2	6.1 ± 0.5
Al	1.5 ± 0.2	28.7 ± 2.0	1.0 ± 0.1
Na	1.1 ± 0.1	4.3 ± 0.5	17.8 ± 1.1
Zr	-	-	8.3 ± 0.1

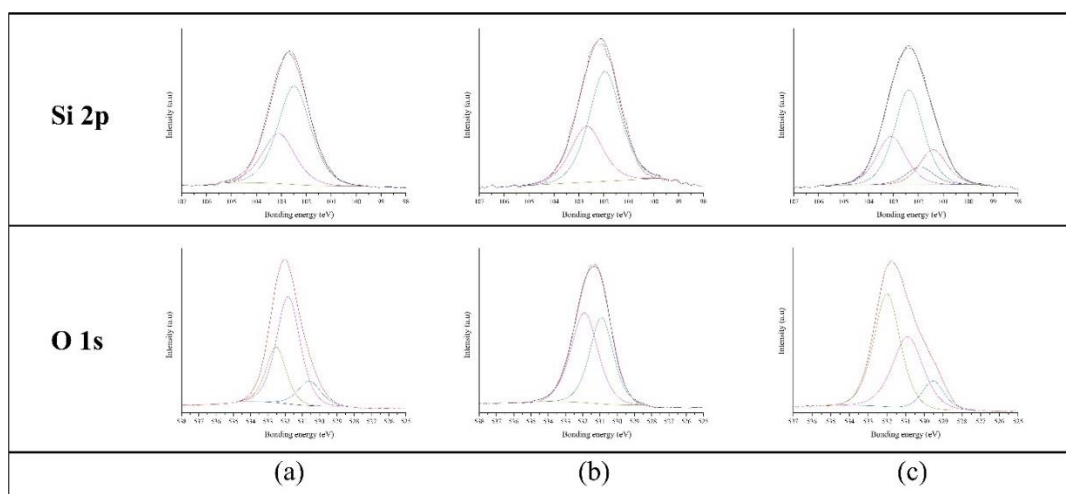


Figure 4.7 : XPS spectra of (a) MAO, (b) MAO-Al and (c) MAO-Zr coatings for Si and O elements.

Owing to the identification of SiO₂ in the structures of the examined MAO coatings, Scheil-Gulliver approach has been applied to TiO₂ - SiO₂ system as depicted in Fig.

4.8, which is found to be identical to the equilibrium diagram for the computed region (figure not shown). The TiO_2 - SiO_2 binary phase diagram showed that two liquids (TiO_2 -rich and SiO_2 -rich) are stable within the compositional limits $X_{\text{SiO}_2} = 0.080$ and 0.846 above the temperature of $1807\text{ }^\circ\text{C}$. Meanwhile rutile and SiO_2 -rich liquid are two phases found within the compositional limits $X_{\text{SiO}_2} = 0$ and 0.938 and between 1807 and $1546\text{ }^\circ\text{C}$. In the SiO_2 -end of the diagram ($0.938 \leq X_{\text{SiO}_2} < 1$), SiO_2 (cristobalite) starts to precipitate from the single SiO_2 -rich liquid upon cooling. Both rutile and SiO_2 (cristobalite) phases form below $1546\text{ }^\circ\text{C}$ throughout the system.

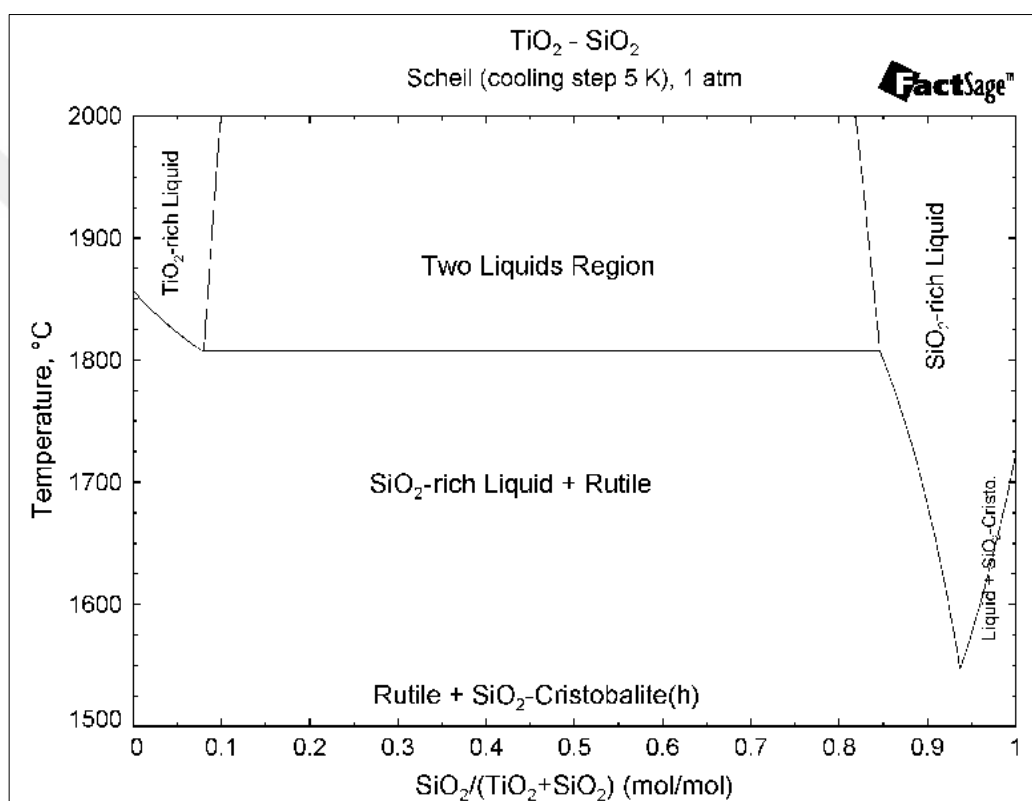


Figure 4.8 : Scheil-Gulliver cooling diagram for the binary TiO_2 - SiO_2 system.

The results of XPS analysis (Fig. 4.7) and thermochemical modelling of TiO_2 - SiO_2 system (Fig. 4.8) confirmed the presence of SiO_2 in the structure of examined MAO coatings. In this respect, the halo appeared below 40° of 2θ on the XRD spectra (Fig. 4.2) could be the result of low critical cooling rate ($2 \times 10^{-4}\text{ K/s}$) of amorphous SiO_2 [157] inhibiting its crystallization during cooling. Thus, it is suggested that rapid cooling favoured amorphous SiO_2 in the MAO coatings.

The average hardness of the examined MAO coatings and the Ti6Al4V alloy taken from the cross-sections are shown in Fig. 4.9. While the hardness of the MAO coating is close to the hardness of the Ti6Al4V alloy, the hardness values of MAO-Al and

MAO-Zr coatings were slightly higher. Although, phase structures could be responsible for the difference in the hardness of the examined coatings, it should be noted that the hardness values of the MAO coatings were below the bulk hardness of TiO₂ (about 1200 HV) with a wider scatter due to microporous nature of the MAO coatings.

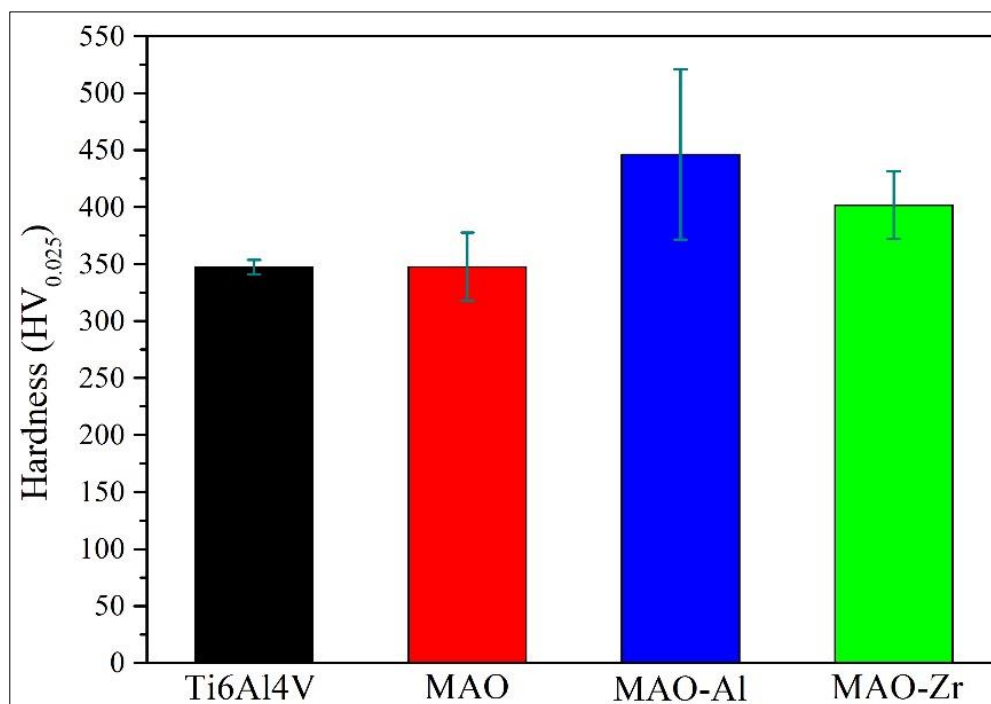


Figure 4.9 : Average hardness of Ti6Al4V substrate and MAO coatings measured from the cross-sections.

4.3.3 Wear characteristics of MAO coatings

Representative 2-D profiles of the wear tracks and quantified wear loss of the examined samples are shown in Fig. 4.10. At first glance, it is evident that wear track areas of the MAO'ed samples are almost negligible as compared to that of the Ti6Al4V alloy, with the exception of MAO-Al sample tested under 3 and 4 N. Wear track areas of MAO'ed samples tested under the load of 2 N were very close to each other. The increase of testing load to 3 N caused a discrepancy in wear track areas of the MAO'ed samples, even though the depth of the wear tracks was still less than the thickness of the coatings. As the testing load increased to 4 N, the wear track area of the MAO-Al sample approached to that of the Ti6Al4V alloy, while the wear track area of the MAO-Zr sample was smaller than that of the MAO sample.

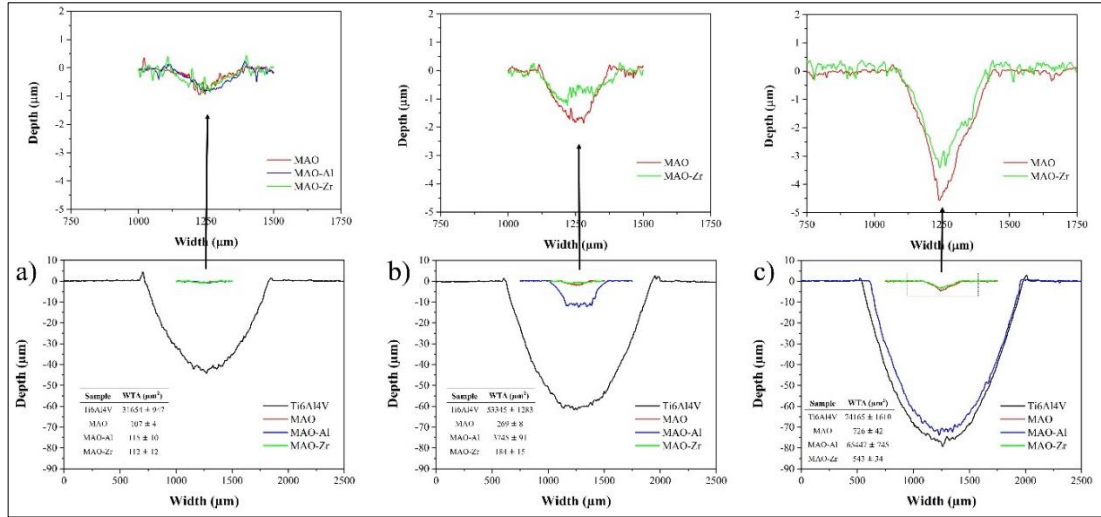


Figure 4.10 : Representative 2-D profiles of the wear tracks developed on the surfaces of examined samples after wear tests conducted under wear test loads of (a) 2 N, (b) 3 N and (c) 4 N. For each wear test load and sample calculated average wear track areas (WTA) are also presented.

Results of the wear tests are quantified in Fig. 4.11 as wear rate (mm^3/Nm), which was calculated by dividing the volume of the wear track (area $\times$ length, mm^3) to testing load (N) and total sliding distance (m). It is very evident that at high testing loads (≥ 3 N) wear rate of the MAO-Al sample got closer to that of the Ti6Al4V alloy, while the lowest wear rate was obtained from MAO-Zr sample. For the highest wear testing load of 4 N generating contact pressure of ~ 1.5 GPa, wear rate of the MAO-Zr sample was about 25% lower than that of MAO sample.

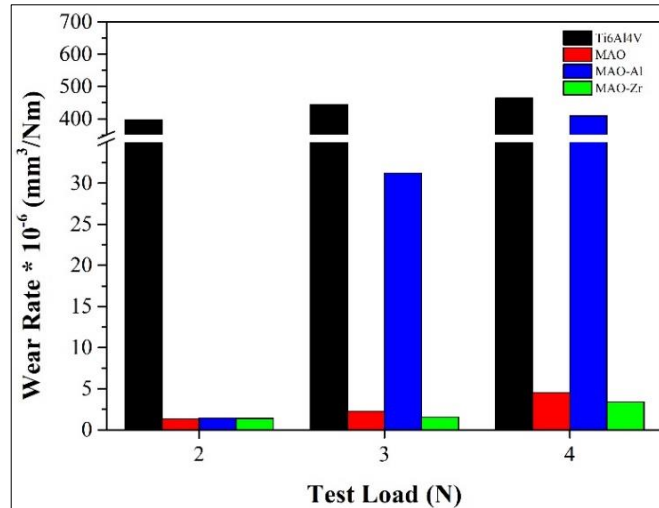


Figure 4.11 : Wear rates of the examined samples calculated for the employed wear test loads.

Friction curves of the examined samples recorded during wear tests are presented in Fig. 4.12. In general, friction coefficient tended to remain constant after a certain

period from the running-in. Unlike smooth friction curves of the MAO'ed samples, where wear progressed under ceramic/ceramic contact (i.e. WC ball/oxide based MAO coating), friction curves of the Ti6Al4V alloy fluctuated in a wide range as an indication of stick-slip phenomenon at the WC ball/Ti6Al4V alloy (i.e. ceramic/metal) contact surface. It has been well established that titanium and its alloys are prone to stick-slip under sliding contact, which defines sequential sticking and sliding between the mating surfaces, owing to their strong adhesion characteristics [129]. However, heavy fluctuations have been observed on the friction curve of the MAO-Al sample after the sliding distance of about 25 m (similar to the friction curve of the Ti6Al4V alloy), which exhibited the highest wear rate among the MAO'ed samples under the test load of 4 N (Fig. 4.11). This observation can be attributed to the complete removal of the coating providing ceramic/metal sliding contact between counterface (WC ball) and substrate (Ti6Al4V alloy), thereafter.

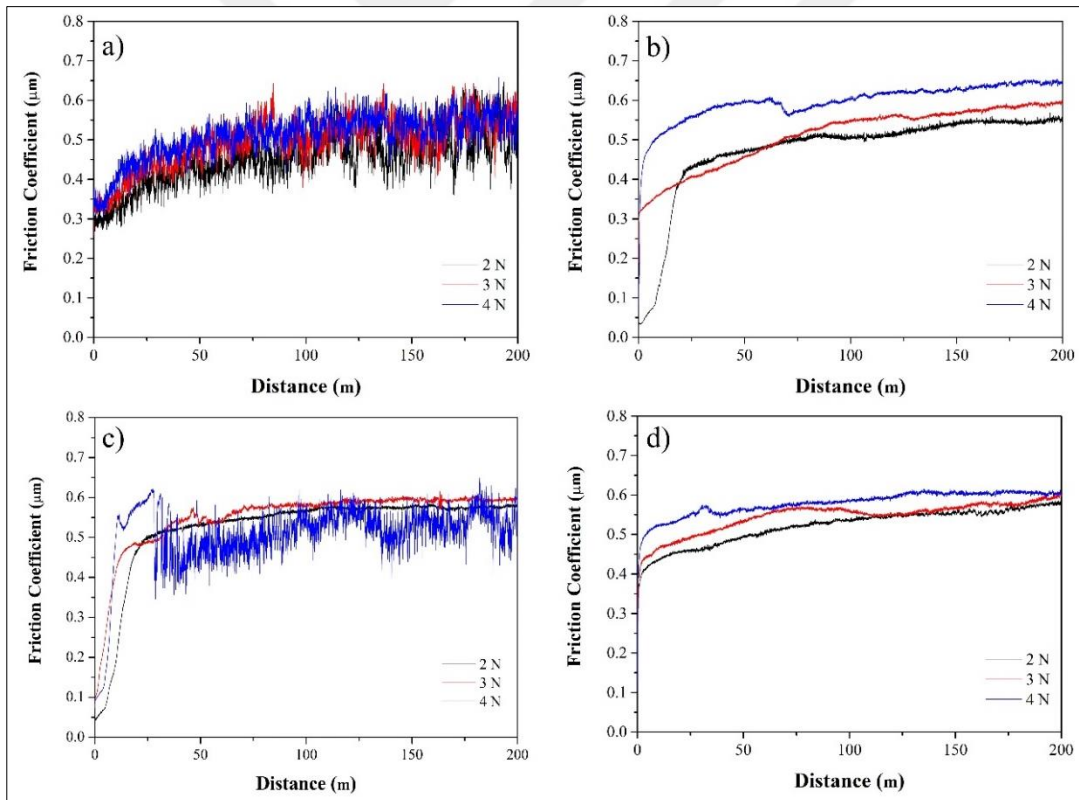


Figure 4.12 : Friction curves of (a) Ti6Al4V, (b) MAO, (c) MAO-Al and (d) MAO-Zr samples worn under wear test loads of 2, 3 and 4 N.

Worn surface SEM images of the examined samples and contact surface optical microscopic images of the counterface (WC ball) are given in Figs. 4.13 and 4.14, respectively. In general, worn surfaces of the Ti6Al4V alloy exhibited a rough and

delaminated topography, which is an indication of plasticity dominated wear. Ploughing action of the counterface also generated grooves aligned with the sliding direction and caused darkening of the contact surface of the counterface. These observations indicated that there was material transfer from the Ti6Al4V alloy to the counterface, which is the characteristic of adhesive wear. It is a well-known fact that titanium and its alloy suffer from severe adhesive wear when they slide over most of the ceramic or metallic engineering materials under high contact pressures [2].

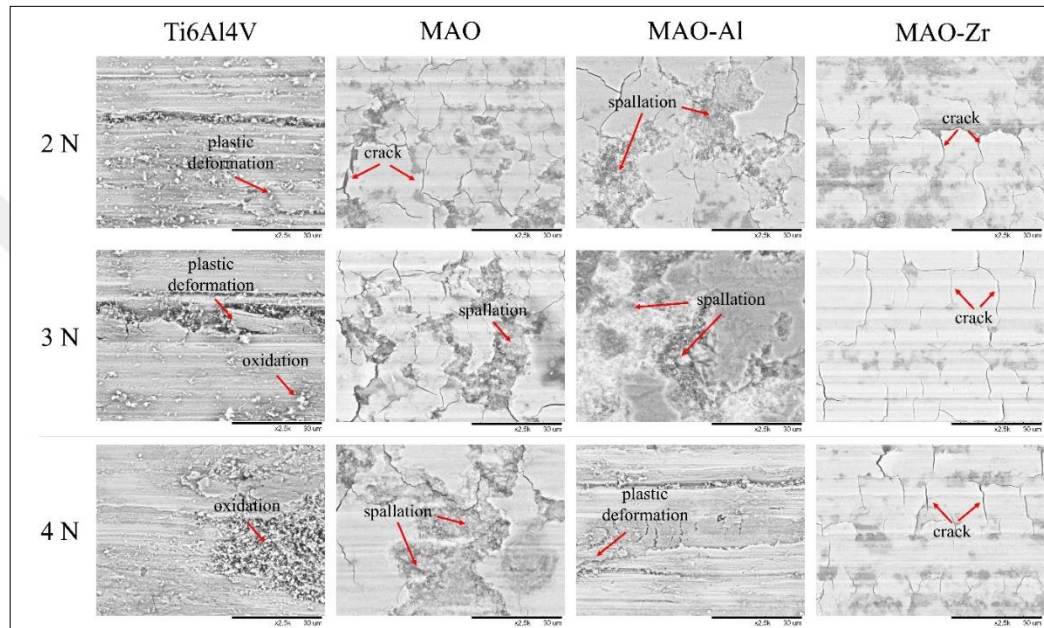


Figure 4.13 : SEM micrographs of wear tracks worn under wear test loads of 2, 3 and 4 N.

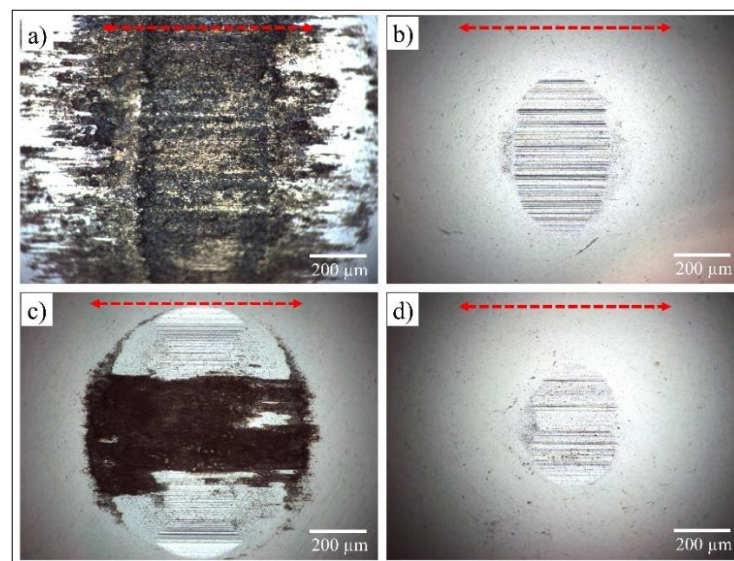


Figure 4.14 : Wear scars formed on the contact surfaces of WC balls used in wear tests of (a) Ti6Al4V, (b) MAO, (c) MAO-Al and (d) MAO-Zr samples under load of 4 N. Arrows are showing the reciprocating sliding directions.

The major difference between worn surfaces of MAO'ed samples and Ti6Al4V alloy is lack of any evidence for plasticity dominated adhesive wear on MAO coatings. This observation can be associated with the very limited plastic deformation ability of ceramics/oxides. Unlike Ti6Al4V alloy, worn surfaces of the MAO'ed samples were relatively smooth but contained micro-crack networks, which are the characteristics of mechanically degraded ceramics under repeated sliding contact via fatigue wear mechanism [33]. The formation of the micro-crack network on the worn surfaces of the MAO'ed samples can be attributed to the porous nature of the MAO coatings, where pores acted as stress risers for easy crack initiation even under very low wear test load. Furthermore, on the worn surfaces of the MAO and MAO-Al samples, local spallation (release of large fragments from the contact surface) was observed in addition to micro-cracks, and became more intense with the increase of wear test load. As compared to the MAO sample, spallation was more severe for MAO-Al sample, so that coating was not detected on its worn surface after testing under 4 N. After complete removal of the MAO-Al coating, wear progressed on Ti6Al4V alloy and therefore, contact surface of the counterface was darkened due to material transfer. However, partial removal of the coating during wear testing as in the case of MAO sample caused scratching at the contact surface of the counterface by the wear particles rather than material transfer. It should be noted that the size of the scar formed on the contact surface of the counterface is proportional with the size of the relevant wear track formed on the examined samples, so that the bigger the wear track area the larger was the size of the scar on the counterface.

Results of the wear tests revealed that application of MAO to Ti6Al4V alloy caused shifting of the wear mechanism from adhesive wear to fatigue wear. Since cracking was more readily favourable than plastic deformation for MAO coatings owing to their ceramic nature, cracks initiated on the contact surface tended to grow towards the subsurface under repeated sliding contact and finally resulted in release of large fragments from the contact surface (spallation) [158] as in the case of MAO and MAO-Al samples. In this respect, spallation free worn surface appearance of the MAO-Zr sample even under the highest test load employed in this study can be attributed to its higher resistance against crack growth, which is related with the fracture toughness.

Mechanical properties of the main structural constituents of the examined MAO coatings are listed in Table 4.3 with the exception of amorphous phase analysed in

Section 4.3.2. Incorporation of Al_2O_3 into the growing TiO_2 during MAO process caused formation of metastable and brittle Al_2TiO_5 type complex oxide (having the lowest fracture toughness and fracture strength in Table 4.3) in the MAO-Al coating. Therefore, it is suggested that formation of Al_2TiO_5 in the structure lowered the fracture toughness of the MAO-Al coating and caused acceleration of spallation, which finally imposed the worst wear resistance. Although fracture toughness of ZrTiO_4 is not available in the open literature to the best knowledge of the authors, it has remarkably higher fracture strength than TiO_2 . It is more likely that presence of ZrTiO_4 along with ZrO_2 and TiO_2 in the structure of MAO-Zr coating retarded growth of the surface initiated cracks and therefore provided much better wear resistance.

Table 4.3 : Mechanical properties of the structural constituents of the fabricated MAO coatings.

Phase	Fracture Toughness ($\text{MPa}\cdot\text{m}^{1/2}$)	Fracture strength (MPa)
TiO_2	2.8 [15]	69-103 [159]
Al_2O_3	3.5-5.2 [160]	282-1084 [15]
Al_2TiO_5	0.5 [161]	25-45 [162]
ZrO_2	4.9-5.8 [163]	2068 [15]
ZrTiO_4	N/A	194-227 [164]

The most important output of this study is to put emphasis on the selection of the additives for electrolytes, when making any attempt to reinforce MAO coatings for wear-related applications. Mechanical properties of the in-situ compounds that could form by plasma induced chemical reactions (between the base metal oxide and additives) play crucial role on the wear resistance of MAO coatings. While brittle compounds (such as Al_2TiO_5 type complex oxide formed in the structure of the MAO-Al coating) can deteriorate the wear resistance, tough ones (such as ZrTiO_4 type complex oxide formed in the structure of the MAO-Zr coating) increase the wear resistance by retarding spallation, under repeated sliding contact.

4.4 Conclusion

In this study, structural features and wear performances of MAO coatings fabricated on Ti6Al4V alloy in a silicate-based electrolyte with and without additions of Al_2O_3

and ZrO_2 particles are examined. Results of the experimental works can be summarised as follows:

1. The morphological features, thickness, roughness, and phase composition of the MAO coatings fabricated on Ti6Al4V showed a strong dependence on the type of the ceramic particle added into the electrolyte. MAO in Al_2O_3 and ZrO_2 added silicate based electrolytes not only caused incorporation of these ceramic particles into TiO_2 based coating but also let formation of their complex oxides (Al_2TiO_5 and ZrTiO_4 , respectively) along with amorphous SiO_2 .
2. Although the hardness of the MAO coatings (between 350 and 450 $\text{HV}_{0.025}$) was close to that of the Ti6Al4V alloy (350 $\text{HV}_{0.025}$), their presences on the surface caused remarkable increment in wear resistance of Ti6Al4V alloy by altering the wear mechanism from adhesive to fatigue wear.
3. While wear test load of 2 N favoured cracking on the contact surfaces of the MAO'ed samples, increasing of wear test load to 3 and 4 N dictated spallation on worn surfaces of MAO and MAO-Al samples, unlike MAO-Zr sample. Spallation was more severe for MAO-Al sample as compared to MAO sample.
4. The poor wear resistance of MAO-Al sample arising from heavy spallation can be associated with the presence of the brittle complex oxide (Al_2TiO_5) in the structure of its coating. On the other hand, ZrTiO_4 type complex oxide in the structure, as in the case of spallation-free MAO-Zr sample, provided better resistance against sliding wear at contact pressures higher than 1 GPa.

4.5 Acknowledgement

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5. SYNTHESIS OF ZIRCONIA INCORPORATED TITANIA LAYER BY MICRO ARC OXIDATION FOR BIOMEDICAL APPLICATIONS ⁴

5.1 Introduction

Titanium and its alloys are attractive materials in the biomedical industry for the manufacturing of implants owing to their low density, low Young's modulus, high tensile strength, and good biocompatibility [165–168]. However, their ease of surface degradation under mechanical contact and poor wear resistance are factors limiting their widespread usage. For example, aseptic loosening occurring shortly after implantation and inflammation of the surrounding tissue, giving rise to the bone resorption (osteolysis) upon release of wear debris into the bloodstream, are crucial problems associated with the poor wear resistance of titanium and its alloys [169,170]. Therefore, surface modification is required for titanium-based implants to extend implantation periods by minimizing *in vivo* surface degradations under mechanical contact.

Among the surface modification processes, micro arc oxidation (MAO) is an attractive technical solution for titanium-based materials due to its suitability for complex geometries and relatively low heat input, which does not alter the microstructure and/or mechanical properties of the substrate [171–174]. MAO generates a thick, hard, and adherent titania (TiO_2) layer over titanium and its alloys, which is generally composed of anatase and rutile forms of TiO_2 [175–177]. Furthermore, adjusting the composition of the electrolyte utilized in the MAO process can create a broad range of altered composition, morphology, and microstructure of the TiO_2 layer. In recent years, research efforts have focused on enhancing the bio- and/or antimicrobial-activities of the TiO_2 layer via adding chemicals containing Ca/P and/or Ag into the electrolyte, respectively [178–180].

⁴This chapter is based on the paper “F. Muhaffel and H. Cimenoglu, Synthesis of zirconia-incorporated titania layer by microarc oxidation for biomedical applications, *Surf. Interface Anal.* 47 (2015) 1166-1173”

While the TiO₂ layer has been reported to protect the titanium-based substrate under mechanical contact [181–183], further efforts to improve its mechanical stability and wear resistance by incorporating graphite, PTFE, MoS₂, and Si₃N₄ particles from the electrolyte have been made [165,184–186]. The increased biocompatibility, chemical inertness, and higher hardness of ZrO₂ motivated authors of present study to synthesize a ZrO₂-reinforced TiO₂ layer for biomedical applications. Although higher hardness has been obtained from ZrO₂-incorporated TiO₂ layers than from TiO₂ layers [187], its durability under sliding contact on Cp-Ti has not yet – to the best of the authors’ knowledge – been documented.

5.2 Material and Methods

Grade 4 quality Cp-Ti discs (10 mm in diameter and 4 mm in thickness) were used as a substrate. Prior to the MAO process, samples were ground with silicon carbide sandpaper to 1200 grit, then cleaned in acetone and distilled water. Cp-Ti samples were subjected to MAO at a current density of 2 A cm⁻² in a base electrolyte as listed in Table 5.1. Pulse frequency and duty cycle were 500 Hz and 60%, respectively. The temperature of the electrolyte was kept at 20 ± 2 °C during the MAO process by a cooling system in order to prevent evaporation of the solution and to regulate the chemical reaction rate. During the MAO process, variation of positive voltage was continuously recorded with a sampling time of 750 ms by using a memory recorder system (Hioki Memory Hicorder 8808). Each sample was processed for 10 min, then rinsed ultrasonically with acetone and distilled water and dried at room temperature. A separate sample group was oxidized under the same process parameters after adding monoclinic ZrO₂ powder (< 325 mesh, Alfa Aesar) to a concentration of 10 g l⁻¹ into the base electrolyte. Hereafter, samples oxidized in the base electrolyte and in the ZrO₂-added electrolyte will be referred to as MAO and MAO-Zr samples, respectively.

Table 5.1 : Electrolyte compositions for MAO process of Cp-Ti.

Electrolyte	Ca(CH ₃ COO) ₂ •H ₂ O (g L ⁻¹)	Na ₂ HPO ₄ (g L ⁻¹)	ZrO ₂ (g L ⁻¹)
Base	41	14.4	-
Base+ZrO ₂	41	14.4	10

Morphology, structure, and mean elemental composition of the exposed surfaces were evaluated after processing using a scanning electron microscope (SEM, Hitachi TM-1000, Jeol NeoScope JCM-6000 and FEI Quanta FEG 250) equipped with energy dispersive spectroscopy (EDS). Phase composition of MAO-exposed surfaces was identified using an X-ray diffractometer (XRD, GBC MMA 027) under Cu-K α radiation at 35 kV and 28.5 mA with a scan range between 20-80° and scanning speed of 2° min⁻¹ at a scan step of 0.020°. Surface roughness was measured by using a 2-D surface profilometer (SP, Veeco Dektak 6M). At least ten successive measurements were conducted on the layers and results were averaged to quantify the mean surface roughness (Ra).

In order to evaluate and compare the bioactivity characteristics in terms of biomimetic apatite forming capability, original Cp-Ti, MAO, and MAO-Zr samples were immersed in 1.5X simulated body fluid (SBF). Samples were vertically soaked in 120 mL SBF in closed screw-capped polypropylene bottles for 3 days. The 1.5X SBF solution was prepared according to Jalota's instruction as shown in Table 5.2 [188]. After soaking for 3 days, samples were removed from SBF, gently rinsed with distilled water, dried in air, and examined on XRD and SEM.

Table 5.2 : SBF composition used in the present study.

Compound	Concentration
NaCl	9.8184 g L ⁻¹
NaHCO ₃	3.4023 g L ⁻¹
KCl	0.5591 g L ⁻¹
Na ₂ HPO ₄	0.2129 g L ⁻¹
MgCl ₂ .6H ₂ O	0.4574 g L ⁻¹
1 M HCl	15 mL L ⁻¹
CaCl ₂ .2H ₂ O	0.5513 g L ⁻¹
Na ₂ SO ₄	0.5513 g L ⁻¹
((CH ₂ OH) ₃ CNH ₂)	9.0855 g L ⁻¹
1 M HCl	50 mL L ⁻¹

Mechanical properties of MAO-exposed surfaces were examined by hardness and scratch tests. Hardness measurements were obtained on cross-sections of the samples

using a depth-sensing micro-hardness tester (CSM Instruments) with a standard Vickers indenter under an indentation load of 100 mN. Hardness values were averaged over eight successful indentations. Crossed scratches were formed on MAO-exposed surfaces under a constant load of 20 N with a scratch tester (CSM Instruments) having a Rockwell C 200 μm radius indenter tip. Scratch length and scratching speed were 2 mm and 2 mm min⁻¹, respectively. Scratching characteristics of the MAO layers were analyzed using the scratch tester and the load was linearly increased from 0.03 N to 20 N under a loading rate of 20 N min⁻¹. The sliding distance and table speed were set to 5 mm and 5 mm min⁻¹, respectively. During progressive scratch testing, the penetration depth and the friction coefficient were recorded to analyze deteriorations in the oxide layers. Upon scratch tests, the scratches and their surroundings were surveyed by SEM. The adherence between the layer and the substrate was evaluated using a Rockwell hardness tester (Zwick ZHR 4150) by penetrating Rockwell C type diamond cone indenter with an applied load of 150 kg. The surrounding area of indent was observed using an optical microscope (OM, Leica ICC50HD).

Wear performances of the Cp-Ti, MAO, and MAO-Zr samples were examined using a reciprocating wear tester (TriboTechnic). Wear tests were conducted in 1.5X SBF at 37 °C under a load of 3 N by rubbing an alumina ball (6 mm in diameter) on the surfaces of the samples with a sliding velocity of 10 mm s⁻¹ for a total sliding distance of 40 m (stroke was 5 mm). The friction coefficient (CoF) was continuously recorded throughout the testing period. After the wear test, samples were cleaned in acetone and dried in air. Geometry of the wear tracks formed on the samples was analyzed by 2-D SP. Volume loss of samples was calculated according to the geometry of the wear tracks and the relative wear resistance (RWR) of the samples was then quantified by dividing the wear volume loss of Cp-Ti into those of the examined samples. Finally, the worn surface of the samples and the contact surface of the alumina balls were examined by SEM and OM, respectively.

5.3 Results

Variation of the positive voltage during processing of MAO and MAO-Zr samples at a constant current density of 2 A cm⁻² is presented in Fig. 5.1. According to the voltage - time curves, Samples were appropriately oxidized in three distinct stages. The process started with anodic oxidation (Stage 1) while the voltage was increased

linearly at a rate of approximately 4 V s^{-1} to the breakdown voltage. In Stage 1, where the dissolution of titanium and passive TiO_2 film formation was more likely, no remarkable difference in voltage between the MAO and MAO-Zr samples was identified. However, the breakdown voltages were slightly different and were observed at near 325 and 350 V for MAO and MAO-Zr samples, respectively. In Stage 2, the increment rate of the processing voltage sharply decreased, while fine sparks were covering the exposed surfaces to generate micro-discharge channels. It is notable that in Stage 2, the oxidation process progressed at a higher voltage for the MAO-Zr sample as compared to MAO sample. In the third stage (started at approximately 400 s), the increment rate of the processing voltage decreased until the end of the process while rare, but intense, sparks appeared on the surfaces. In Stage 3, the applied voltage of the MAO-Zr and MAO samples attained similar values.

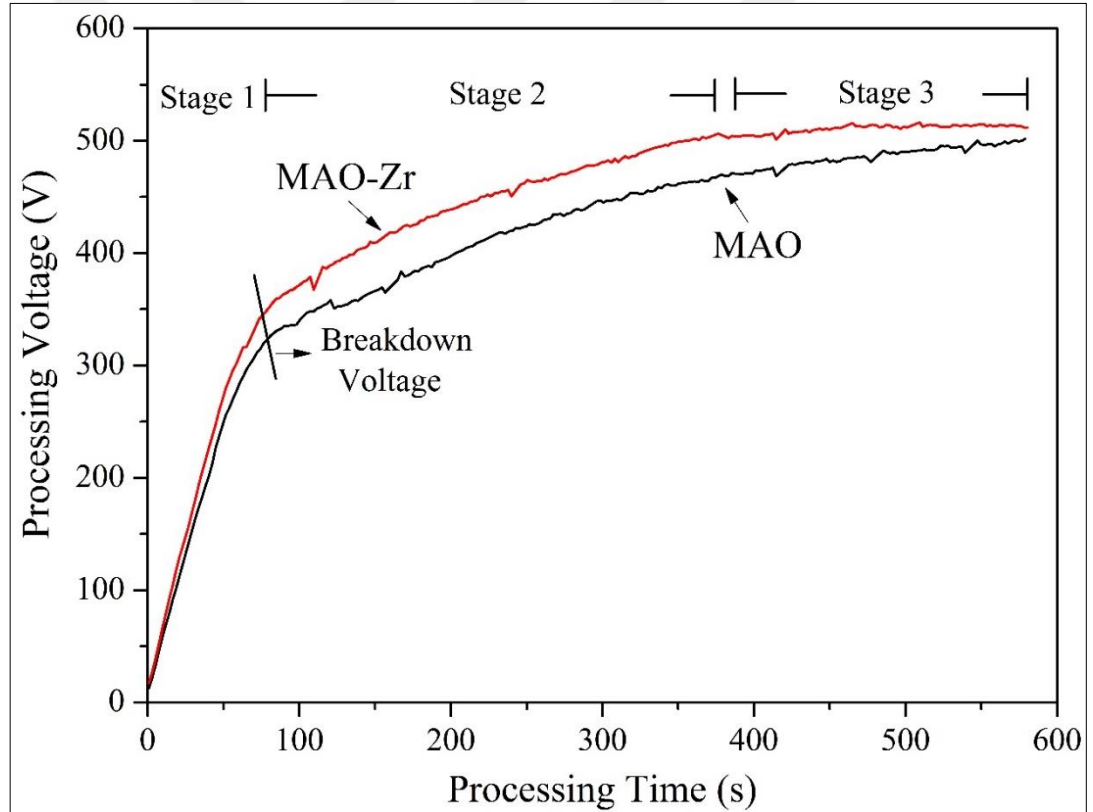


Figure 5.1 : Variation of the voltage during processing of MAO and MAO-Zr samples.

Results of XRD analyses conducted on the MAO and MAO-Zr samples are shown in Fig. 5.2. The XRD spectra of the MAO sample predominantly showed the rutile form of TiO_2 . Peaks representative of TiO_2 in anatase form, dicalcium phosphate dihydrate (DCPD), and calcium titanate (CaTiO_3) were also present on relevant spectra. In the

case of MAO-Zr sample, the most intense peak corresponded with zirconium titanate (ZrTiO_4). Peaks representing ZrO_2 (in the form of tetragonal and monoclinic) also appeared on the XRD spectrum in addition to the peaks corresponding to TiO_2 , DCPD, and CaTiO_3 . In comparison to the XRD spectrum of the MAO sample, peaks associated with the rutile form of TiO_2 were shifted to lower angles and broadened on the XRD spectrum of the MAO-Zr sample. It should be noted that α -titanium peaks observed in XRD spectra (Fig. 5.1) are due to penetration of the X-rays beneath the oxide layer.

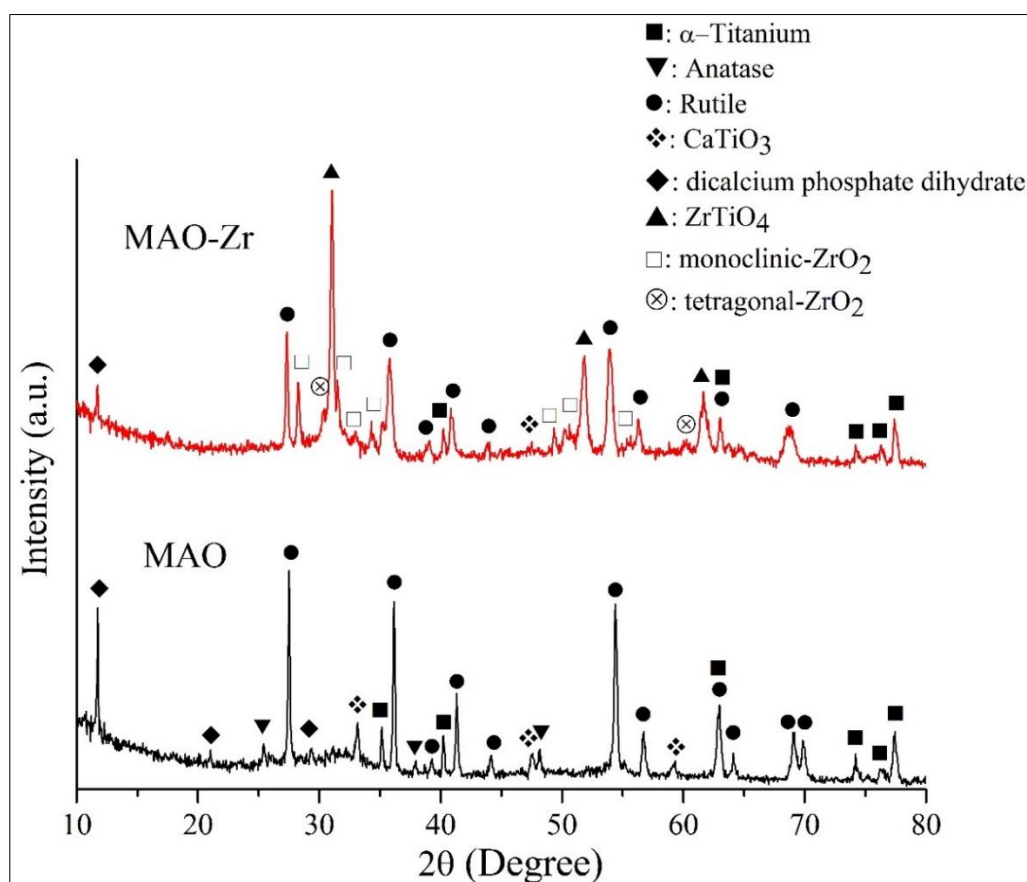


Figure 5.2 : XRD spectra of MAO and MAO-Zr samples.

Surface and cross-sectional SEM micrographs of the MAO and MAO-Zr samples are shown in Fig. 5.3. Oxide layers exhibited the micro-porous morphology. EDS analyses confirmed the deposition of Ca and P on the surfaces to form CaTiO_3 and DCPD, as identified by XRD analysis (Fig. 5.2). Unlike that of the MAO sample, the oxide layer of the MAO-Zr sample was enriched by Zr (17.4 wt.%). Cross-section examinations revealed that the thickness of both oxide layers was approximately 18 μm . The oxide layer of the MAO-Zr sample was in a more compact nature as compared to the oxide layer of the MAO sample.

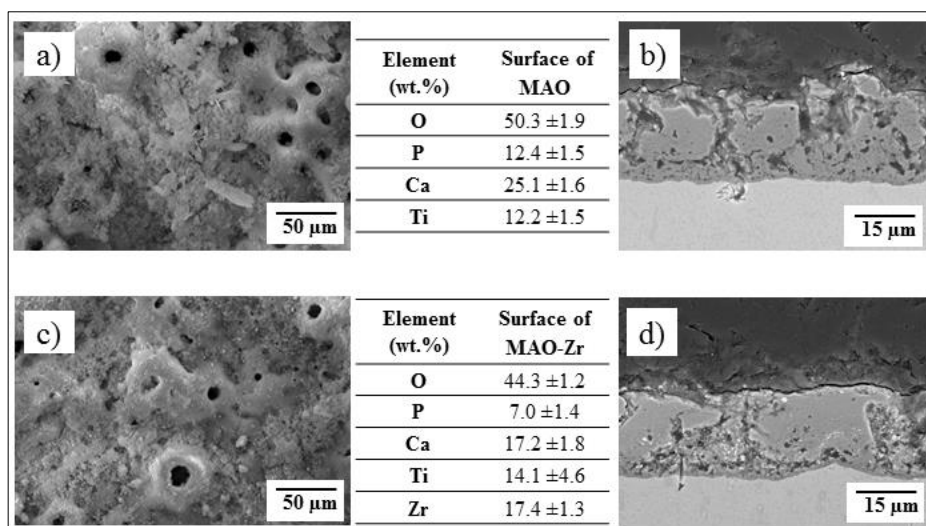


Figure 5.3 : Surface and cross-sectional SEM micrographs and corresponding surface EDS analyses of (a,b) MAO and (c,d) MAO-Zr samples.

A high magnification cross-section SEM micrograph of the oxide layer formed on the MAO-Zr sample, along with EDS results, is shown in Fig. 5.4. ZrO₂ particles were apparent as bright spots (Area B in Fig. 5.4) and located mostly around the pore channels. Also, compact regions of the oxide layer (Area A in Fig. 5.4) were enriched by Zr.

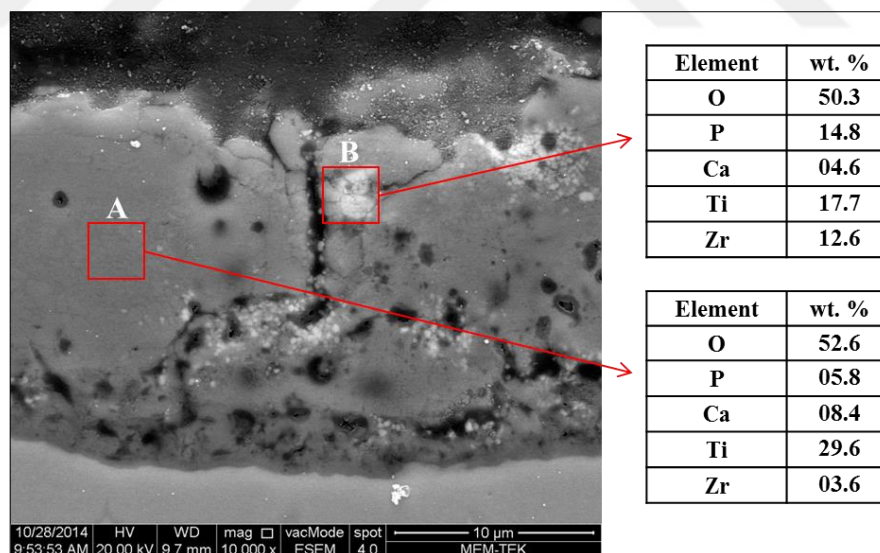


Figure 5.4 : High magnification cross-sectional SEM micrograph of MAO-Zr sample and EDS analyses of A and B coded areas.

Average surface roughness (Ra) and hardness of the oxide layers formed over MAO and MAO-Zr samples are listed in Table 5.3. Although the surface roughness of the oxide layers was almost in the same range, the oxide layer of the MAO-Zr sample exhibited higher hardness than the oxide layer of the MAO sample.

Table 5.3 : Average surface roughness (Ra) and hardness values of the oxide layers formed on MAO and MAO-Zr samples.

Sample	Ra, μm	Hardness (HV _{0.01})
MAO	2.2 ± 0.2	718 ± 119
MAO-Zr	1.9 ± 0.1	881 ± 148

SEM micrographs and corresponding XRD spectra obtained after the bioactivity tests of the samples are shown in Figs. 5.5 and 5.6, respectively. Surfaces of the MAO and MAO-Zr samples were fully covered by a biomimetically formed apatite layer, however, no indication of apatite deposition has been detected on the surface of the Cp-Ti sample in same testing period. It should be noted that micro-cracks detected on the apatite layers of MAO and MAO-Zr samples are due to stresses generated during sample drying upon removal from the SBF solution [168].

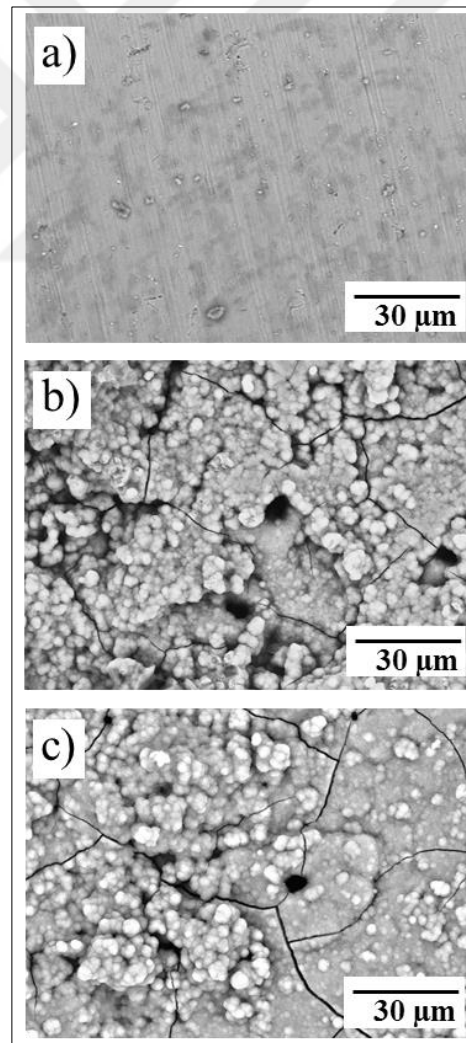


Figure 5.5 : SEM micrographs of (a) Cp-Ti, (b) MAO and (c) MAO-Zr after immersion in SBF for 72 h.

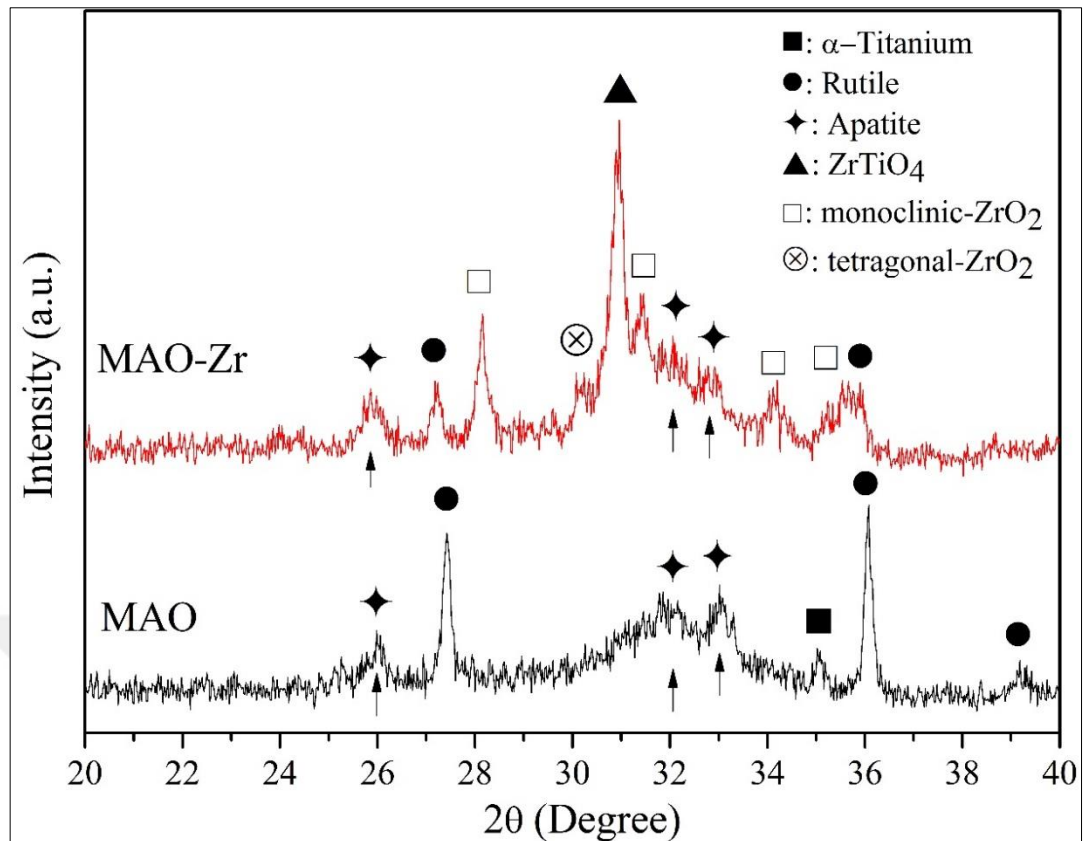


Figure 5.6 : XRD spectra of MAO and MAO-Zr samples after immersion in SBF for 72 h.

SEM micrographs of the crossed scratches formed on the oxide layers are shown in Fig. 5.7. Scratch tests imposed spallation type failures around the intersection points of the scratches and conformal cracks in the scratch tracks. When the size of the spallation area and the intensity of the conformal cracks are of concern, severity of failure developed in the oxide layers can qualitatively be assessed as major and minor for MAO and MAO-Zr samples, respectively.

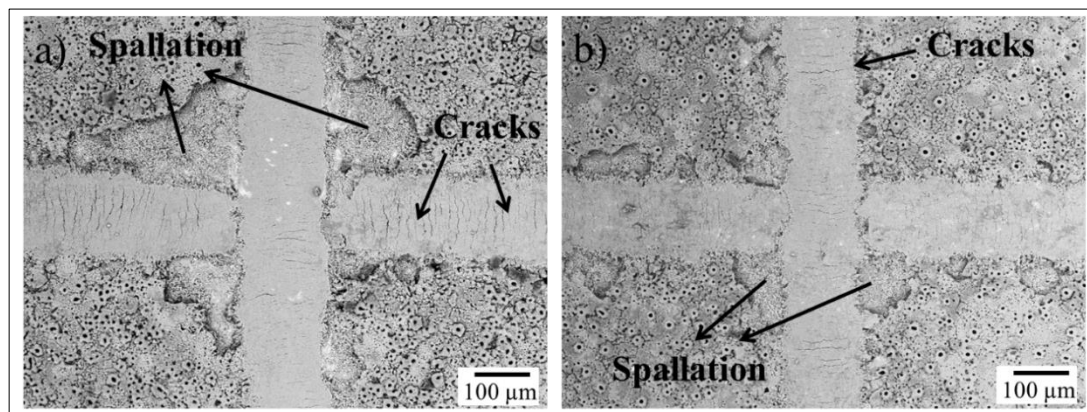


Figure 5.7 : SEM micrographs of the scratches formed on (a) MAO and (b) MAO-Zr samples under constant load of 20 N.

The scratching and frictional behaviors of the MAO and MAO-Zr layers were analyzed with the results of scratch tests under progressive loading up to 20 N as illustrated in Fig 5.8. The residual depths reached under maximum load (20 N) were below the thickness of the layers and quantified as 17 μm and 12 μm for MAO and MAO-Zr samples, respectively. In accordance with results of indentation tests (Fig. 5.7), MAO-Zr sample layer was exposed to lower residual penetration depths than that of the MAO sample throughout scratch tests. Higher scattering in the friction curve of the MAO sample was observed in comparison to the curve associated with the MAO-Zr sample. Furthermore, Rockwell C adhesion test, as shown in Fig. 5.9, showed a better adhesion for MAO-Zr sample as compared to MAO sample when the detached area at the periphery of the indent was considered.

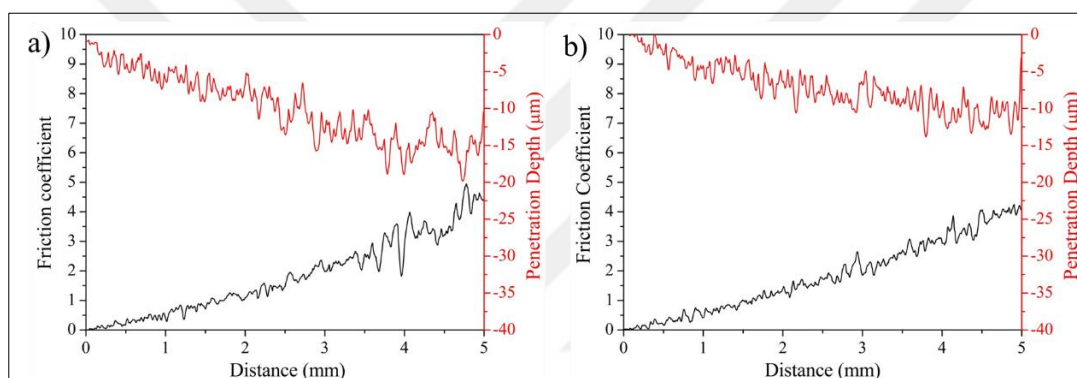


Figure 5.8 : Residual depth/Friction coefficient – Sliding distance graphs and SEM micrographs of worn surfaces of (a) MAO and (b) MAO-Zr samples evaluated by scratch test.

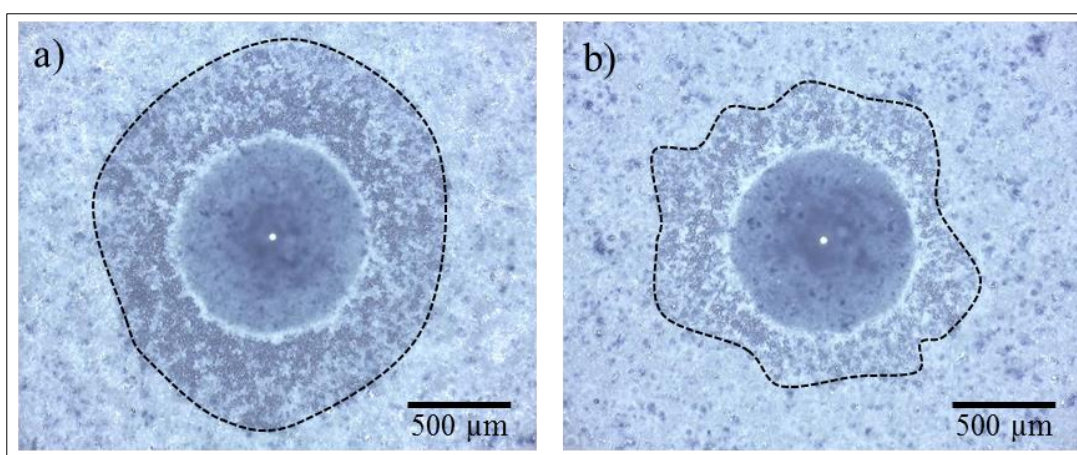


Figure 5.9 : OM image showing periphery of indent (detached area is surrounded) after Rockwell C adhesion test conducted for (a) MAO and (b) MAO-Zr samples.

Wear test results are listed in Table 5.4 in terms of RWR and CoF. MAO and MAO-Zr samples exhibited superior wear resistance and lower CoF values than Cp-Ti, which

has a worn surface topography that can be characterized by a plastically deformed, grooved, and delaminated appearance (Fig. 5.10). Material removed from the surface of the Cp-Ti sample was transferred to the alumina ball and caused a dark-colored contact surface. Unlike the Cp-Ti sample, there was no evidence of plastic deformation on the worn surfaces of the MAO and MAO-Zr samples or material transfer to the contact surface of the alumina ball. The oxide layer of the MAO-Zr exhibited higher RWR than the oxide layer of MAO sample (about 16%).

Table 5.4 : Relative Wear Resistance values and average friction coefficients (CoF) obtained from the sliding wear tests conducted in SBF solution.

Sample	RWR	CoF
Cp-Ti	1.0	0.43
MAO	7.4	0.36
MAO-Zr	8.6	0.38

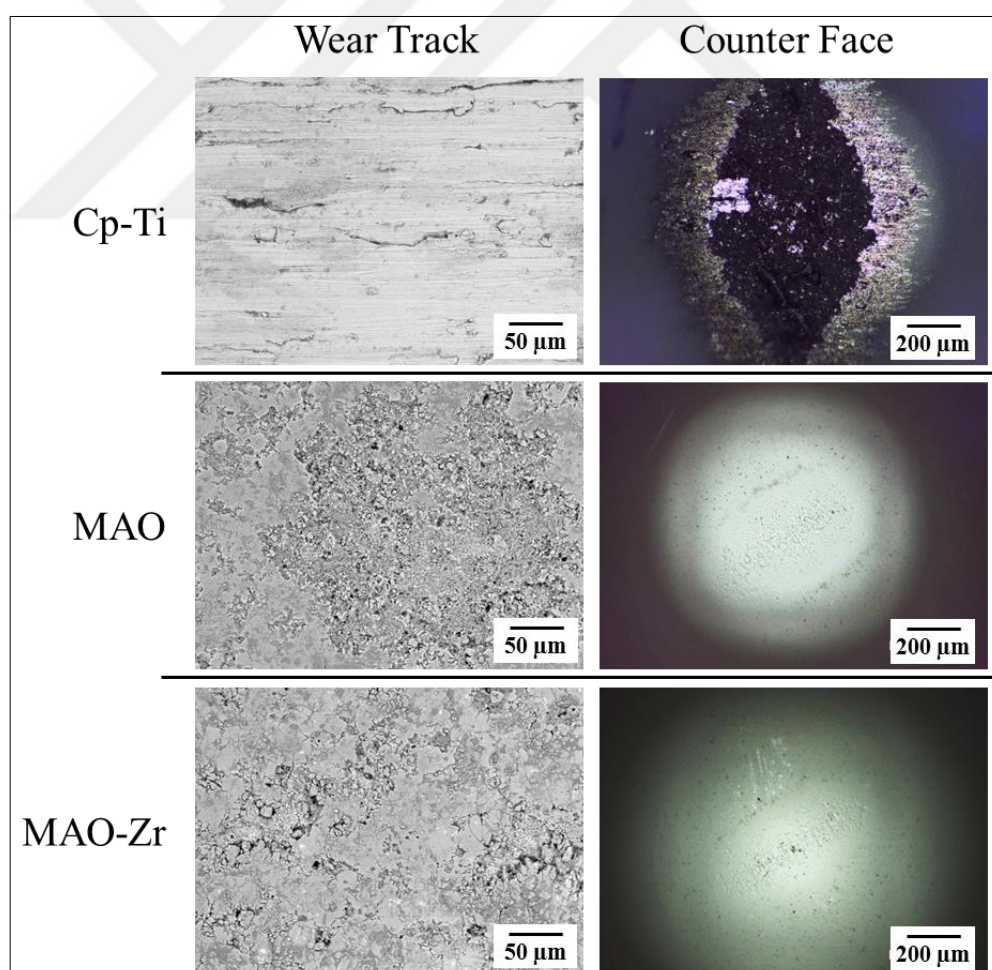


Figure 5.10 : SEM micrographs of wear tracks of Cp-Ti, MAO and MAO-Zr samples and corresponding OM images of alumina balls.

High magnification SEM micrographs of the worn surface are depicted in Fig. 5.11 for the MAO-Zr and MAO samples. In general, sliding contact of the alumina ball caused a smoothing and spallation of the oxide layer. Spallation was more dominant for the MAO sample in comparison to the MAO-Zr sample.

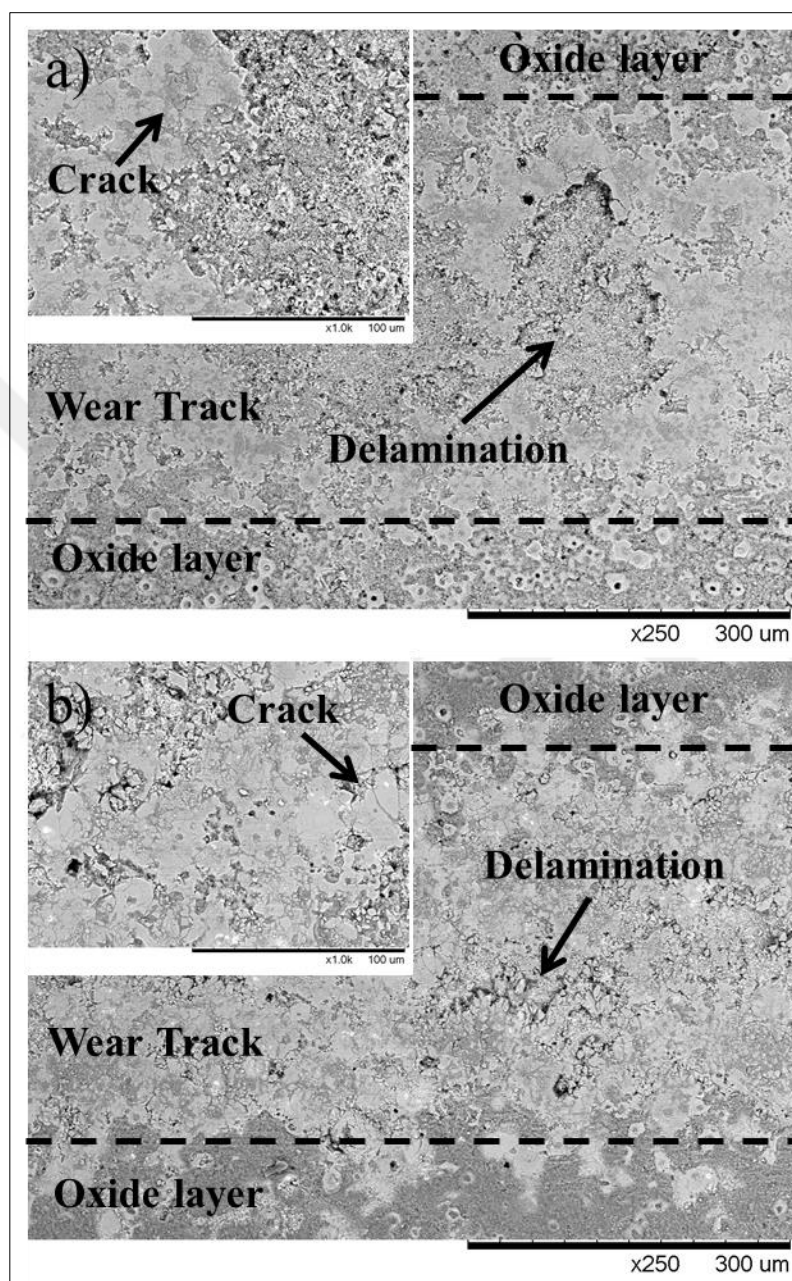


Figure 5.11 : High magnification SEM micrographs of wear tracks of (a) MAO and (b) MAO-Zr samples.

5.4 Discussion

Application of the MAO process in calcium acetate hydrate and disodium hydrogen phosphate anhydrous containing base electrolyte generated an 18 μm thick, micro-

porous TiO_2 layer (in rutile and anatase forms) on the surfaces of Cp-Ti samples (Fig. 5.3). During processing, Ca and P incorporated from the electrolyte formed biocompatible compounds (DCPD and CaTiO_3) in the TiO_2 layer (Fig. 5.2). Introduction of monoclinic ZrO_2 powder into the electrolyte encouraged Zr-related oxides (ZrTiO_4 and ZrO_2) to form in the oxide layer (Fig. 5.2) and caused a progression of the MAO process at higher voltage levels as seen in Fig. 5.1. The higher breakdown voltage observed for the MAO-Zr sample, in contrast to that of the MAO sample, can be associated with the melting temperature of ZrO_2 (2750 °C), which is higher than that of TiO_2 (1843 °C) [189]. During the MAO process, migration of ZrO_2 particles from the electrolyte towards the substrate due to electrophoretic drift [190] caused accumulation of ZrO_2 particles in tetragonal and monoclinic crystal structures predominantly at the vicinity of pores. Since tetragonal ZrO_2 is stable above 1170 °C, transformation of monoclinic ZrO_2 particles added to the electrolyte into the tetragonal ZrO_2 can be attributed to the progress of MAO (Fig. 5.1) at higher voltages (i.e. higher heat input), leading to an increase in the temperature of the exposed surface. High temperatures at the exposed surface also activated the reaction between TiO_2 and ZrO_2 to form ZrTiO_4 in the oxide layer, which is stable above 1100 °C on the TiO_2 - ZrO_2 phase diagram. As evidenced by the broadening and shifting of TiO_2 peaks on the relevant XRD spectra (Fig. 5.2), Zr ions dissolved in TiO_2 formed a solid solution with a larger lattice parameter. Thus, the greater ionic radius of Zr, as opposed to that of Ti, induced a larger lattice parameter for TiO_2 [191]. Additionally, the more compact nature of the oxide layer formed in the ZrO_2 powder added electrolyte (Fig. 5.3) was due to better sintering as the result of the higher temperature of the exposed surface during the MAO process.

In association with the changes in its structural features, the oxide layer formed in the ZrO_2 added electrolyte exhibited better durability than the oxide layer formed in the base electrolyte. Higher hardness (Table 5.3), better scratching characteristics (Figs. 5.7 and 5.8) and improved adhesion strength (Fig. 5.9) indicate an enhanced mechanical stability of the oxide layer against sinking under axial stress and cracking/flaking under shear stress, respectively. Therefore, during wear testing, the counter-face (alumina ball) penetrated to shallow depths and the shear stress generated during sliding contact involved the detachment of smaller wear debris from the oxide layer formed in the ZrO_2 -added electrolyte.

Regardless of electrolyte composition utilized in the MAO process, oxide layers of MAO and MAO-Zr samples efficiently protected the substrate from the destructive action of the counter-face by increasing RWR and reducing CoF (Table 5.4); this is in accordance with the results of previous studies [192,193] and provided remarkable improvement in bioactivity as confirmed by SBF immersion tests (Figs. 5.5 and 5.6). The crucial role of biocompatible compounds present in the TiO_2 layer on biomimetic apatite layer formation in SBF has been well documented [194–196]. In contrast to results obtained by Shin et al. [190] that showed better bioactive properties from ZrO_2 -incorporated oxide layer formed on Cp-Ti by MAO process, this work did not show a significant difference in bioactivities of MAO and MAO-Zr samples. They attributed higher bioactivity of the ZrO_2 -incorporated oxide layer to its higher surface roughness leading to easy nucleation of biomimetic apatite in SBF solution. Since oxide layers formed in base and in ZrO_2 -added electrolytes have similar surface roughness (Table 5.3) and contain identical biocompatible compounds (Fig. 5.2), no considerable difference in precipitation characteristics of biomimetic apatite was identified between them in the SBF tests conducted in the current study.

5.5 Conclusion

In the present study, the characteristics of the oxide layers formed on Cp-Ti substrates by MAO process in ZrO_2 -free and ZrO_2 (10 g l^{-1}) added electrolytes were compared by structural surveys, SBF tests, hardness measurements, scratch and wear tests. Findings of the present study can be summarized as follows:

- The addition of ZrO_2 powder into the electrolyte not only introduced ZrO_2 particles and generated a new ZrTiO_4 -type oxide, but also improved the compactness of the TiO_2 layer.
- Changes in the microstructure resulted in higher hardness, better adhesion strength and scratch resistances obtained from the oxide layer formed in ZrO_2 -added electrolyte, which also preserved its enhanced bioactivity.
- In association with the improved hardness and scratch resistance, the oxide layer formed in the ZrO_2 -added electrolyte exhibited higher wear resistance in SBF than the oxide layer formed in the base electrolyte. This is due to the reduced contribution of spallation to the progress of wear under sliding contact.

5.6 Acknowledgement

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6. ROLE OF COUNTERFACES WITH DLC AND N-BASED COATINGS ON FRICTIONAL BEHAVIOUR OF AZ31 MAGNESIUM ALLOY SUBJECTED TO PLASMA ELECTROLYTIC OXIDATION (PEO) PROCESS ⁵

6.1 Introduction

The transportation industry's continuous pursuit to improve the vehicle fuel economy embraces utilization of lightweight Mg-based alloys with high strength-to-mass ratio. Yet, the high wear rates of these alloys limit their use in components subjected to sliding contact [4]. The surfaces of Al-, Mg- and Ti-based alloys that are being developed for lightweight components used in the transportation industry are normally subjected to high wear and high friction if they operate under dry sliding contact. Although the mechanisms of wear are different in each of these alloys the application of plasma electrolyte oxidation (PEO) process that uses electrochemical reactions in alkaline electrolytes has emerged as an effective method to improve both corrosion and wear resistance of lightweight alloys by forming ceramic coatings consisting mostly of oxides of PEO treated alloys. However, the high coefficient of friction (COF) values that were commonly recorded during sliding against different types of counterface materials turned out to be one of the main deficiencies of PEO treated alloys, restricting their more extensive use in wear related applications as discussed in the literature [197,198]. The use of PEO process on Mg alloy surfaces has drawn considerable technological interest, and as a result several studies have been undertaken in order to investigate the roles of process parameters on the formation of MgO based coatings during this process [199–202]. The tribological properties of these coatings were also studied. For example, the surfaces of commercially pure Mg samples that were treated in electrolytes containing sodium silicate and sodium phosphate [203] using current densities of 0.060–0.140 A/cm² revealed that the resulting PEO coatings consisted of a mixture of spinel Mg₂SiO₄ and MgO when

⁵ This chapter is based on the paper “S. Bhowmick, F. Muhaffel, G. Sun, H. Cimenoglu, A.T. Alpas, Role of counterfaces with DLC and N-based coatings on frictional behaviour of AZ31 magnesium alloy subjected to plasma electrolytic oxidation (PEO) process, Surf. Coatings Technol. 397 (2020) 125977”

produced using a sodium silicate electrolyte, $\text{Mg}_3(\text{PO}_4)_2$ and MgO using the sodium phosphate electrolyte. The PEO coatings produced in a sodium silicate solution exhibited higher wear resistance than those produced in a sodium phosphate solution.

The high hardness of 260–470 HV of the former coatings compared to 175–260 HV for those produced in sodium phosphate electrolyte was suggested to be the reason for their high wear resistance. Liang et al. [204] synthesized PEO coatings on an AM60B Mg alloy in silicate and phosphate electrolytes, and reported that the coating produced from the silicate electrolyte was compact and consisted of a mixture of MgO and Mg_2SiO_4 , while the one formed in phosphate electrolyte was more porous and mainly composed of a single MgO phase. The PEO coating produced from a silicate electrolyte had a high hardness and provided a low wear rate but exhibited a high COF value of 0.80 against a Si_3N_4 ball. A slightly higher wear rate was recorded for the PEO coating produced from a phosphate electrolyte and this was accompanied by a COF of 0.60. It was noted that the uncoated AM60 had a COF value of 0.31 against the same counterface. Jin et al. [205] deposited a MgO coatings on AZ91D samples using two different PEO voltage modes, namely by direct current and high-frequency bipolar pulsing. Compared to the uncoated AZ91D alloy sliding against WC balls, PEO coatings produced by either of these processes reduced the wear rates, but at the same time they showed high COF values of 0.70 and 0.55 compared to the uncoated alloy. Recently, Muhaffel and Cimenoglu [206] established that an electrolyte with 10 g/l NaAlO_2 + 5 g/l Na_3PO_4 + 2 g/l KOH provided an optimized electrolyte composition for producing AZ91 alloy surfaces with PEO coatings composed of MgO , MgAl_2O_4 and AlPO_4 that were resistant to both dry and wet (0.9 wt% NaCl solution) sliding. However, the recorded COF of 0.51 for PEO coated AZ91 was higher than that of the uncoated AZ91 when sliding against counterfaces made of alumina balls in dry condition.

Therefore, previous studies that investigated tribological behaviour of the PEO treated Mg alloys established a trend of reduced wear (typically 50%), but higher friction compared to the base alloys. These studies put emphasis on the effects of electrolyte composition and PEO process parameters but lesser consideration was given to the role of the counterface materials. However, it became obvious that almost always higher COF values (> 0.5) resulted compared to uncoated Mg alloys sliding against steel, alumina and WC counterfaces. Reduction of the COF simultaneously with the

wear rate is critical for certain tribo-systems such as engine components. The current study was undertaken in order to determine the role of counterfaces on the frictional properties of PEO coated AZ31 alloy along with their effect on alloy's wear resistance. The recognition that low COF values could be achieved by utilizing diamond-like carbon (DLC) coated counterfaces when they were placed in sliding contact against Al, Mg and Ti alloys [207,208] provided the primary incentive for using DLC coated counterfaces against PEO treated and untreated AZ31 surfaces. For comparison with DLC, the tribological properties of more conventional counterfaces coated with nitride based (N-based) hard coatings were also studied. The N-based coatings including TiN, TiCN, and CrN represent a common commercial group of coatings, also used as in specific applications such as piston ring and die coatings. These applications are relevant to the industrial use of Mg alloys in lightweight components.

Previous laboratory scale tribological studies performed on the uncoated Mg alloys sliding against DLC coated counterfaces can be found in references [209–214]. Bhowmick and Alpas [209] studied the frictional behaviour of a cast AZ91 grade Mg alloy using a non-hydrogenated ($H < 2$ at.%) diamond-like carbon (NH-DLC) counterface. During dry sliding in air with 45% relative humidity (RH), a COF value of 0.27 ± 0.06 was measured and a lower COF of 0.11 ± 0.01 was observed when distilled water spray was used. The NH-DLC coated drills mitigated magnesium adhesion and reduced the drilling torques of AZ91 during minimum quantity lubrication (H₂O-MQL) using drills coated with NH-DLC. Matsumo and Osakada [210] observed a low COF of 0.08 when hydrogenated diamond-like carbon (H-DLC) coated counterfaces were placed in sliding contact against samples made of ZK60 grade (6% Zn and 0.5% Zr) Mg alloy, but COF > 0.25 were recorded when counterfaces with TiC/TiCN/TiN multilayer coatings were used. Matsumoto et al. [211] also studied the tribological behaviour of AZ31 alloy against H-DLC and TiAlN coated tools using a tapered plug inserted into the hole of a billet, and measuring the plug penetration load. By examining the penetration load-stroke curves, they estimated the COF values between the AZ31B and the plug, and showed that H-DLC had a lower COF of 0.10 than when TiAlN with a COF of 0.15 was used. Dohda et al. [212] studied the tribological characteristics of dies coated with H-DLC, and N-based coatings in contact with AZ31 alloy in ironing process conducted at different temperatures. For TiN coating in contact with AZ31 alloy, the COF values were 0.2 at 150 °C, 0.35 at

200 °C and 0.4 at 250 °C. In case of DLC coatings, the COF values were lower, namely 0.08 at 150 °C, 0.12 at 200 °C, and 0.4 at 250 °C. Konca et al. [213] studied the frictional behaviour of NH-DLC coatings against commercial purity Mg (99.9 wt%) samples tested under ambient air and argon atmospheres. In argon, NH-DLC coating showed a very low steady state COF (μS) of 0.05 after an initial running-in period. Carbonaceous material transfer from the NH-DLC to the contact surface of the Mg pin was observed. Changing the test atmosphere from argon to ambient air increased the COF to 0.40, which was accompanied by the formation of oxidized Mg debris and a higher wear rate. Bhowmick et al. [215] studied the friction and wear behaviour of HDLC coatings sliding against AZ91 Mg alloy in air. Although a low μS value of 0.11 was recorded at a RH of 40% the μS value of H-DLC-AZ91 tribosystem increased with an increase in RH of the test atmosphere. Carbonaceous transfer layers were formed on the AZ91 surfaces, and carbon atoms in these layers were passivated by OH according to the Fourier transform infrared (FTIR) and micro-Raman spectroscopy. In this study the experimental work was focussed on measuring the COF values of PEO coated AZ31 alloy against selected counterface coatings and also determining the wear rates. As indicated earlier, oxide coatings formed as a result of PEO process serve to increase the wear resistance of base alloys but the COF values of PEO treated surfaces remain high during sliding against different types of counterfaces. The main purpose of the investigations undertaken in this work was therefore to examine the possibility of reducing the COF values of the PEO coated Mg alloys by using a suitable coating for the counterface without using liquid or solid lubricants. Following the sliding contact experiments, the mechanisms of sliding-induced damage and interfacial material transfer phenomena were examined in order to rationalize the roles of the counterface materials on the COF of PEO treated AZ31.

6.2 Experimental Approach

6.2.1 Description of plasma electrolytic oxidation (PEO) process

Rectangular samples of 15 mm $\times$ 15 mm $\times$ 4 mm were machined from the as-cast AZ31 (Mg-3 wt% Al-1 wt% Zn) alloy for the PEO treatment of their surfaces. The hardness of the AZ31 alloy was measured as 0.74 GPa using a Vickers micro-hardness tester (Wilson Tukon 1102). Following grinding and polishing of the surfaces using standard metallographic procedures, samples were placed in an electrolytic bath with

an electrolyte consisting of 15 g/l sodium metasilicate (Na_2SiO_3 , Aldrich) and 2 g/l potassium hydroxide (KOH, Aldrich). PEO treatment was conducted using a current density of 2.2 A/cm^2 for a duration of 240 s. During the PEO process the temperature of the electrolyte was maintained at $293 \pm 2 \text{ K}$ using a cooling system in order to control the rates of the chemical reactions on the surface of the samples. Upon completion of the PEO process the coated sample surfaces were cleaned ultrasonically in acetone and distilled water and then dried in air.

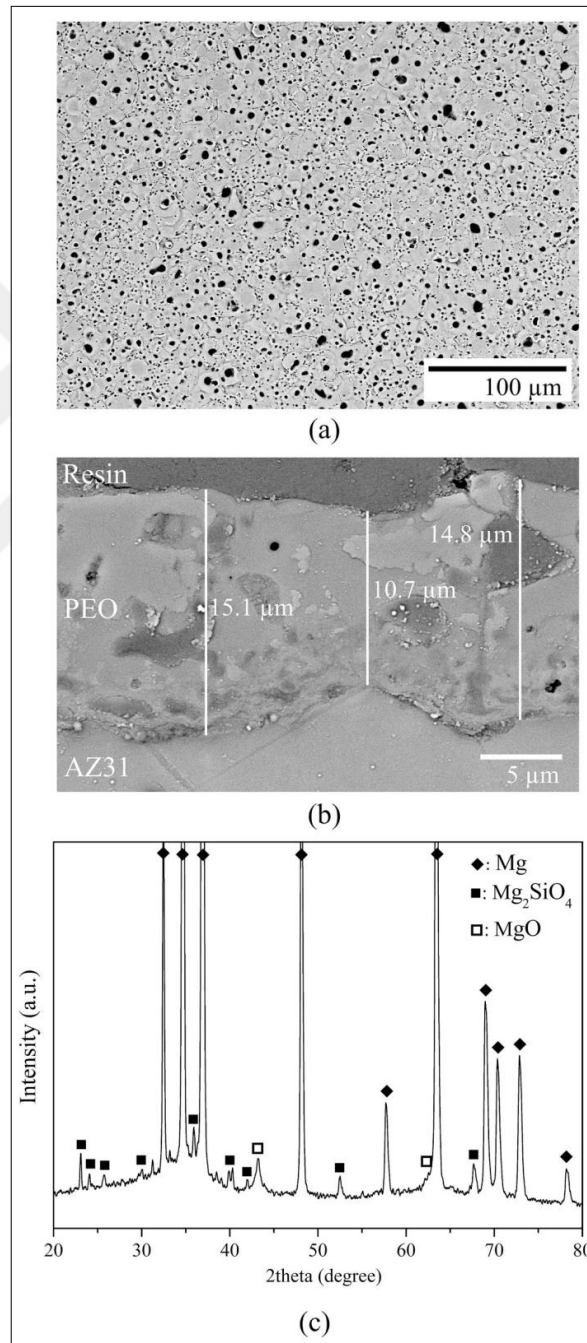


Figure 6.1 : (a) Surface and (b) cross sectional back-scattered electron micrographs and (c) XRD spectrum of the PEO coated AZ31.

Backscattered electron scanning electron microscopy (BSE-SEM) images taken from the surface and cross-section of the PEO treated AZ31 samples are shown in Fig. 6.1(a and b) along with the XRD spectrum of the coated surface obtained using Cu-K α radiation (Fig. 6.1c). The PEO coating exhibited a characteristic microporous surface morphology (Fig. 6.a), and the phase structure of the coating was identified as a mixture of MgO and Mg₂SiO₄ type of oxides (Fig. 6.1c). The coating had an average thickness of 13 μ m, measured on several sections such as the one shown in Fig. 6.1b. The arithmetic average surface roughness (Ra) of the coatings was measured as 0.69 ± 0.07 μ m using an optical surface profilometer (WYKO NT-1100). The hardness of the PEO coated surfaces was 5.49 ± 0.51 GPa.

6.2.2 Counterface materials: uncoated, H-DLC, TiCN, TiN and CrN coated bearing steel

Counterfaces used in the sliding contact tests against the uncoated AZ31 and PEO coated AZ31 samples consisted of uncoated SAE 52100 grade bearing steel balls of 6.0 mm in diameter, and the steel balls with the same diameter coated with H-DLC and N-based coatings. The H-DLC coatings were deposited on the SAE 52100 steel balls using an unbalanced magnetron sputtering system, which consisted of one chromium and two graphite targets. Butane was used as the precursor gas to achieve the desired 40 at.% of hydrogen content of the main body of the H-DLC coating as determined using Elastic Recoil Detection (ERD) analysis technique after the deposition. A 0.1 μ m thick Cr interlayer was initially deposited on the steel substrate surface to enhance interfacial adhesion. The N-based coatings deposited on the SAE 52100 grade steel balls comprised of TiN, TiCN and CrN. The first two of these coatings e.g., TiN and TiCN were deposited using a cathodic arc evaporation technique, while CrN was deposited using magnetron sputtering. Table 6.1 lists the measured thickness values of the coatings deposited on the SAE 52100 steel along with their hardness (H) and elastic modulus (E) values calculated from the load-displacement curves obtained using a Berkovich type nano-indenter tip that penetrated to depth of 200 nm from the coating surfaces. The H and E values for each surface reported in Table 6.1 were calculated by averaging measurements taken from at least 40 indentation impressions.

Table 6.1 : Thickness, hardness and elastic modulus values of the coatings deposited on SEA 52100 steel ball and used as counterfaces.

Coatings and substrate	Thickness, μm	H, GPa	E, GPa
TiN	1.0	14.0	280
TiCN	1.0	15.0	252
CrN	3.5	21.9	336
DLC (40%H)	1.5	11.4	103
52100 Steel	-	6.9	210

6.2.3 Determination of coefficient of friction values and wear rates

Sliding contact tests were performed using a tribometer (CSM Instruments, Switzerland, model ISC 450) operated in the ball-on-flat configuration inside an environmental enclosure. Tests were run at a constant linear sliding speed of 0.02 m/s and under a normal load of 1.0 N. A low constant load of 1.0 N was applied in order to compare performances of different counterface coatings under a loading condition where the wear rates were low and the COF values were typically high. A low sliding speed of 0.02 m/s was used to prevent frictional heating. Three sliding tests were performed on uncoated AZ31 and PEO coated AZ31 alloy against each type of counterface described in Section 2.2. Tests were conducted in an air atmosphere with the humidity controlled at 32% RH. A fresh counterface was used for each test. The initial running-in and the steady state COF values (μ_R and μ_S , respectively) were determined from the friction curves recorded during the tests. Usually a peak in the friction curve was formed during the initial running-in period, and the maximum value of the COF peak observed in this period was recorded as μ_R . The μ_S value (e.g., for some PEO coated AZ31) was calculated from the arithmetic mean of the steady-state portion of the friction curve, typically attained after 500 sliding revolutions. Otherwise average COF values obtained after 500 revolutions were noted (e.g., for some uncoated AZ31). For uncoated AZ31 and PEO coated AZ31, the COF values calculated in this way for each of the three tests conducted against a particular counterface material were reported as the average COF, or average μ_S when applicable, for this tribocouple.

The volumetric wear losses of the uncoated AZ31 and PEO coated AZ31 were estimated from the area profiles of the cross-sections of the wear tracks taken from four different locations along a circular track with a typical radius of 1.5 mm using an optical surface profilometer as described in [214,216,217]. The reported wear rates were the average values obtained from the three tests conducted for each tribocouple.

The morphological and compositional features of the contact surfaces subjected to sliding contact damage were examined using an SEM (FEI Quanta 200 FEG) equipped with an energy dispersive X-ray (EDS) spectrometer. Functional group analyses of the worn surfaces and the tribolayers were carried out using a Fourier-transform infrared (FTIR) spectrometer (Bruker Alpha-T). The background calibration of FTIR spectra was done using a reference sample coated with Au. Data for each spectrum were recorded in between 4000 and 500 cm^{-1} with a scanning rate of 24 scan/min.

6.3 Results

6.3.1 COF of AZ31 and PEO coated AZ31 against H-DLC and N-based coatings

Initially three types of N-based coatings, namely TiCN, TiN and CrN, were tested against uncoated AZ31 in air with a constant humidity level of 32% RH. Friction tests conducted using counterfaces coated with TiCN, TiN and CrN placed in sliding contact against AZ31 resulted in high COF values similar to the frictional behaviour of the 52100 steel counterface running against AZ31 as shown in Fig. 6.2(a). The COF values of AZ31 calculated for sliding periods between 500 and 1000 revolutions were 0.34 ± 0.04 for the 52100 steel, 0.36 ± 0.04 for TiN, 0.38 ± 0.06 for CrN and 0.33 ± 0.07 for TiCN counterfaces. It should be noted that in all cases the friction curves were characterized by large fluctuations about the mean COF values, which increased with the number of revolutions. The large fluctuations coincided with the observation that the detached material fragments transferred back and forth between the worn AZ31 surface and the counterface during sliding contact. During the course of this process, the worn surfaces and the transferred material became oxidized. Metallographic and spectroscopic evidence for the surface damage mechanisms will be examined in more detail in Section 3.4. The frictional behaviour of H-DLC sliding against uncoated AZ31 differed from the other counterfaces as their friction curves initially exhibited a distinct running-in period with high μ_R , which was followed by a stable friction trend characterized by small fluctuations (± 0.01). This stage of the COF curve can be considered as the steady state; During most of the steady state stage μ_S was 0.13 but a gradual increase of μ_S to 0.14 was observed for > 1000 revolutions in Fig. 6.2(a). The two additional sliding tests conducted on AZ31 using HDLC and other counterfaces that are not shown in Fig. 6.2(a) provided trends consistent with those shown this

figure. The results obtained from the three sliding tests performed using these counterfaces against uncoated AZ31 are shown in Fig. 6.3 for each tribo-couple in the form of bar charts.

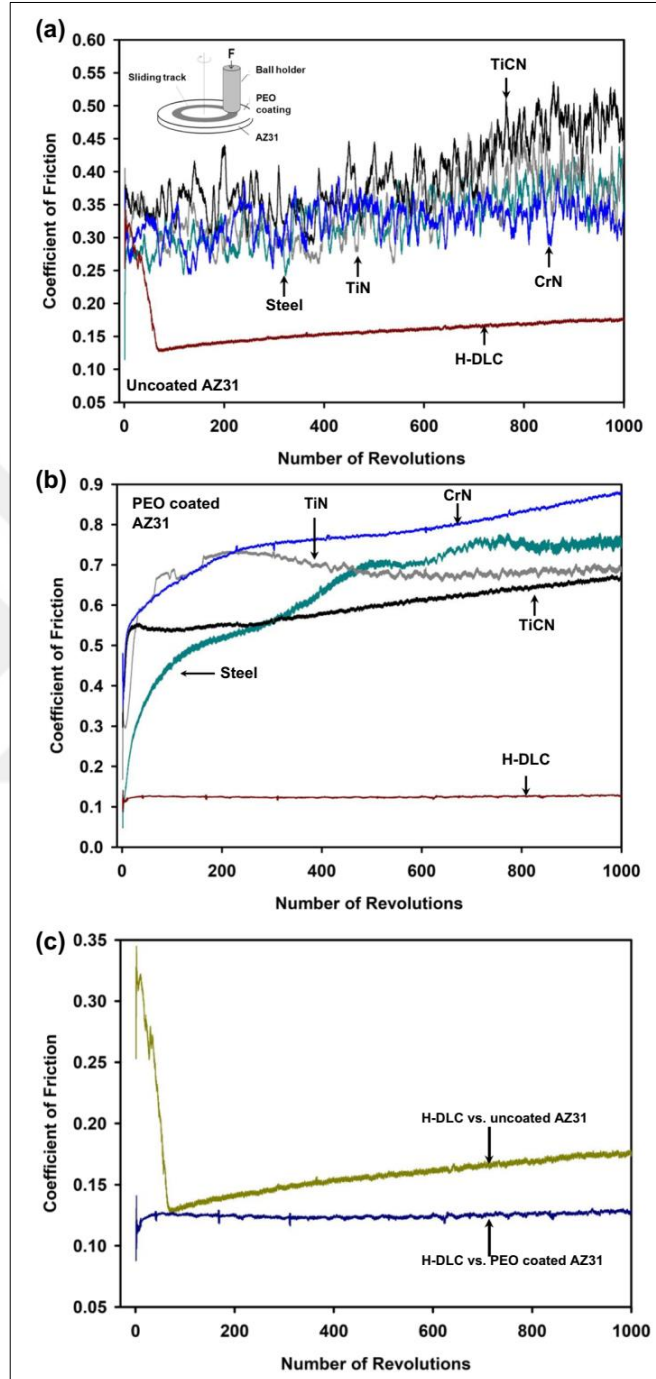


Figure 6.2 : Variations of the COF with the number of revolutions for uncoated 52100 steel, TiN, CrN, TiCN and H-DLC tested against (a) uncoated AZ31; (b) PEO coated AZ31; (c) variations of the COF with the number of revolutions when H-DLC slid against uncoated and PEO coated AZ31. A schematic view of experimental set-up showing the friction arm, load, a ball holder and a PEO coated sample is inserted in (a).

Typical COF vs. number of revolutions plots obtained for PEO coated AZ31 sliding against H-DLC, N-based coated and the uncoated SAE 52100 steel counterfaces are shown in Fig. 6.2(b). For the tests shown in this figure COF values of PEO coated AZ31 were increased with the number of revolutions and reached 0.87 for CrN, 0.63 for TiCN and 0.65 for TiN (at 1000 cycles). These COF values were within the same range as that of PEO coated AZ31 running against the steel counterface. The most important aspect of Fig. 6.2(b) is that when PEO coated AZ31 was tested against H-DLC coated counterface, following an initial running-in period with a low μ_R of 0.16, a steady state regime with a μ_S of 0.13 ± 0.02 was reached. Comparison of friction trends of uncoated AZ31 and PEO coated AZ31 tested against H-DLC can be observed from Fig. 6.2(c) that shows that both μ_R and μ_S were low when the H-DLC coated counterface was placed in contact against the uncoated and PEO coated AZ31. It is also observed that in case of PEO coated AZ31, the μ_S was not only low but also remained constant throughout the duration of the sliding tests.

Comparison of Fig. 6.2(a) and (b) shows that when counterfaces with N-based coatings (and uncoated 52100) were run against the PEO coated AZ31, the resulting COF values were higher than against the uncoated AZ31. However, the mean COF values obtained using these counterfaces sliding against PEO coated AZ31 were characterized by small fluctuations indicating that the material transfer and back transfer events between the interfaces were lessened. The mitigation of material transfer phenomenon could be attributed to the fact that PEO coated surfaces had a higher hardness than uncoated AZ31, and also PEO coatings increased the oxidative resistance of the Mg alloy. The average COF values obtained from the three sliding tests performed using each type of counterface materials running against PEO coated AZ31 are summarized in Fig. 6.3 with their standard deviations. As the counterfaces with N-based coatings provided COF curves with similar trends (Fig. 6.2b), the TiCN counterface was selected as the representative of this type of coatings for comparison with DLC coated counterfaces as described in the following sections.

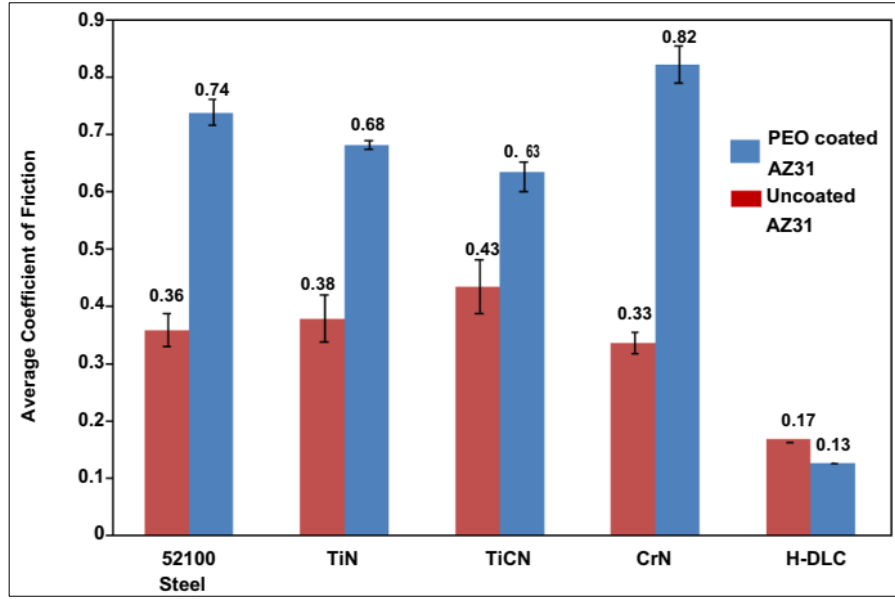


Figure 6.3 : Average COF values obtained from three tests when uncoated AZ31 and PEO coated AZ31 were tested against uncoated steel, TiN, TiCN, CrN, and HDLC. The COF values given are either average steady state COF (μs) of three tests or average COF values of three tests calculated between 400 and 1000 revolutions (see Fig. 2).

6.3.2 Wear track morphologies and wear rates of AZ31 and PEO coated AZ31 against selected counterfaces

Optical surface profilometry measurements were performed on the wear tracks of uncoated and PEO coated AZ31 samples after the sliding contact tests and the typical 3-D morphologies are shown in Fig. 6.4a–d. The average and maximum track depth were $0.96 \pm 21 \mu m$ and $1.17 \mu m$ for uncoated AZ31 while sliding against TiCN coated counterface, for which a representative image of wear track is shown in Fig. 6.4a. The use of H-DLC counterface reduced the average depth of wear track to $0.45 \pm 11 \mu m$ and maximum depth to $0.56 \mu m$ (Fig. 6.4b). PEO coated AZ31 samples exhibited less wear damage against all types of counterfaces and the largest depth of wear scar was always smaller than the coating thickness. The average and maximum wear scar depths on PEO coated AZ31 were $0.66 \pm 11 \mu m$ and $0.77 \mu m$ when sliding against TiCN coated counterface (Fig. 6.4c). Sliding against H-DLC counterface resulted in the lowest average wear depth of $0.11 \pm 0.6 \mu m$ on PEO coated AZ31 surface and the maximum track depth was only $0.17 \mu m$ (Fig. 6.4d).

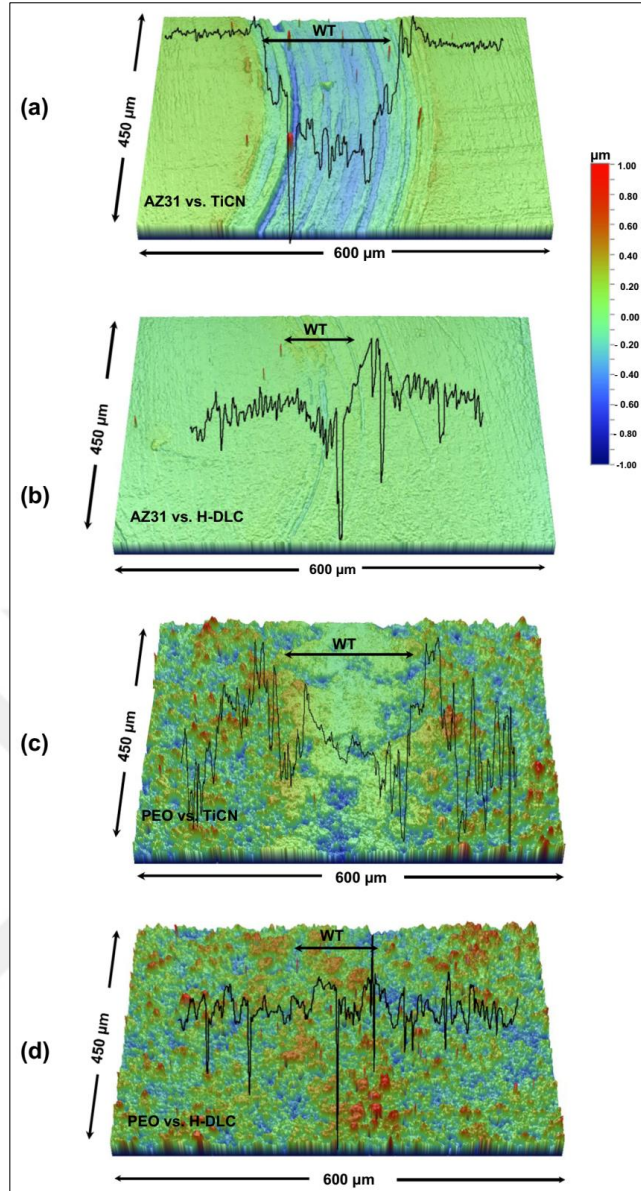


Figure 6.4 : 3-D surface profilometry images of wear tracks formed on the AZ31 samples after sliding against (a) TiCN and (b) H-DLC coated 52100 steel balls; 3-D surface profilometry images of wear tracks formed on the PEO coated AZ31 samples after sliding against (c) TiCN and (d) H-DLC coated 52100 steel balls. 2-D surface roughness profiles at the central position of each image are superimposed on 3-D images. WT indicates the width of the wear track.

The volumetric wear rates of uncoated AZ31 and PEO coated AZ31 were calculated from 3-D optical surface profilometry data as described in Section 2.3 and it was found that for uncoated AZ31, the normalized wear rate was $2.12 \times 10^{-5} \text{ mm}^3/\text{Nm}$ when sliding against uncoated 52100 steel, and $3.98 \times 10^{-5} \text{ mm}^3/\text{Nm}$ against TiCN coated 52100 steel. A slight decrease in the normalized wear rate to $1.98 \times 10^{-5} \text{ mm}^3/\text{Nm}$ was observed when H-DLC coated counterface was used. On the contrary, for PEO coated AZ31, the normalized wear rate was $1.89 \times 10^{-5} \text{ mm}^3/\text{Nm}$ when sliding against

uncoated 52100 steel, and $2.79 \times 10^{-5} \text{ mm}^3/\text{Nm}$ against TiCN coated 52100 steel. No measurable wear could be recorded on PEO coated AZ31 running against H-DLC counterface. The worn track surface features and their compositions are analysed further using SEM/EDS and FTIR techniques and the results are presented in Sections 3.3 and 3.4.

6.3.3 SEM and EDS examination of counterface contact surfaces against AZ31 and PEO coated AZ31

BSE-SEM and EDS observations showed that the contact surfaces of uncoated 52100 steel and TiCN coated counterface were covered with material transferred from AZ31 that was oxidized during the sliding process to form MgO transfer layers. A representative BSE image of the transfer layer formed on the contact surface of 52100 steel ball during the test conducted against uncoated AZ31 is shown in Fig. 6.5(a) with the corresponding EDS elemental maps for Fe, Mg and O (Fig. 6.5(b–d)). Formation of MgO transfer layers on the counterface is a common feature of Mg alloys subjected to dry sliding [218,219]. A BSE image of the transfer layer formed on TiCN coated ball during the test conducted against uncoated AZ31 is shown in Fig. 6.5(e) along with the corresponding EDS elemental maps for Ti, Mg and O in Fig. 6.5(f–h) again revealing the formation of an oxidized transfer layer. On the other hand, sliding tests conducted against H-DLC did not lead to the formation of a transfer layer on the contact surface of the counterface as shown in Fig. 6(a) but some powdery debris particles could be observed around the edges of the contact area. From the elemental EDS maps of C, Mg and O in Fig. 6.6(b–d), it can be suggested that some transferred Mg and O incorporating debris particles were formed; hence possibly debris particles that can be observed at the periphery of the contact surface were MgO.

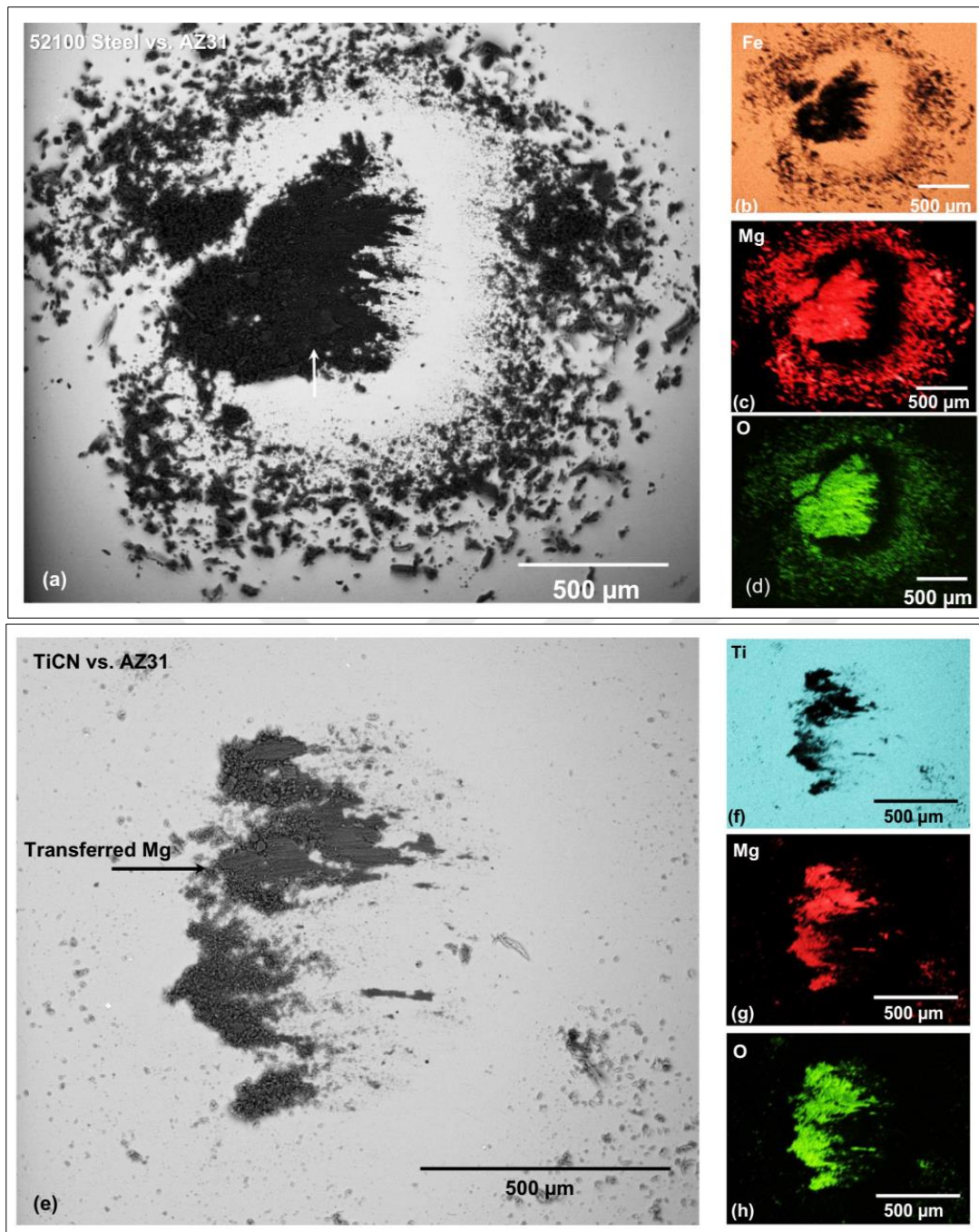


Figure 6.5 : (a) Back scattered electron image of the 52100 steel surface tested against uncoated AZ31 for 1000 revolutions. The elemental EDS maps taken from the contact area shown in (a) are for (b) Fe, (c) Mg, and (d) O. (e) Back scattered electron image of the TiCN coated steel tested against AZ31 for 1000 revolutions. The elemental EDS maps taken from area shown in (e) are for (f) Ti, (g) Mg, and (h) O.

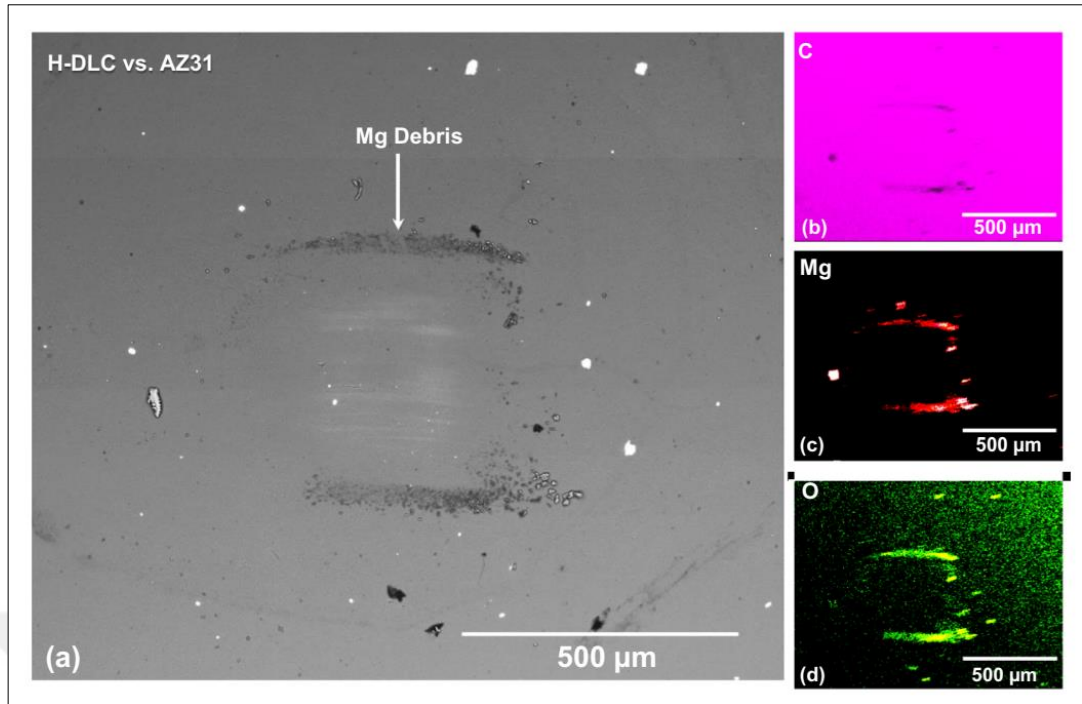


Figure 6.6 : (a) Back scattered electron image of the H-DLC coated steel tested against uncoated AZ31 for 1000 revolutions. The elemental EDS maps taken from the contact shown in (a) are for (b) C, (c) Mg, and (d) O. The Mg debris is indicated by the arrow.

The uncoated 52100 steel counterface running against the PEO coated AZ31 had a large wear area and was subjected to plastic deformation. Mg and O were detected in the debris transferred from the PEO coated AZ31 during sliding (Fig. 6.7[a–d]). A BSE image of TiCN coated counterface after sliding against PEO coated AZ31 is shown in Fig. 6.7(e) and revealed that the surface of TiCN did not show evidence for formation of transferred MgO particles unlike the same counterface running against uncoated AZ31 (Fig. 6.5e). The lack of a transfer layer is evident from the EDS elemental maps shown in Fig. 6.7(f–g). Similar observations were made in case of H-DLC sliding against PEO coated AZ31. According to the BSE image (Fig. 6.8a) and EDS elemental compositional maps (Fig. 6.8(b–d)), the contact surface of H-DLC counterface ran against PEO coated AZ31 consisted predominantly of carbon and some oxide particles were formed outside the contact area.

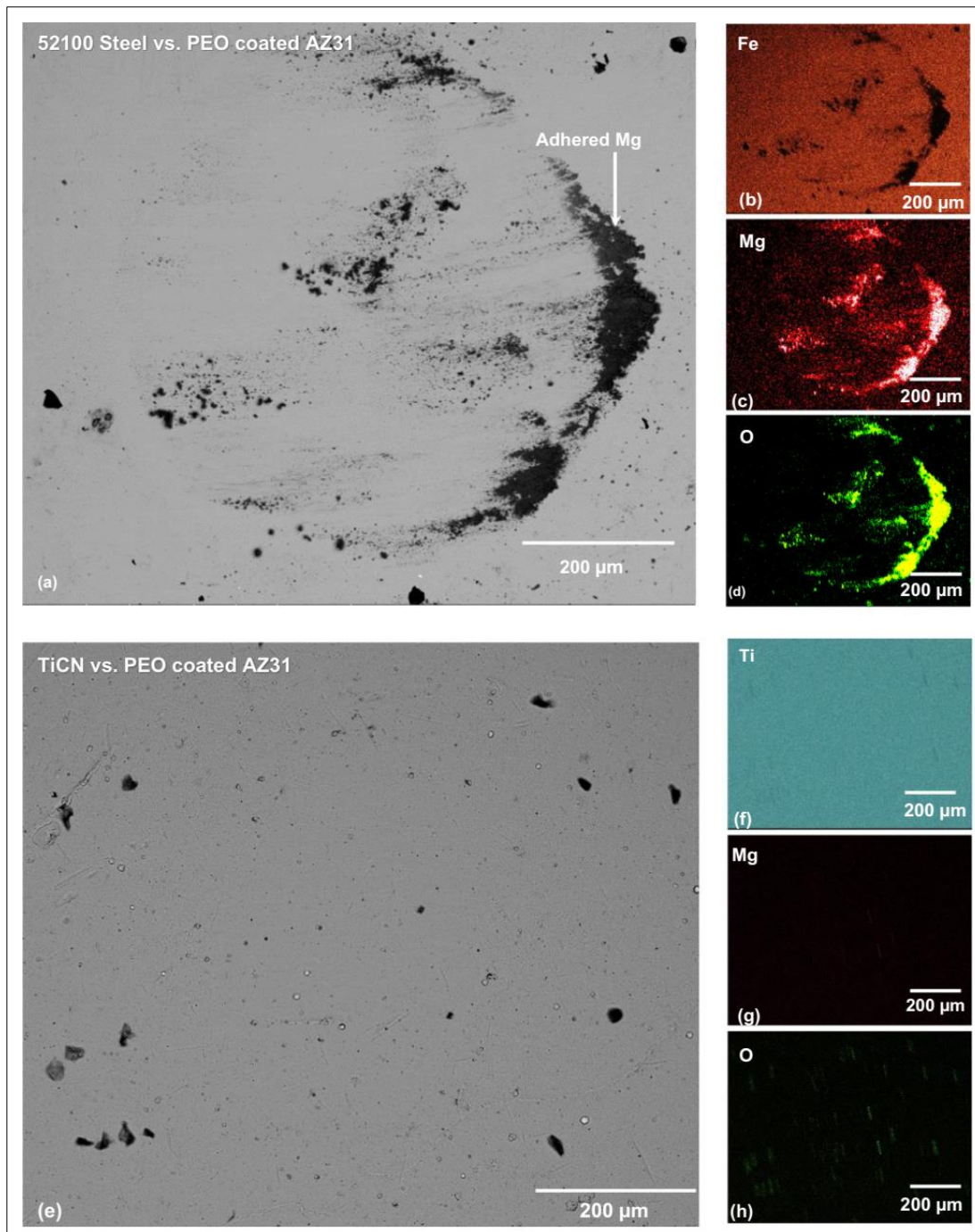


Figure 6.7 : (a) Back scattered electron image of the uncoated 52100 steel against PEO coated AZ31 for 1000 revolutions. The elemental EDS maps taken from the contact area shown in (a) are for (b) Fe, (c) Mg, and (d) O. (e) Back scattered electron image of the TiCN coated steel tested against PEO coated AZ31 for 1000 revolutions. The elemental EDS maps taken from the contact area shown in (e) are for (f) Ti, (g) Mg, and (h) O.

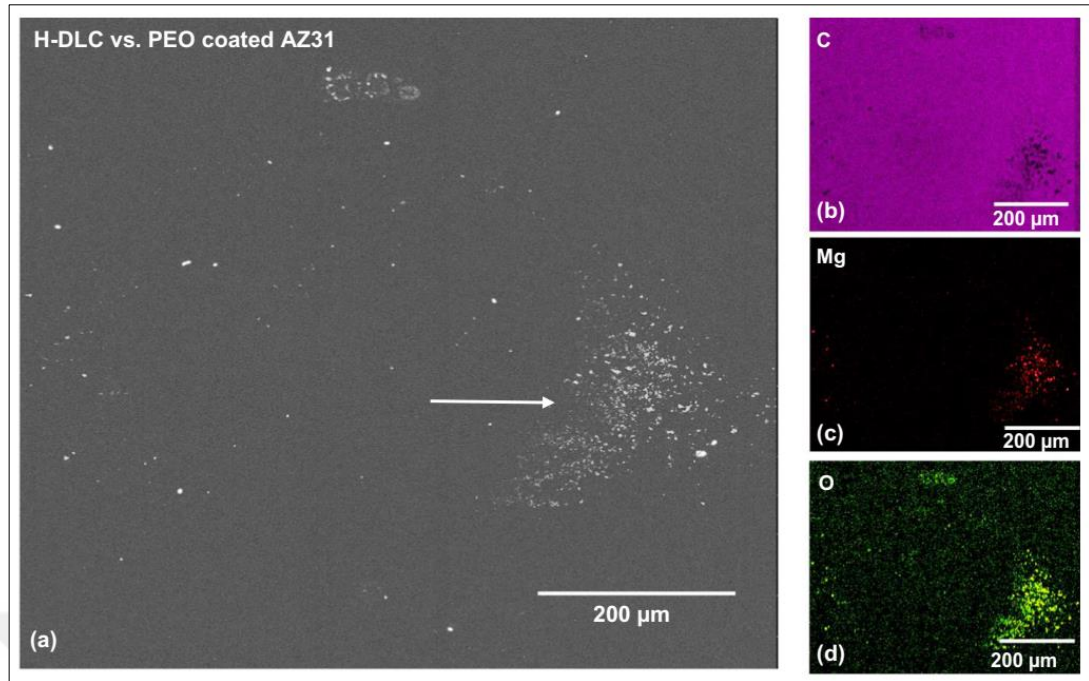


Figure 6.8 : (a) Back scattered electron image of the H-DLC coated steel tested against PEO coated AZ31 for 1000 revolutions. The elemental EDS maps taken from the contact area shown in (a) are for (b) C, (c) Mg, and (d) O. The MgO debris is indicated by the arrow.

6.3.4 Characterization of wear tracks formed on AZ31 and PEO coated AZ31

The BSE images of the wear tracks that were formed on the uncoated AZ31 surfaces during sliding contact are shown in Fig. 6.9(a–c). Considering the morphologies of wear tracks of AZ31 generated during sliding contact against 52100 steel (Fig. 6.9a), TiCN (Fig. 6.9b), and H-DLC coated counterfaces (Fig. 6.9c), tested for the same sliding distance of 1000 revolutions, it becomes clear that the wear tracks were wide when 52100 steel (575 μm) and TiCN (565 μm) counterfaces were used, but running against H-DLC resulted in a narrower wear track of 200 μm wide. Dark patches of material layers were formed on the wear tracks of ZA31 and identified as MgO. These observations and also observations made during the course of sliding tests suggested that these fragments were back transferred from the counterface surfaces during sliding contact as indicated earlier. The MgO coverage of the wear track increased with sliding, which could be the cause of increase in COF values with the number of revolutions shown in Fig. 6.1(a).

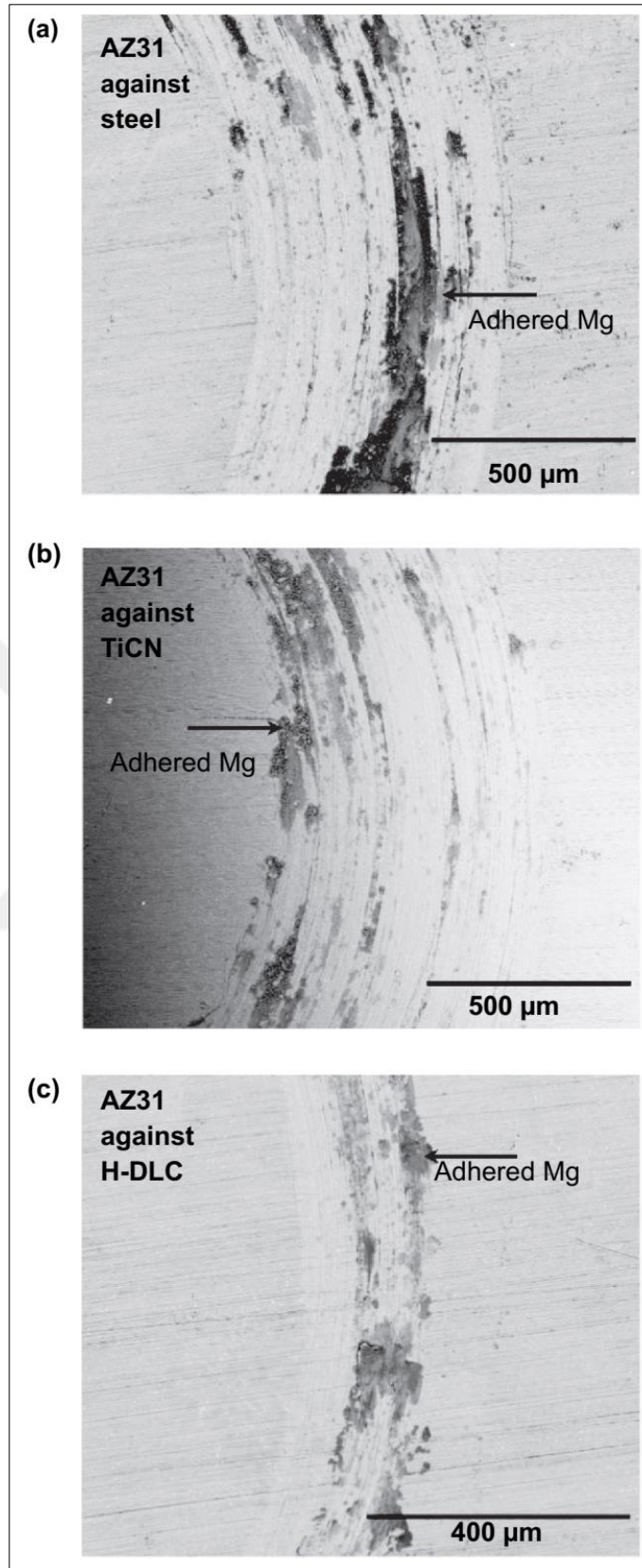


Figure 6.9 : Typical back scattered electron images of wear tracks formed on uncoated AZ31 surface when tested against (a) uncoated 52100 steel, (b) TiCN and (c) H-DLC after 1000 revolutions. The adhered layers are MgO indicated using arrows. WT indicates the width of the wear track.

Examination of the wear tracks formed on the PEO coated AZ31 surfaces by SEM revealed some significant differences in the wear track morphologies and in the compositions of transfer layers. One of the notable aspects of sliding contact with 52100 steel was the occurrence of Fe transfer from the steel. These layers are shown in the BSE image in Fig. 6.10(a), and examination of the corresponding elemental EDS maps of Fe and O suggested that they were iron oxide layers. There was no evidence of material transfer from TiCN to the wear tracks of PEO coated AZ31 (Fig. 6.10b). On these wear tracks the asperities appeared to be subjected to plastic deformation and were flattened. BSE images of the wear tracks formed on the PEO coated AZ31 sliding against H-DLC revealed a wear track that is not easily distinguishable from the rest of the surface due to low wear damage. Some open surface pores that were initially present on the unworn surface were no longer visible, which could be due to formation of thin transfer layers (Fig. 6.10c). A higher magnification BSE image (Fig. 6.10d) of the wear track indeed revealed formation of a transfer layer on the wear track. The corresponding EDS map for C shown in Fig. 6.10(e), and the EDS spectrum of this area shown in Fig. 6.10(f) confirmed that the transfer layers incorporated carbonaceous material. A likely interpretation of the formation of these layers is material transfer from the H-DLC to the PEO coated AZ31 surface during the sliding process. This carbonaceous layer appears to play an important role in reducing the COF as will be discussed in Section 4.

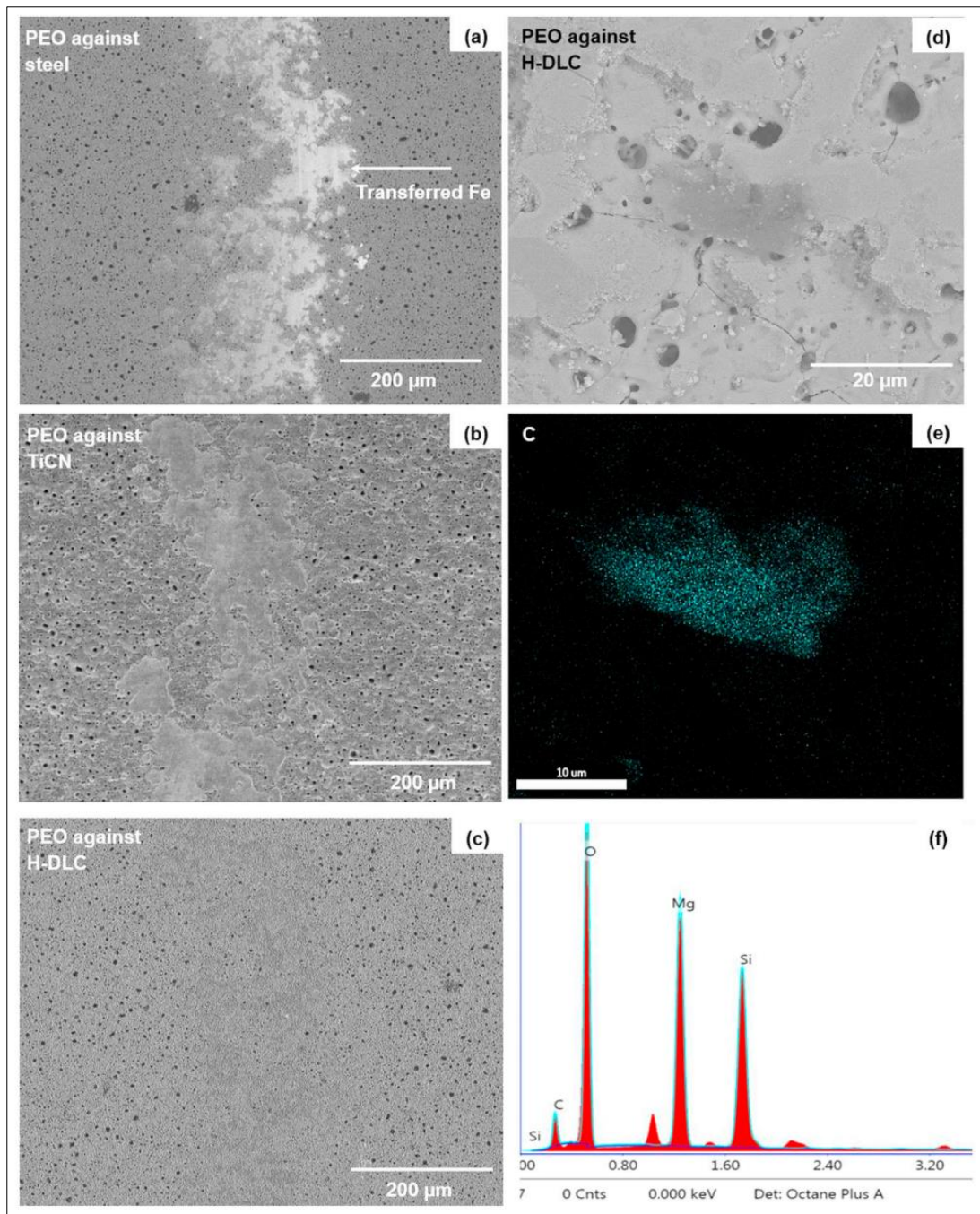


Figure 6.10 : Typical back scattered electron images of wear tracks formed on PEO coated AZ31 surface when tested against (a) uncoated 52100 steel, (b) TiCN, (c) H DLC after 1000 revolutions, (d) PEO wear track at higher magnification showing transferred DLC, (e) EDS map of carbon distribution of (d) and (f) EDS spectrum of the area shown in (e).

The FTIR spectra taken from the wear tracks formed on AZ31 and PEO coated AZ31 surfaces as a result of sliding against H-DLC coated counterfaces are shown in Fig. 6.11(a) and (b). The characteristic IR bands of C-H, O-H and C-O were apparent on the wear tracks of both uncoated and PEO coated AZ31. Additional bands of Mg-O and Si-O were detected on the wear tracks of PEO coated AZ31. The IR bands

observed at 2900 cm^{-1} were significant as they corresponded to the (C-H) groups [214,220,221]. Thus, FTIR results suggested that wear tracks exhibited layers that incorporated hydrocarbon compounds possibly formed as a result of the material transfer from H-DLC coated counterface.

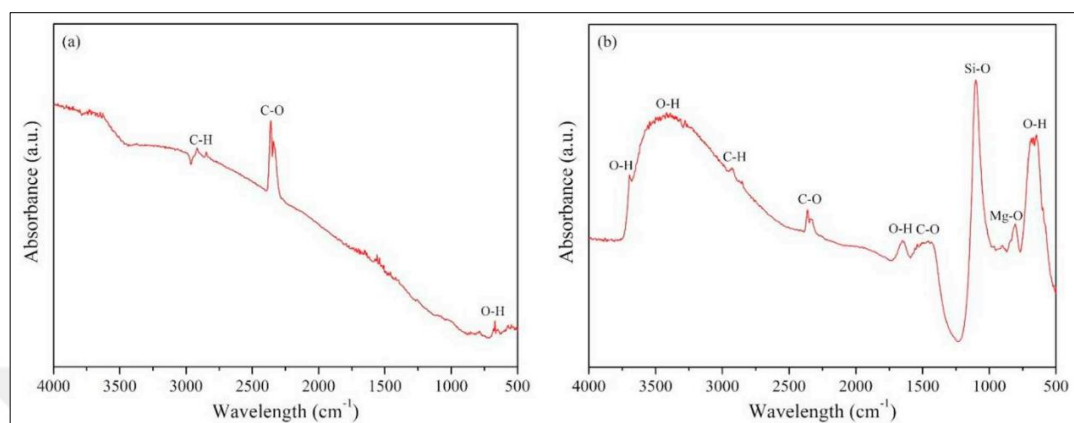


Figure 6.11 : FTIR spectra of the wear tracks formed on (a) uncoated AZ31 and (b) PEO coated AZ31 after sliding against H-DLC.

6.4 Discussion of Mechanisms for Low and Stable Friction of H-DLC Against PEO Coated AZ31

It is pertinent to start the discussion by considering the friction curves generated when AZ31 and PEO coated AZ31 were put in sliding contact against counterfaces with N-based coatings (and uncoated steel). In case of uncoated AZ31 placed in sliding contact against counterfaces other than the H-DLC, the material transfer occurred from the sample surfaces to these counterfaces (Fig. 6.6) and some (oxidized) Mg was back transferred to AZ31's wear tracks. The transfer and back transfer events were likely responsible for the large fluctuations of the COF curves in Fig. 6.2a. One possible reason for the stable COF values with low fluctuations observed during PEO coated AZ31 sliding against these counterfaces (Fig. 6.2b) would be the inherently porous nature of the PEO treated surfaces (Fig. 6.1a), which would likely to provide stronger mechanical adhesion and help to retain the transfer layers formed during sliding better than the AZ31 surfaces. Thus, a hard PEO layer would not only reduce wear of AZ31 (Figs. 6.3 and 6.4) but also act like a robust substrate, which would prevent detachment of tribolayers that were already formed. However, the wear on the counterfaces running against PEO coated AZ31 were more extensive compared to the wear of counterfaces running against uncoated AZ31, as shown in Figs. 6.5 and 6.6; This is an

undesirable effect of the high hardness of the PEO coating with a rough surface morphology. Consequently, the PEO coating would increase the wear resistance of AZ31, but at the same time the COF of the tribosystem increased too, notwithstanding the fact that the COF curves in this case were more stable than when running against uncoated AZ31 surfaces. The use of H-DLC counterface against AZ31 reduced the wear of this material in agreement with the literature [215,222] and also reduced the COF to the lowest level compared to other counterfaces tested (Fig. 6.3). Still Mg (and MgO) transfer to H-DLC (Figs. 6.8 a-d) and back transfer to AZ31 (Fig. 6.9c) was not entirely alleviated and as these events continued a slight increase in the COF to 0.17 was observed (Fig. 6.2c).

PEO coated AZ31 displayed a low steady-state COF (Fig. 6.2c) and a low wear (Fig. 6.10c) when sliding against H-DLC compared to counterfaces made of steel and N-based coatings. The COF of PEO coated AZ31 running against H-DLC coated counterface was also characterized by low fluctuations and maintained a constant steady state value. This was due to the transfer of H-DLC to the wear track of PEO coated AZ31. Transfer of counterface material to the wear tracks also occurred when PEO coated AZ31 was put in sliding contact against steel (Fig. 6.10a) and N-based coatings (e.g. Fig. 6.10b). However, the C-based composition of transfer layer (Fig. 6.10(d–e)) was an important factor for producing a low COF; FTIR spectra taken from the wear tracks formed on PEO surfaces (Figs. 6.11(a, b)) provided additional evidence for the transfer of carbonaceous material from H-DLC to the wear tracks on PEO coated AZ31. Several complementary interpretations exist for the low COF of the H-DLC coatings in ambient air including easy shearing of the CeC interfaces [223], and passivation of the surface carbon atoms at both side of the interface by hydrogen [215,224,225]. It is evident that once the Clayers on the surface of PEO coated AZ31 is formed and remain adhered to the contact surface, a low and constant COF of 0.13 could be attained. Thus, a disadvantage that the PEO coatings over the uncoated AZ31, namely generation of higher COF values, despite providing low dry sliding wear rates, can be overcome by using an H-DLC counterface in tribological components requiring durable lightweight materials.

6.5 Summary and Conclusions

This study investigated the roles of counterface materials on the friction and wear behaviour of PEO coated AZ31 grade Mg alloy in comparison with the base AZ31 alloy. It was shown that the type of counterface used had a significant effect on the coefficient of friction (COF) of PEO coated AZ31 alloy. The main results can be summarized as follows:

- i) When AZ31 was put in dry sliding contact with H-DLC coated counterface a low COF of 0.17 was observed. In comparison, COF values > 0.36 with high fluctuations resulted when counterfaces made of SAE 52100 steel and those coated by TiN, TiCN, CrN were used. MgO transfer layers originating from the wear tracks of AZ31 were formed on the counterface surfaces with the exception of H-DLC.
- ii) PEO coated AZ31 provided lower wear compared to AZ31 when the same counterfaces were used. The COF values for PEO coated AZ31 obtained when steel counterfaces and those with N-based coatings were used were higher than those of AZ31 but the friction curves were more stable, with lesser fluctuations conceivably due to the retention of transfer layers at the sliding interfaces as a result of higher hardness and the porous morphology PEO coated surfaces.
- iii) The use of H-DLC coated counterface against PEO coated AZ31 reduced the COF simultaneously with the wear due to the formation of carbonaceous transfer layers on the wear tracks. The COF of this tribosystem was stable, and once a steady state friction regime was reached the COF remained constant at 0.13. It was concluded that utilization of H-DLC coated counterfaces against PEO coated Mg alloys can broaden application of these alloys to tribological components where low friction and wear are needed along with low mass.



7. WEAR AND CORROSION CHARACTERISTICS OF NOVEL ALUMINA COATINGS PRODUCED BY MICRO ARC OXIDATION ON AZ91D MAGNESIUM ALLOY ⁶

7.1 Introduction

Owing to its attractive properties such as high hardness, chemical inertness, wear resistance and melting point, thick ($> 20 \mu\text{m}$) alumina coatings are usually utilized in engineering applications to protect metals and its alloys against degradations caused by mechanical loads and/or chemical attacks and/or thermal effects [226–229]. Thermal spraying, in which alumina powder is sprayed onto the substrate in a semi molten state, is a widely used technique for coating alumina on metal surfaces [230–233]. When magnesium and its alloys are of concern, deposition of semi molten alumina particles by thermal spraying may lead to some complications arising from the low melting point and poor oxidation resistance of magnesium, thermal expansion mismatch between the alumina coating and the magnesium substrate and generation of undesirable microstructure in magnesium due to the excessive heat [234].

Being motivated by lower processing temperatures of CS and MAO processes, present study was initiated to form a protective alumina layer on magnesium and its alloys by eliminating the potential problems of thermal spraying. Cold spraying, is based on acceleration of powder in a gas stream towards the substrate at lower temperatures relative to thermal spraying [235], hence it provides coating of the heat sensitive metals such as aluminum, titanium and magnesium successfully without oxidation [236–238]. Furthermore, introduction of ceramic particles into the metal powders improves the deposition efficiency of CS [239] and generates denser and harder metal matrix composite layers as compared to monolithic ones [240]. It should be mentioned that, the protective nature of the CS layers against corrosion and wear is not sufficient for the harsh service conditions.

⁶ This chapter is based on the paper “O. Tazegul, F. Muhaffel, O. Meydanoglu, M. Baydogan, E. S. Kayali, H. Cimenoglu, Wear and corrosion characteristics of novel alumina coatings produced by micro arc oxidation on AZ91D magnesium alloy, Surf. Coatings Technol. 258 (2014) 168-173”

On the other hand MAO, which is based on electrochemical reactions developing under a certain applied voltage in alkaline electrolytes to form an oxide of the substrate, recently, appeared as an attractive process to develop protective oxide layers on light metals such as aluminum, magnesium, titanium and their alloys. In this respect, there is a vast number of studies in the literature [85,241–247] reporting remarkable enhancement in the wear and corrosion resistances of aluminum and its alloys upon covering their surfaces with alumina layer via MAO process.

In this study, an attempt has been made to produce a multi-layered coating on AZ91D alloy by sequential use of CS and MAO processes. More specifically, obtaining a multi-layered coating consisting of an alumina layer with an aluminum layer (monolithic or composite) beneath it has been aimed. To the knowledge of the authors, reports on production of multi-layered coatings on magnesium alloys by combination of CS and MAO processes are scarce in the open literature. In a recently published study [248], MAO process was employed after deposition of monolithic aluminum by CS onto AZ91 magnesium alloy. Although, remarkably better protection was obtained against corrosion attack, the coating did not exhibit multi-layered characteristics due to the extension of oxidation beyond the aluminum layer during MAO process.

7.2 Materials and Methods

In the present study, 15x15x4 mm samples machined from the as-cast AZ91D alloy (~81 HV) were used as the substrates. Prior to MAO, aluminum (99.5% purity, Alfa-Aesar) and aluminum matrix alumina reinforced composite layers were deposited on the samples by CS process. Composite layer deposition was employed by using a mixture of aluminum powder with α -alumina particles (99.3% purity, Praxair) which constituted 20 % of the total volume. CS process was conducted by the Rusonic Model K-201 equipment and powder was accelerated by air at an inlet pressure of 6 bar. The particle sizes of the aluminum and alumina powders used in this work were <44 μm and ~12 μm , respectively. The CS layers (>200 μm) were ground and polished prior to MAO process. The hardness of the monolithic and composite layers was measured as 57 HV_{0.025} and 78 HV_{0.025}, respectively. MAO was employed in an electrolyte containing 0.18 mol/L sodium aluminate (NaAlO₂, Alfa Aesar) and 0.035 mol/L potassium hydroxide (KOH, Aldrich) at 400 V. The frequency and the duty cycle of the MAO process were 500 Hz and 60%, respectively. While CS deposited samples

were oxidized for 20 min, AZ91D sample was oxidized until reaching nearly the similar MAO thickness with those of CS deposited samples. During the MAO process, the temperature of the electrolyte was kept at 20 ± 2 °C by a cooling system in order to regulate the chemical reaction rate on the surface of the samples. After the MAO process samples were cleaned ultrasonically in acetone, distilled water and dried in air. As a reference, a sample of the as-cast AZ91D alloy was also oxidized in the same electrolyte. Hereafter, the samples subjected to MAO process were coded as MA, CS-0 and CS-20 for the magnesium alloy substrate (AZ91D), monolithic aluminum layer deposited substrate and composite aluminum layer deposited substrate, respectively.

In the scope of the present study, structural examinations of the samples were made by utilizing a Scanning Electron Microscope (SEM, Hitachi TM-1000) and an X-ray Diffractometer (XRD, GBC MMA). SEM examinations were conducted on the surfaces and the cross-sections of the samples. For cross-sectional SEM examinations, samples were gently cut and then ground and polished by following standard metallographic procedures. XRD analyses were performed with a scan rate of $2^\circ/\text{min}$ and a step angle of 0.02° under Cu-K α radiation.

Hardness of the oxide layers was measured from the cross-sections of the specimens by using a depth sensing micro hardness tester (CSM Instruments) with a Vickers indenter, under an indentation load of 250 mN. In order to plot hardness profiles of the oxide layers, hardness values obtained after five successful indentations made at the same cross-sectional distance from the surface were averaged. Adhesion of the MAO coatings was analyzed using a scratch tester (CSM Instruments) having a standard Rockwell C indenter. The load range, sliding distance and sliding speed were set as 0.05–20 N, 5 mm and 5 mm/min, respectively. During scratch testing acoustic emission was recorded to analyze deteriorations in the oxide layers. After the test, the scratches were examined by SEM.

Dry sliding wear performances of the samples were determined by a reciprocating wear tester (Tribotech) against Al₂O₃ ball having a diameter of 6 mm. Wear tests were executed under a load of 5 N, sliding speed of 10 mm/s, stroke of 5 mm and total sliding distance of 100 m under normal atmospheric conditions (22 ± 1 °C and $30 \pm 2\%$ humidity). Friction coefficient values were recorded during the tests. After the wear tests, wear tracks were examined by a surface profilometer (Veeco Dectac 6M)

and SEM. Wear scars formed on the Al_2O_3 balls were imaged by an optical microscope (OM, Leica ICC50HD).

Electrochemical corrosion behavior of the samples was conducted in 3.5 wt.% NaCl solution open to air by utilizing Gamry PCI4/750. All potentials were measured with respect to a saturated calomel electrode. Platinum electrode rod served as the counter electrode for current measurement. Samples were immersed into the 3.5 wt.% NaCl solution and allowed to be stabilized for 20 min in order to ensure a steady open circuit potential. The potentiodynamic polarization tests were conducted from -1.0 V and 0.5 V versus open circuit potential with a scan rate of 2 mVs^{-1} . From the polarization curve, the corrosion parameters were evaluated by Tafel extrapolation method by Gamry Echem Analyst v.5.68 software.

7.3 Results and Discussion

The XRD patterns of the oxidized samples are shown in Fig. 7.1. Upon application of the MAO process, MA was covered with an oxide layer composed of magnesium aluminate (MgAl_2O_4) and magnesia (MgO) phases, while the oxide layers of CS-0 and CS-20 samples were consisted of α -alumina ($\alpha\text{-Al}_2\text{O}_3$) and γ -alumina ($\gamma\text{-Al}_2\text{O}_3$) phases. Detection of magnesium and aluminum peaks on the XRD patterns can be attributed to the penetration of the X-rays beyond the oxide layers.

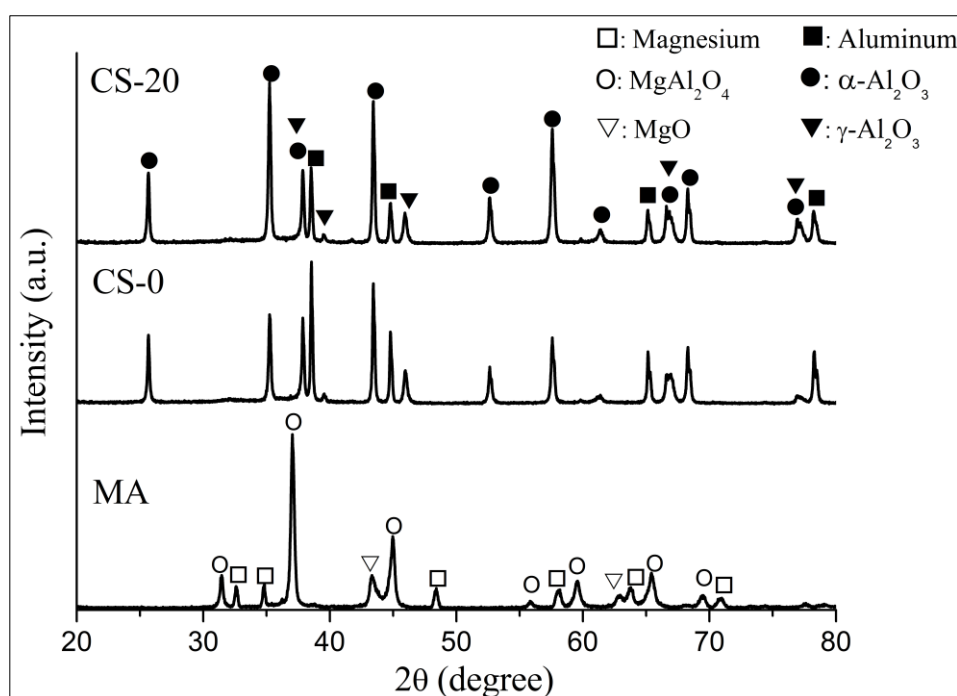


Figure 7.1 : XRD patterns of oxidized samples.

The growth mechanism of oxide layer (containing MgAl_2O_4 and MgO phases) on the MA can be attributed to the reactions took place between magnesium, aluminum and oxygen during MAO processing [203,249,250]. While the reactions between magnesium of the substrate and oxygen formed MgO , high aluminum content of the substrate and presence of aluminum ions in the electrolyte both induced the formation of MgAl_2O_4 phase in the oxide layer [251–255]. When the CS-0 is of concern, the reaction between aluminum and oxygen in the electrolyte favored formation of an oxide layer consisting of α - and/or γ -alumina [244,256]. Since α -alumina is thermodynamically more stable than γ -alumina at high temperatures, generation of α -alumina during MAO may be related to relatively high heat input during processing [257]. XRD analyses (Fig. 7.1) revealed that the peak intensities of α -alumina were higher for CS-20 sample than CS-0 sample. Principally, α -alumina reinforcement in CS deposited layer can be responsible for the increase in α -alumina phase on the surface. On the other hand, the reduction of aluminum matrix volume fraction by using α -alumina particles in the composite layer suggested that the aluminum matrix of the CS-20 sample experienced higher heat input (caused by localization of voltage and current) than CS-0 sample and this may favored α -alumina formation during MAO process.

The SEM micrographs of the oxidized samples are presented in Fig. 7.2. Although, their phase compositions were different (Fig. 7.1), oxide layers of MA, CS-0 and CS-20 samples exhibited typical rough morphology of MAO, containing spherical micro-pores in various sizes (in between 0.5 and 4 μm). The formation of these micro-pores generally have been ascribed to evolution of high voltage discharge channels formed when molten oxide and gases are pulled out during processing [258]. Furthermore, micro-cracks were detected especially at the flat regions of the oxide layers. However, they were not connected with each other and relatively short in length. Micro-cracking of the oxide layers was mainly related with thermal stresses caused by the fast solidification of molten oxide in the relatively cold electrolyte [259,260]. In comparison to the oxide layers of the MA and CS-0 samples, the flat region was wider on the oxide layer of the CS-20 sample owing to the reduction in number of pores. These observations suggest blocking of volcano appearance of discharge channels by the reinforcing α -alumina particles of the composite layer.

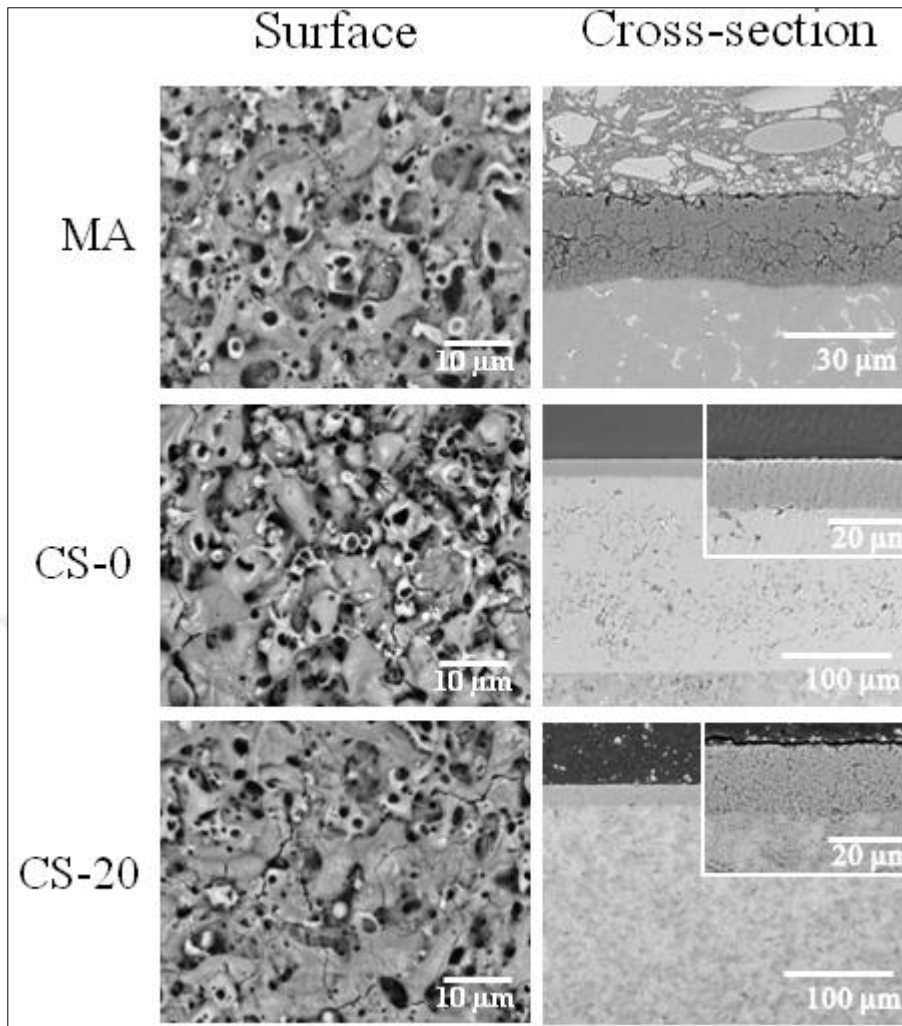


Figure 7.2 : SEM micrographs of the surfaces and cross sections of oxidized samples.

Cross-sectional examinations (Fig. 7.2) revealed that, the most compact and dense oxide layer has grown on the CS-0 sample, whereas oxide layer on the MA sample has defective nature characterized by a network of discontinuities extending through the thickness. In the case of CS-20 sample, progress of oxidation in the aluminum matrix resulted in the formation of interfaces between the growing oxide layer and reinforcing α -alumina particles and therefore, the oxide layer grew on CS-20 sample was less dense than that of CS-0 sample. As a result of the higher affinity of magnesium to oxygen than aluminum, oxide layer grew on MA sample was thicker than CS-0 and CS-20 samples. The thicknesses of the oxide layers were measured as; 37.9 ± 0.9 , 22.3 ± 0.8 and 28.3 ± 1.3 μm for MA, CS-0 and CS-20 samples, respectively. In the case of the CS samples, accelerated growth of the alumina layer may be related to the exposure of CS-20 sample to higher heat input than CS-0 sample during the MAO process. Cross-sectional SEM examinations, also confirmed that interfaces between the oxide

layers and the underlying substrate or CS layers were free from any discontinuities such as pores and cracks.

The results of the hardness measurements conducted on the oxide layers are shown as hardness – distance from surface profiles in Fig. 7.3. As a general trend, hardness was low at the regions close to the surface (300-400 HV at a distance of 5 μm) and increased at further distances from the surface (850-1600 HV at depth of 20 μm). Measurement of low hardness values close to the outermost regions can be attributed to the higher micro-porosity concentration [261,262]. Furthermore, incorporation of chemical species of the electrolyte and low crystallinity due to rapid cooling rate may also lead low hardness at these regions [183,262]. The contribution of the phase composition on the hardness of the oxide layers became more evident at distances longer than 15 μm . In this respect, higher hardness of the oxide layers of CS-0 and CS-20 samples than the oxide layer of MA sample can be associated with the higher hardness of alumina than that of MgO [263,264]. Furthermore, presence of high amount of α -alumina in the oxide layer of the CS-20 sample (Fig. 7.1) provided higher hardness in comparison to the oxide layer of CS-0 sample. In a previous work, relatively low hardness of the alumina layer formed by MAO process was associated with generation of γ -alumina as well as insufficient sintering of α -alumina [265].

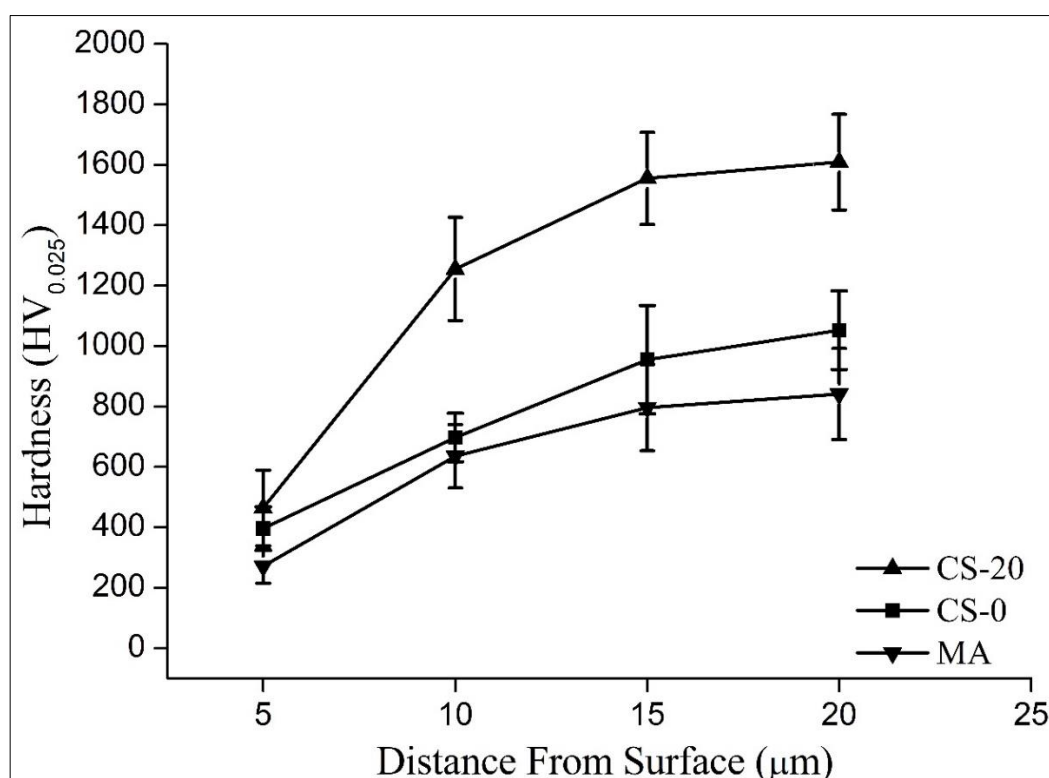


Figure 7.3 : Micro-indentation measurements of hardness of oxidized samples.

The results of the scratch tests are presented in Fig. 7.4 including the acoustic emission – force plots and the SEM images of the scratches. The oxide layer of the MA sample exhibited poor scratch resistance as compared to the oxide layers of the CS-0 and CS-20 samples. As can be seen in Fig. 7.4a, the tip of the scratch tester penetrated beyond the oxide layer and contacted with the substrate when the load reached 4 N. This low scratch resistance of the oxide layer can be arising from its defective nature and relatively lower hardness as mentioned above. In the case of CS-0 sample (Fig. 7.4b), after cohesive failures observed at the half of the test (about 10 N) due to the tensile stress induced by plastic deformation, adhesive cracks appeared at both sides of the scratch track when the test load reached 18 N. At the end of the scratch track, significant spallation was also detected. The oxide layer of the CS-20 sample (Fig. 7.4c) exhibited excellent resistance against scratching at the maximum test load of 20 N without remarkable changes on the acoustic emission – force plot. In this respect, no cracks and delamination were detected around the scratch track formed on its oxide layer. This phenomenon can be associated with higher hardness of the oxide layer (Fig. 7.3) and its good adhesion with the underlying composite layer.

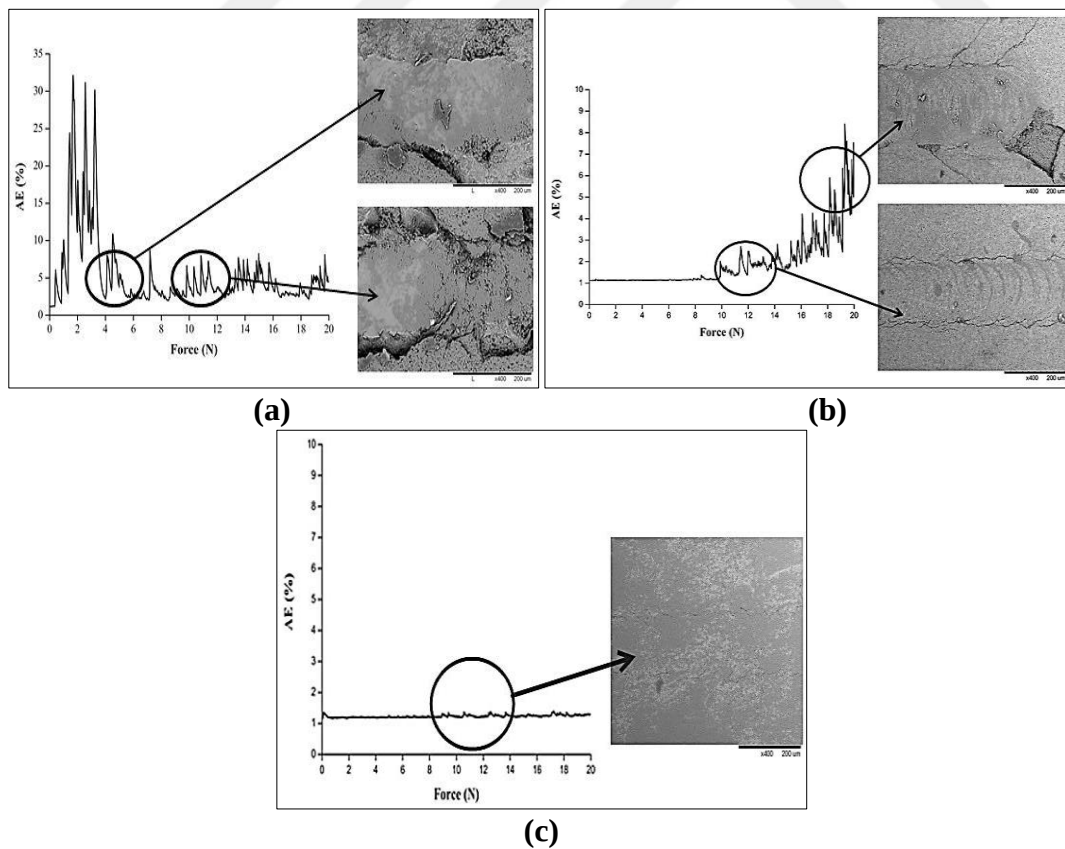


Figure 7.4 : Acoustic emission (AE) - force graphs and SEM micrographs of worn surfaces of (a) MA, (b) CS-0 and (c) CS-20 samples evaluated by scratch test.

The results of the wear tests are quantified in Table 7.1 in terms of the relative wear rates and the average friction coefficients recorded during the wear tests. Relative wear rates were low for the samples which exhibited low friction coefficients. This suggests that contact interface plays a crucial role of on the tribological performance of the examined tribo-couples. The contact surface appearances of the examined samples and the counter face (alumina ball) are shown in Fig. 7.5. The worn surface of the CS-0 sample contained many micro-cracks and local detachment areas indicating the dominant wear mechanism as delamination. However, the delaminated particles did not attach to the contact surface of the alumina ball whose wear scar had a grooved morphology indicating that it was worn by micro abrasion during the wear tests. In the case of CS-20/alumina ball tribo-couple, even though the alumina ball was subjected to micro-abrasion, evidence of delamination was not clearly identified on the worn surface of the CS-20 sample. Its smooth and crack free morphology can be associated with better wear resistance and lower friction coefficient than those of CS-0 sample.

Table 7.1 : Average relative wear rates and average friction coefficients of samples.

Sample	Relative Wear Rate	Average Friction Coefficient
MA	1.0	0.30
CS-0	1.8	0.44
CS-20	0.7	0.24

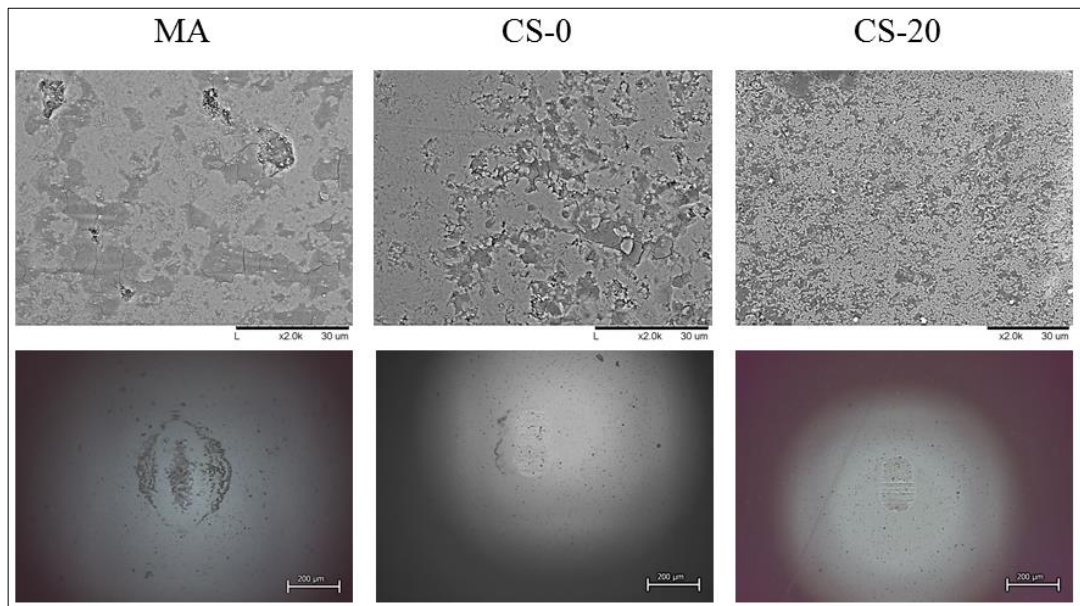


Figure 7.5 : SEM images of worn tracks of oxidized samples and wear scars of Al_2O_3 balls.

Among the examined samples, MA sample exhibited moderate tribological performance. The worn surface of the MA can be characterized by micro-cracked and delaminated nature. Limited delamination at contact surface of the MA sample provided better wear resistance and lower friction coefficient as compared to those of the CS-0 sample. Sticking of the delaminated particles on the contact surface of alumina ball prevented its direct contact with the oxide layer and therefore inhibited the progress of abrasion on alumina ball.

Potentiodynamic polarization curves of the examined samples are shown in Fig. 6. Anodic and cathodic Tafel constants (β_a and β_c), corrosion potential (E_{corr}), and corrosion current density (i_{corr}) determined by extrapolation method of Tafel plots are given in Table 7.2. Furthermore, polarization resistance (R_p) values of samples (Table 7.2) were calculated with Stern-Geary relationship given below [266].

$$R_p = \frac{\beta_a \beta_c}{2.3 i_{corr} (\beta_a + \beta_c)} \quad (7.1)$$

It can be clearly seen from the values given in Table 7.2 that E_{corr} value of the CS-0 sample was nearly half orders of MA sample in magnitude, while CS-20 sample had a slightly more negative E_{corr} than that of CS-0 sample. On the other hand, CS-0 and CS-20 samples exhibited about 1.5 and 19 times lower i_{corr} values compared with that of MA sample, respectively. Furthermore, it should be noted that CS-0 and CS-20 samples had 1.6 and 17 times higher R_p values with respect to MA sample.

Table 7.2 : Results of potentiodynamic polarization tests applied to MA, CS-0 and CS-20 samples.

Sample	β_a (V _{SCE} /decade)	β_c (V _{SCE} /decade)	E_{corr} (V _{SCE})	i_{corr} (μ A/cm ²)	R_p (Ω .cm ²)
MA	0.120	0.285	-1.317	18.7	1961
CS-0	0.128	0.295	-0.681	12.8	3028
CS-20	0.174	0.134	-0.897	0.98	33337

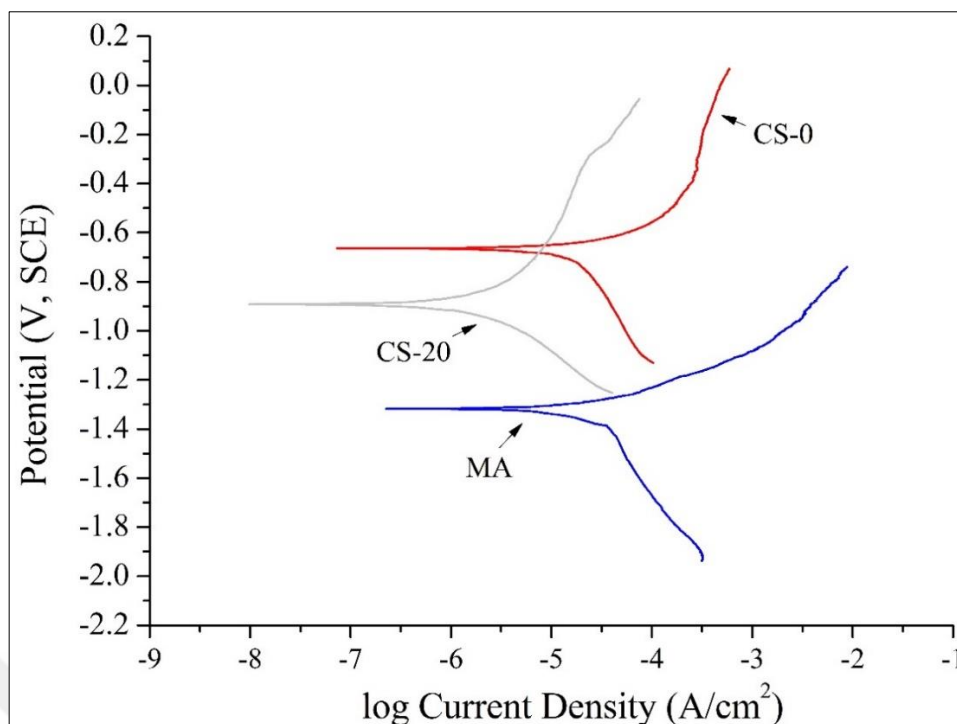


Figure 7.6 : Potentiodynamic polarization curves for MA, CS-0 and CS-20 samples immersed in 3.5 wt.% NaCl solution.

Although the oxide layers are expected to be protective against chemical deterioration, the progress of corrosion on the examined samples can be explained by penetration of corrosive solution into the pores and/or micro-cracks of the oxide layers [248]. In addition to its more defective nature of the surface of MA sample, low thermodynamic stability of MgO than alumina [267,268] should also be considered when analyzing the poor corrosion performance of the MA sample in comparison to CS-0 and CS-20 samples. Based on the anodic branch of potentiodynamic polarization curves as representing the different pitting corrosion potential, pitting corrosion on the surface of CS-20 sample was delayed for a longer period than those of MA and CS-0 samples. On the other hand, i_{corr} and R_p values indicated far better corrosion resistance of CS-20 sample than that of CS-0 sample. It is suggested that presence of high amount of α -alumina as reinforcing particles in the oxide layer, which is thermodynamically more stable than γ -alumina, provided better protection from corrosive (chloride ions) environment. This indicates that α -alumina reinforcement in CS aluminum layer decreased the vulnerability of the MAO coating to chloride ions. According to the E_{corr} values listed in Table 7.2, CS-20 sample became more active than CS-0 sample at more negative potentials. This may arise from the denser nature of the oxide layer of CS-0 sample in comparison to that of the CS-20 sample.

7.4 Conclusion

Sequential application of CS and MAO processes successfully formed hard and adherent alumina layer with an underlying aluminum (monolithic or composite) layer over AZ91D magnesium alloy. As compared to the MAO treated state of the AZ91D alloy, application of MAO after cold spraying of alumina reinforced aluminum matrix composite layer provided superior enhancement in both dry sliding tribological performance against alumina ball and corrosion resistance in 3.5 wt.% NaCl solution.

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8. CONCLUSIONS AND RECOMMENDATIONS

The key findings of the modifications of MAO coatings on magnesium, titanium and aluminium alloys are summarised below:

- MAO coatings improved the corrosion and wear resistance of the AZ91 Mg alloy. When compared to the reference electrolyte, Na_3PO_4 added electrolytes generated MAO coatings with much-improved corrosion and corrosion wear resistances due to inhibition of the development of corrosion products ($\text{Mg}(\text{OH})_2$ and MgCl_2) by AlPO_4 as exposed to 0.9 wt% of NaCl solution. An increment of the electrolyte concentration of Na_3PO_4 from 5 g/l to 10 g/l slightly degraded the corrosion-wear efficiency of the formed MAO coating and imposed higher surface roughness.
- The usage of ZrO_2 particles in the electrolyte not only yielded the incorporation of ZrO_2 particles but also produced new ZrTiO_4 -type oxide in the MAO coating and enhanced the compactness of the TiO_2 layer. Modified microstructural features have resulted in higher stiffness, better adhesion, and increased scratch resistance for the oxide layer formed in ZrO_2 -added electrolyte, whereas retaining improved bioactivity. In combination with increased hardness, adhesion, and scratch resistance, the oxide layer developed in the ZrO_2 -added electrolyte demonstrated better wear resistance in SBF containing environment than the oxide layer formed in the base electrolyte. This is due to the decreased contribution of spallation to the development of wear under sliding contact.
- The morphological properties, hardness, surface roughness, and phase composition of the MAO coatings manufactured on Ti6Al4V alloy demonstrated an explicit dependency on the type of ceramic particle introduced to the electrolyte. The addition of Al_2O_3 and ZrO_2 particles in silicate-based electrolytes induced not only the absorption of these ceramic particles into the TiO_2 -based MAO coating but also the generation of their complex oxides (Al_2TiO_5 and ZrTiO_4 , respectively) alongside amorphous SiO_2 . The low wear resistance of the MAO-Al sample resulting from heavy spalling was associated

with the formation of the brittle complex oxide (Al_2TiO_5) in the composition of the MAO coating. Nevertheless, on the other side, ZrTiO_4 form complex oxide in the microstructure, as in the case of a spallation-free MAO-Zr sample, imposed much higher resistance to sliding wear at contact pressures greater than 1 GPa.

- The MAO coating on the 7075 aluminium alloy synthesized in the ZrO_2 -free electrolyte was monolithic and Al_2O_3 -based, but the MAO-Zr coating synthesized in the m- ZrO_2 containing electrolyte comprised of two distinct oxide layers as; the ZrO_2 particle (in the form of monoclinic and tetragonal) incorporated in the Al_2O_3 -based outer layer and the monolithic Al_2O_3 -based inner layer. From the mathematical calculations obtained from the results of the wear tests utilised at 300 °C, the maximum contact pressures which do not cause the removal of the coating until the 10^6 contact cycles were determined to be 331 and 851 MPa for the MAO and MAO-Zr coatings, respectively.
- Usage of the H-DLC coated counterface against MAO'ed AZ31 magnesium alloy lowered the COF during sliding action, and simultaneously, the wear loss was reduced due to the creation of carbonaceous transfer layers on the wear tracks. The COF of this tribosystem was stable, and after a steady-state friction regime had been achieved, the COF held steady at 0.13 till the end of the test. This was presumed that the use of H-DLC coated counterfaces against MAO coated magnesium alloys can expand the application of these alloys to tribological components where low friction and wear are required together with low weight.
- Sequential application of CS and MAO processes successfully formed hard and adherent alumina layer with an underlying aluminium (monolithic or composite) layer over AZ91D magnesium alloy. Compared to the MAO treated state of the AZ91D alloy, application of MAO after cold spraying of alumina reinforced aluminium matrix composite layer provided superior enhancement in both dry sliding tribological performance against alumina ball and corrosion resistance in 3.5 wt.% NaCl solution.

The recommendations for future works to be carried out on improving wear performance of MAO'ed light metals can be classified as follows:

- i) Modifying MAO coating with various additives to reduce COF
- ii) Increasing the hardness and strength of the substrate underneath the MAO coating
- iii) Applying post-treatment to the MAO coating to reduce COF

The wear performance of MAO coatings can be improved by reducing COF that occurred between MAO coating and sliding contact. Thus, some solid lubricants such as graphite, MoS_2 , $\text{h-B}_4\text{N}$ etc., can be added to the electrolytes used during the MAO process. These solid lubricants are known well for reducing COF because their layered structure can be incorporated into the MAO coating without jeopardizing the hardness of the coating. Apart from modifying the produced MAO coating, the wear performance of MAO coating, especially at high temperatures, can be enhanced by increasing the hardness and strength of the substrate. Under this scope, oxidation and nitration of titanium alloys provide higher hardness and strength for the surface of the alloy along with a thick diffusion layer. Thereupon, the MAO coating synthesised on oxidised or nitrided surfaces can employ better wear performance at high temperatures, where metallic substrate loses strength and hardness. Another approach for enhancing the wear performance of MAO'ed light metals can be applying post-treatment on fabricated MAO coating. Polymer-based lubricants such as polytetrafluoroethylene can be impregnated into the pores of MAO coating, and during sliding contact, they can effectively reduce COF and, therefore, the wear rate.



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