

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**WEAR BEHAVIOUR OF MULTILAYER COATED
WE43 MAGNESIUM ALLOY**



M.Sc. THESIS

Mertcan KABA

Department of Metallurgical and Materials Engineering

Materials Engineering Programme

JULY 2020

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**WEAR BEHAVIOUR OF MULTILAYER COATED
WE43 MAGNESIUM ALLOY**

M.Sc. THESIS

**Mertcan KABA
(506171417)**

Department of Metallurgical and Materials Engineering

Materials Engineering Programme

Thesis Advisor: Prof. Dr. Hüseyin ÇİMENÖĞLU
Thesis Co-Advisor: Prof. Dr. Uğur MALAYOĞLU

JULY 2020

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

**ÇOK KATMANLI KAPLANMIŞ WE43 MAGNEZYUM ALAŞIMININ
AŞINMA DAVRANIŞI**

YÜKSEK LİSANS TEZİ

**Mertcan KABA
(506171417)**

Metalurji ve Malzeme Mühendisliği Anabilim Dalı

Malzeme Mühendisliği Programı

**Tez Danışmanı: Prof. Dr. Hüseyin ÇİMENÖĞLU
Eş Danışman: Prof. Dr. Uğur MALAYOĞLU**

TEMMUZ 2020

Mertcan Kaba, a M.Sc. student of ITU Graduate School of Science Engineering and Technology student ID 506171417, successfully defended the thesis entitled “WEAR BEHAVIOUR OF MULTILAYER COATED WE43 MAGNESIUM ALLOY”, which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor:	Prof. Dr. Hüseyin ÇİMENÖĞLU Istanbul Technical University	
Co-advisor:	Prof. Dr. Uğur MALAYOĞLU Dokuz Eylul University	
Jury Members:	Prof. Dr. Murat BAYDOĞAN Istanbul Technical University	
	Prof. Dr. M. Lütfi ÖVEÇOĞLU Istanbul Technical University	
	Prof. Dr. Erdem ATAR Gebze Technical University	

Date of Submission : 15 June 2020
Date of Defense : 29 July 2020





To my family,



FOREWORD

First of all, I would like to express my sincere thanks to my supervisor Prof. Dr. Hüseyin ÇİMENÖĞLU not only for his guidance and support during this thesis but also for his valuable suggestions in my professional life. It is an honour to be his assistant for me. I also want to serve my special thanks to my co-supervisor Prof. Dr. Uğur MALAYOĞLU for his guidance and support from my bachelor studies to this thesis.

I would like to acknowledge the Mechanical Metallurgy Research group, especially Prof. Dr. Murat BAYDOĞAN, Lect. Faiz MUHAFFEL and Res. Assist. Doğukan ÇETİNER for their supports during my studies.

Lect. Faiz MUHAFFEL is specially acknowledged for his kind and precious helps during coating processes, experimental works and evaluation of the results. Also, I want to give may thanks to Dr. Kadir TEKİN for his support in performing corrosion tests and analysing the test results. I want to thank Dr. Sezgin CENGİZ for his support and different point of view. I would like to give my thanks to M.Sc. Mert ALTAY and M.Sc. Nurhan ERK for their helps during my thesis. Dr. Grzegorz Cempura is also acknowledged for SEM/EDS studies at AGH University of Science and Technology.

Additionally, I want to thank to İTÜ BAP office for the contribution to my thesis with a project number of MYL-2018-41253. On the other hand, I would like to acknowledge the TÜBİTAK and TEYDEB for the projects (217M275 and 5160013, respectively), which I participated in and financially supported me during my early master studies. I also specially acknowledge Doç. Dr. Birgül BENLİ for her guidance and support during TÜBİTAK project.

And the most importantly, I would like to express my gratitude to my brother and my parents for their presence and support in my entire life. Mr. Serhat AKTAŞ and Mr. Tugay TÜZÜN are also acknowledged for their valuable friendship and their patient during this study.

Also, I want to give my special thanks to Res. Assist. Mehtap ARSLAN for her kind support, patient and her valuable presence.

June 2020

Mertcan KABA
(Metallurgical and Materials Engineer)

TABLE OF CONTENTS

	<u>Page</u>
TABLE OF CONTENTS.....	xi
ABBREVIATIONS	xiii
LIST OF TABLES	xv
LIST OF FIGURES	xvii
SUMMARY	xix
ÖZET.....	xxi
1. INTRODUCTION.....	1
2. MAGNESIUM ALLOYS	3
2.1 Mg Alloys for High Temperature Applications	6
3. MICRO-ARC OXIDATION OF MAGNESIUM ALLOYS	11
3.1 Principles of MAO Process	11
3.2 Literature Review on MAO Coatings Formed on WE Series Mg Alloys.....	16
3.2.1 New approach to MAO of Mg alloys.....	21
4. EXPERIMENTAL STUDIES.....	25
4.1 Material and Coating Processes	25
4.1.1 Material	25
4.1.2 Cold spray coating	26
4.1.3 Micro-arc oxidation coating.....	29
4.2 Structural Characterization of the MAO Coatings	30
4.2.1 XRD analysis	30
4.2.2 SEM/EDS analysis	31
4.2.3 Micro-hardness measurements.....	31
4.3 Electrochemical Corrosion Tests	31
4.4 Wear Tests.....	32
5. RESULTS AND DISCUSSION	35
5.1 Structure of the MAO Coatings	35
5.1.1 MAO coating fabricated on the WE43 alloy	35
5.1.2 MAO coating fabricated on the CSed WE43 alloy	38
5.2 Electrochemical Corrosion Behaviour	42
5.3 Wear Behaviour.....	44
5.3.1 Effect of the testing load	45
5.3.2 Effect of the testing temperature	54
6. CONCLUSIONS	65
REFERENCES.....	67
CIRRICULUM VITAE	77

ABBREVIATIONS

ASTM	:	American Society for Testing and Materials
CS	:	Cold Spray
EDS	:	Energy Dispersive Spectroscopy
HV	:	Vickers Hardness
MAO	:	Micro-Arc Oxidation
OM	:	Optical Microscope
PEO	:	Plasma Electrolytic Oxidation
SEM	:	Scanning Electron Microscope
XRD	:	X-Ray Diffractometer



LIST OF TABLES

	<u>Page</u>
Table 2.1: Some of the important physical and mechanical properties of pure Mg ...	5
Table 3.1: Widely applied surface treatment techniques for Mg and its alloys	11
Table 3.2: Variation in the coating thickness and surface roughness with electrical parameters.	15
Table 3.3: Effect of the electrolyte composition on the phase structure of the MAO coatings	16
Table 3.4: Wear loss data calculated for the WE43 and MAO coated WE43 samples	20
Table 4.1: The chemical composition of the WE43 alloy	25
Table 4.2: Process parameters for WE43+MAO and WE43+CS+MAO samples....	30
Table 4.3: Process parameters for reciprocating ball-on-plate and unidirectional ball-on-disc wear tests.	33
Table 5.1: Results of the EDS analysis conducted in the Regions O and I of the cross-section of the WE43+MAO sample.....	38
Table 5.2: Results of the EDS analysis conducted in Region X of the cross-section of the WE43+CS+MAO sample.	41
Table 5.3: Results of the potentiodynamic polarization tests conducted on the examined samples in 3.5 wt. % NaCl solution.....	43
Table 5.4: Calculated specific wear rates and the max. depth of the wear tracks of the examined samples tested at 1 and 4 N.....	47
Table 5.5: Results of the contact stress and depth of the maximum shear stress calculations for the examined samples tested at 1 and 4 N.....	54
Table 5.6: Calculated specific wear rates of the examined samples tested at 25 °C, 250 °C, and 320 °C.	57



LIST OF FIGURES

	<u>Page</u>
Figure 2.1: Some components made of Mg alloys in automotive and aerospace industries.	4
Figure 2.2: Alloy development route.	6
Figure 2.3: Creep curves of the commercially available Mg alloys after testing at 150 °C under 50 MPa stresses.....	7
Figure 2.4: (a) Change in the yield strength of the Mg alloys with temperature and (b) creep strength of Mg alloys tested at 200 °C.....	8
Figure 2.5: Corrosion potentials of some Mg alloys in 3.5 wt. % NaCl media.	9
Figure 3.1: (a) Schematic illustration of MAO system and (b) electrolysis cell in aqueous electrolyte.....	12
Figure 3.2: Spark formation during MAO of Mg alloys.....	13
Figure 3.3: Voltage-time graph recorded during MAO process of a Mg alloy.	14
Figure 3.4: SEM images of the MAO coating produced on a Mg alloy taken from (a) surface and (b) cross-section.....	15
Figure 3.5: (a) Voltage-time graph recorded during MAO process and (b) surface and (c) cross-sectional SEM images of the MAO coating.....	17
Figure 3.6: (a) Polarization curves and cross-sectional SEM images of the (b) WE43 alloy and (c) MAO coating after corrosion tests.....	17
Figure 3.7: Cross-sectional SEM images of the MAO coating (a) before and (b) after corrosion tests.	19
Figure 3.8: Surface and cross-sectional SEM images of the multilayer coatings....	22
Figure 3.9: Cross-sectional SEM images of the multilayer coatings having different CS and MAO layer thicknesses.....	23
Figure 4.1: XRD pattern of the examined WE43 alloy.....	26
Figure 4.2: (a) OM and (b) SEM image taken from the WE43 alloy after etching. .	26
Figure 4.3: Commercial Dymet K-10-01 (Al+60 wt.% Al ₂ O ₃) powder mixing used in CS process.....	27
Figure 4.4: XRD pattern of the WE43+CS sample.....	28
Figure 4.5: (a) Cross-sectional SEM image of the WE43+CS sample and (b) high magnification SEM image taken from the region B shown in (a).	28
Figure 4.6: Results of the EDS analysis conducted on the (a) Al matrix, (b) alumina particles and (c) bright particles (Stainless steel) at the BSE-SEM image of the WE43+CS sample sown in Figure 4.5b.	29
Figure 4.7: MAO unit and an example for spark formation on the sample during process.	30
Figure 4.8: Standard three electrode corrosion flat cell setup used in this study for polarization tests.....	32
Figure 5.1: XRD pattern of the WE43+MAO sample.	35
Figure 5.2: SEM images taken from the (a,b) surface and (c,d) cross-section of the WE43+MAO sample.....	36
Figure 5.3: Coating structure and discharge types formed after MAO process on Mg alloy.	37

Figure 5.4: Elemental mapping analysis of the WE43+MAO sample showing the presence of Mg, O, Na, Al and Zr.	37
Figure 5.5: XRD pattern of the WE43+CS+MAO sample.	39
Figure 5.6: SEM images taken from the (a,b) surface and (c,d) cross-section of the WE43+CS+MAO sample.	40
Figure 5.7: Elemental mapping analysis of the WE43+CS+MAO sample showing the presence of Al, O, Fe, Cr and Mg.	41
Figure 5.8: Potentiodynamic polarization curves for the examined samples tested in 3.5 wt. % NaCl solution.	43
Figure 5.9: Friction curves of the examined samples tested at the load of (a) 1 N and (b) 4 N.	45
Figure 5.10: 2-D profiles taken from the wear tracks of the examined samples tested at the load of (a) 1 N and (b) 4 N.	46
Figure 5.11: Worn surface SEM images of the examined samples tested at the load of 1 N.	48
Figure 5.12: OM images of the wear scars formed on the alumina ball counterfaces used in wear testing of the examined samples at a load of 1 N.	49
Figure 5.13: Worn surface SEM images of the examined samples tested at the load of 4 N.	52
Figure 5.14: OM images of the wear scars formed on the alumina ball counterfaces used in wear testing of the examined samples at a load of 4 N.	53
Figure 5.15: Friction curves of the samples tested at (a) 25 °C, (b) 250 °C, and (c) 320 °C.	55
Figure 5.16: 2-D profiles taken from the wear tracks of the examined samples tested at (a) 25 °C, (b) 250 °C, and (c) 320 °C.	56
Figure 5.17: BSE-SEM images taken from the worn surface of the WE43 sample after wear testing at 25 °C, 250 °C, and 320 °C.	59
Figure 5.18: Worn surface SEM images of the WE43+CS sample tested at the temperature of 25 °C, 250 °C, and 320 °C.	61
Figure 5.19: Worn surface SEM images of the WE43+MAO sample tested at the temperature of 25 °C and 250 °C.	62
Figure 5.20: Worn surface SEM images of the WE43+CS+MAO sample tested at the temperature of 25 °C, 250 °C, and 320 °C.	63

WEAR BEHAVIOUR OF MULTILAYER COATED WE43 MAGNESIUM ALLOY

SUMMARY

Perspective on decreasing the weight of the components in order to reduce CO₂ emission has led the manufacturers in automotive and aerospace industries to consider the application of magnesium alloys owing to their high specific strength (strength to weight ratio). However, the limited strength of the magnesium alloys, especially above 120 °C, restricts their extensive usage. For this reason, instead of widely-used aluminium and zinc containing alloys such as AZ31 and AZ91, WE series magnesium alloys containing yttrium and rare earth elements have been developed for high temperature application up to 300 °C. Considering its high temperature and creep resistances, WE series alloys are attractive for aerospace and automotive industries. However, similar to the most widely used ones, this new alloy also suffers from poor wear and corrosion resistance due to low hardness and high surface reactivity. Therefore, in order to enhance wear and corrosion resistance of WE series alloys, modification of the surfaces by various techniques appears as an essential technical solution.

In this respect, micro-arc oxidation (MAO) process, which forms magnesium oxide-based coatings, has been successfully employed on many commercially available grades of magnesium alloys. In the open literature, a few numbers of MAO studies have been conducted on the WE series alloys with the aim of improving the corrosion resistance. To the author's best knowledge, only one study is available in the open literature stating improvement in room temperature wear resistance of WE43 alloy by MAO process, which formed a coating consisting of magnesium oxide and magnesium silicate. However, magnesium oxide-based coatings did not provide sufficient protection against corrosion and wear due to their lower hardness and poor compactness. From this point of view, higher hardness of aluminium oxide (alumina) as compared to magnesium oxide motivated some researchers to fabricate multilayer coatings on magnesium alloys by applying cold spray and MAO processes sequentially. Thus, after the coating of magnesium alloys with aluminium or aluminium matrix composites by cold spray technique, MAO process has been employed to form aluminium oxide-based coatings at the outermost surface. The multilayer coating composed of alumina and aluminium or aluminium matrix composite layer exhibited superior wear and corrosion resistance than that of monolayer magnesium oxide-based coating.

In the scope of this study, which was initiated mainly with the aim of improving high temperature wear resistance, multilayer (aluminium matrix composite/alumina) coating was fabricated on the WE43 magnesium alloy by subsequently applying CS and MAO process. While commercially available alumina particle reinforced aluminium matrix powder was used in the cold spray process, MAO processes were conducted in an aluminate-based electrolyte. In order to compare the properties of multilayer coating with monolayer magnesium oxide coating, WE43 alloy was also subjected to the MAO process. Structural characterization of the fabricated coatings was done by using

an optical microscope, energy dispersive spectroscopy equipped scanning electron microscope, and a X-ray diffractometer. Additionally, hardness measurements were conducted on the cross-section of the fabricated coatings by Vickers indenter. Corrosion behaviour of the coatings was also investigated by performing electrochemical polarization tests in 3.5 wt. % sodium chloride (NaCl) media. After electrochemical polarization tests, corrosion potential and current densities of the examined samples along with the polarization resistance were calculated using the Tafel extrapolation method.

Furthermore, the wear behaviour of the examined samples was determined by dry sliding wear tests via using tribometer with two different configurations against alumina ball counterface. Firstly, the effect of the testing load on the wear behaviour was investigated by reciprocating tribometer in the ball-on-flat configuration under the testing load of 1 and 4 N. Then the influence of the testing temperature was also examined by high temperature tribometer in the ball-on-disc configuration at 25 °C, 250 °C, and 320 °C. After wear tests, wear tracks formed on the contact surfaces of the examined samples were investigated by 2-D surface profilometer. Worn surface of the samples was also examined by SEM to determine the operative wear mechanisms.

Structural examinations revealed that the outermost surface of the multilayer coating consisted of alpha and gamma alumina while monolayer coating composed of magnesium oxide and magnesium aluminate with an average hardness of 1129 HV_{0.025} and 311 HV_{0.025}, respectively. It should be noted that porous nature of the monolayer magnesium oxide coating plays a critical role in its low hardness. Results of the wear tests showed that hard multilayer coating exhibited remarkably better wear resistance than that of monolayer magnesium oxide coating both at room and high temperatures. Furthermore, the multilayer coating exhibited better durability at high temperatures and high loads, so that it was possible to detect the protective nature of the multilayer coating at 320 °C under 2 N and at room temperature under 4 N. However, monolayer magnesium oxide layer completely removed from the contact surface during testing at 250 °C under 2 N and at room temperature under 4 N. In addition, electrochemical corrosion tests conducted in 3.5 wt. % NaCl revealed much higher corrosion resistance of the multilayer coating as compared to monolayer magnesium oxide coating.

ÇOK KATMANLI KAPLANMIŞ WE43 MAGNEZYUM ALAŞIMININ AŞINMA DAVRANIŞI

ÖZET

Magnezyum alaşımları hafifliği ve yüksek özgül mukavemeti nedeniyle uzay, havacılık ve otomotiv sektörü için cazip mühendislik malzemelerinden biridir. Mg alaşımları otomotiv ve havacılık sektörlerinde kullanımları sırasında yaklaşık olarak 150-320°C aralığında sıcaklığa maruz kalmaktadır. Yaygın olarak kullanılan ve alüminyum ve çinko içeren AZ serisi magnezyum alaşımları 120 °C üzerindeki sıcaklıklarda mukavemetini koruyamadığı için itriyum ve nadir toprak elementlerinin eklenmesiyle 300 °C ye kadar mukavemetini koruyan WE serisi magnezyum alaşımları geliştirilmiştir. Ancak yüksek yüzey aktivitesi, kararsız kimyasal özellikleri ve düşük sertliği geliştirilen bu alaşımların korozyon ve aşınma direncini düşürerek kullanımını sınırlandırmaktadır. Yüksek sıcaklıklarda yüksek mukavemet ve sürünme direnci gerektiren uygulamalarda kullanılması planlanan WE serisi alaşımların korozyon ve aşınma direncinin geliştirilmesi amacıyla yüzeylerinin sertliğini ve kararlılığını arttırmak için yüzey modifikasyon işlemlerinden geçmesi gerekmektedir.

Yüzeyde oksit esaslı sert seramik kaplama oluşturan mikro-ark oksidasyon (MAO) yöntemi çevre dostu olması ve altlık üzerinde herhangi bir olumsuz etkiye neden olmaması nedeniyle hafif metaller (alüminyum, magnezyum ve titanyum) için çekici bir yöntem olarak öne çıkmaktadır. Literatürde WE serisi alaşımların MAO yöntemi ile magnezyum oksit esaslı seramik kaplanması üzerine birkaç çalışma yer almaktadır. Bu çalışmalar özellikle WE serisi Mg alaşımlarının korozyon direncinin geliştirilmesine ve biyolojik uygulamalarda kullanımının artırılması üzerine odaklanırken, aşınma direncinin geliştirilmesi üzerine yapılan çalışmalar az sayıdadır. WE serisi alaşımlar üzerinde oluşturulan MAO kaplamaların yüksek sıcaklıklardaki aşınma davranışı ise daha önce çalışılmamıştır. Ayrıca, MAO yöntemi ile oluşturulan magnezyum oksit esaslı kaplamalar aşınma ve korozyona karşı düşük sertlikleri ve sıkıştırılabilirlikleri nedeniyle sınırlı koruma sağlamaktadır. Bu doğrultuda birkaç araştırmacı magnezyum alaşımları üzerinde soğuk sprej (cold spray, CS) ve MAO yönteminin birlikte uygulanmasıyla en üst katmanda yüksek sertliğe sahip alüminyum oksit (alümina) altta ise monolitik alüminyum ya da alüminyum matrisli kompozitten oluşan çok katmanlı kaplama üretimi üzerinde çalışmıştır. Geliştirilen bu çok katmanlı kaplamanın magnezyum oksit esaslı monolitik kaplamalara kıyasla çok daha üstün aşınma ve korozyon direnci kazandırdığı literatürde belirtilmiştir.

Bu çalışma kapsamında WE43 magnezyum alaşımının özellikle yüksek sıcaklıklardaki aşınma direncinin artırılması amacıyla soğuk sprej ve MAO yönteminin birbirini takip eden şekilde uygulanmasıyla yüzeyde çok katmanlı alüminyum oksit esaslı kaplama üretilmiştir. “Çok katmanlı” kaplamanın üretiminde ilk olarak alümina parçacık takviyeli alüminyum matrisli kompozit tozlar WE43 alaşımı üzerine soğuk sprej yöntemiyle kaplanmış. Ardından elde edilen CS kaplama tabakası üzerinde alüminat esaslı elektrolit içerisinde MAO yöntemiyle alüminyum oksit kaplama tabakası üretilmiştir.

Ayrıca referans olarak WE43 alaşımı da MAO yöntemiyle kaplanarak “tek katmanlı” magnezyum oksit esaslı kaplama elde edilmiştir.

Elde edilen kaplamaların yapısal karakterizasyonu optik mikroskop, enerji dağılım spektroskopisi donanımlı taramalı elektron mikroskobu ve X-ışını difraktometresi yardımıyla gerçekleştirilmiştir. Ek olarak, kaplanmış malzemelerin kesitlerinden Vickers batıcı uç kullanılarak sertlik ölçümleri yapılmıştır. Çok katmanlı ve monolitik MAO kaplamaların korozyon davranışlarının incelenmesi amacıyla ağ. % 3.5 sodyum klorür (NaCl) çözeltisi içerisinde elektrokimyasal polarizasyon testleri uygulanmıştır. Elektrokimyasal polarizasyon testleri sonucunda elde edilen eğrilerden Tafel ekstrapolasyon yöntemi yardımıyla numunelerin korozyon potansiyelleri, korozyon akım yoğunlukları, anodik ve katodik Tafel sabitleri hesaplanmıştır. Ayrıca korozyon dirençlerini sayısal olarak ifade edebilmek için numunelerin polarizasyon dirençleri de hesaplanmıştır.

Kaplamaların aşınma davranışlarının belirlenmesi amacıyla iki farklı konfigürasyonda tribometre kullanılarak kuru ortamda alümina bilyaya karşı kayma aşınması testleri gerçekleştirilmiştir. İlk olarak, ileri-geri salınımlı düz yüzeyde sürtünen bilya (ball-on-flat) konfigürasyonuna sahip aşınma cihazı kullanılarak oda sıcaklığında 1 N ve 4 N yük altında testler gerçekleştirilip test yükünün numunelerin aşınma davranışlarına etkisi incelenmiştir. Tek yönlü çalışan disk üzerinde sürtünen bilya (ball-on-disc) konfigürasyonuna sahip yüksek sıcaklık aşınma test cihazı kullanılarak da 2 N yük altında 25 °C, 250 °C ve 320 °C sıcaklıklarda testler yapıp test sıcaklığının aşınma davranışlarına etkisi belirlenmiştir. Aşınma testlerinin ardından yüzeyde oluşan aşınma izleri 2-D temaslı yüzey profilometresi yardımıyla incelenerek aşınma kayıpları hesaplanmıştır. Ayrıca, aşınma mekanizmalarının belirlenmesi amacıyla aşınan yüzeyler taramalı elektron mikroskobu kullanılarak incelenmiştir. Ek olarak, aşınma testlerinde kullanılan bilyaların temas yüzeyleri de optik mikroskopta incelenmiştir.

Yapısal incelemeler sonucunda elde edilen çok katmanlı kaplamanın üst yüzeyinde alfa ve gama fazları halinde alüminyum oksitin bulunduğu tespit edilmiştir. WE43 alaşımı üzerinde oluşturulan tek katmanlı MAO kaplamanın içeriğinde ise magnezyum oksit ve magnezyum alüminat bulunmaktadır. Kaplamaların kesitleri incelendiğinde altlık malzemeye iyi bağlanma gösterdikleri belirlenmiştir. Çok katmanlı alümina esaslı kaplamanın sertliği kesitten ortalama 1129 HV_{0.025} seviyesinde ölçülürken tek katmanlı magnezyum oksit esaslı kaplamanın sertliği ise ortalama 311 HV_{0.025} mertebesinde. Magnezyum oksitin alüminyum oksite göre düşük sertliğinin yanı sıra tek katmanlı magnezyum oksit kaplamanın daha poröz yapıda olmasının düşük sertliğe neden olduğu düşünülmektedir.

Aşınma test sonuçlarına göre, çok katmanlı sert alüminyum oksit esaslı kaplamanın hem oda sıcaklığında hem de yüksek sıcaklıklarda tek katmanlı poröz magnezyum oksit esaslı kaplamaya kıyasla daha yüksek aşınma direncine sahip olduğu belirlenmiştir. Ayrıca, çok katmanlı kaplama hem 2 N yük altında 320 °C sıcaklığa kadar hem de oda sıcaklığında 4 N yüke kadar yapısal bütünlüğünü korurken tek katmanlı magnezyum oksit esaslı kaplama 2 N yük altında 250 °C sıcaklıkta ve oda sıcaklığında 4 N yük altında aşırı hasara uğrayıp yüzeyden ayrılmaktadır. Çok katmanlı alüminyum oksit kaplamanın sert ve yoğun yapısının, daha poröz olan düşük sertliğe sahip tek katmanlı magnezyum oksite göre daha iyi aşınma direnci sağladığı sonucuna varılmıştır.

Diğer taraftan, yapılan elektrokimyasal polarizasyon testlerinin sonuçlarına göre magnezyum oksitten daha yüksek kararlılığa sahip olan (sıkıştırılabilirliği yüksek) alümin-

yum oksit içeren çok katmanlı kaplamanın en iyi korozyon direnci gösterdiği belirlenmiştir. Aynı şekilde altlık malzemenin korozyon direnci magnezyum oksit esaslı tek katmanlı kaplama yardımıyla geliştirilse de magnezyum oksidin poröz yapısı nedeniyle korozyona karşı istenen koruma elde edilememiştir. Bu sonuçlar ışığında WE43 alaşımı üzerinde alümina esaslı çok katmanlı kaplama üretilmesi ile korozyon direncinin yanı sıra hem oda sıcaklığında hem de yüksek sıcaklıklarda aşınma direncinde kayda değer artış elde edilmiştir. Soğuk spreyci yöntemi ile oluşturulan alüminyum matrisli kompozit katmana alüminadan farklı seramik parçacıkların (zirkonya vb.) takviye edilmesinin çok katmanlı kaplamaların özelliklerini bir üst seviyeye taşıyabileceği düşünülmektedir. Ayrıca daha üstün aşınma direncinin MAO kaplama sırasında kullanılan elektrolite parçacık (zirkonya vb.) takviyesi ile de elde edilebileceği öngörülmektedir. Elde edilen çok katmanlı kaplamaya çeşitli takviyelerin yapılarak aşınma davranışının incelenmesinin de ileriki çalışmalar için önemli bir motivasyon kaynağı olabileceği değerlendirilmiştir.





1. INTRODUCTION

Magnesium (Mg) and its alloys, which have the lowest density among the other structural metals (steel and aluminium), have paid significant attention to be applied in automotive and aerospace industries in the light of lowering components to reduce CO₂ emission as an environmental-friendly approach. In addition to their high specific strength, Mg alloys have remarkable advantageous such as good castability and high recyclability [1,2]. For the case of the automotive industry, aluminium, zinc, and/or manganese containing AZ and AM series Mg alloys have been commonly used in the production of many components. However, poor mechanical properties of these alloys at high temperatures (>120 °C) restrict their extensive usage for components subjected to 147 °C and 327 °C, such as support parts near the air-craft engines and pistons of the engine blocks in the racing car [3,4]. Therefore, yttrium and rare earth elements containing WE series Mg alloys were developed to overcome this challenge due to their high creep resistance up to 300 °C.

Although mechanical properties (i.e, creep resistance) of the WE series alloys are sufficient for the high temperature applications, their high surface reactivity and low hardness make WE series alloys prone to corrosion and wear similar to other commercially available Mg alloys. Considering WE series Mg alloys to be used in aerospace and automotive industries, their surfaces should be modified to enhance wear and corrosion resistance by several surface treatments. In this respect, micro-arc oxidation (MAO) process, also called as plasma electrolytic oxidation (PEO), is the most attractive and environmentally friendly technique to produce oxide-based ceramic coatings having high hardness on the surface of light metals (Al, Mg, and Ti) without any destructive effects on the substrate [5–7]. In the open literature, a limited number of studies investigating the properties of the MAO coatings produced on the WE series Mg alloys were reported [8–11]. Although these studies mainly focused on the improvement in corrosion resistance of MAO coating produced on WE series alloys, their wear behaviour was only examined by Malayoğlu et al. [11]. However, wear resistance of

the MAO coated WE series alloys at high temperature was not determined in the open literature to the best of the author's knowledge.

On the other hand, these coatings provided limited protection against corrosion and wear due to the lower hardness and lower compactness of the magnesium oxide [12,13]. Further improvement in wear and corrosion resistance can be achieved by producing aluminium oxide on the Mg alloys' surface. In this respect, some researchers, which dealt with the application of thermal spray processes on AZ series alloys, reported that the corrosion and wear resistance of the substrates were successfully enhanced [14,15]. However, the application of the thermal spray on the Mg alloys was restricted due to its detrimental effects such as the generation of excessive heat input on the substrate. Thus, a novel approach to produce aluminium oxide (alumina) layer on the surface of Mg alloys was introduced as the combined application of cold spray (CS) with the MAO process [16,17]. Researchers, who developed multilayer coating on AZ series Mg alloys, reported remarkable improvement in the wear and corrosion resistance of the substrate compared to monolayer coatings. Nevertheless, wear behaviour of these multilayer coatings on any Mg alloys at high temperatures was not studied yet.

This study mainly focused on improving wear resistance of the WE43 alloy at high temperatures by producing alumina containing multilayer coating via subsequently applying CS and MAO process. As a reference, MAO process also was performed on WE43 alloy to fabricate monolayer coating consisting of magnesium oxide. Corrosion behaviour of the coatings was examined by conducting electrochemical polarization tests in 3.5 wt. % sodium chloride (NaCl) media. Moreover, the effects of the testing load and temperature on the wear behaviour of the examined samples were determined by dry sliding wear tests against alumina ball counterface.

2. MAGNESIUM ALLOYS

Magnesium (Mg) and its alloys have gained significant attention in automotive and aerospace industries, especially for decreasing the weight in many components as an environmental-friendly approach to reduce CO₂ and NO_x emission. Besides having the lowest density ($\sim 1.7 \text{ g/cm}^3$) among the other structural metals, the advantages putting forward to Mg and its alloys are listed below [1,18–20];

- High strength to weight ratio (specific strength),
- Better castability arising from its less susceptibility to hydrogen porosity and good fluidity,
- Good damping capacity,
- Good weldability and machinability
- High recycling ability.

Despite their advantages, the usage of Mg and its alloys has been restricted by some disadvantageous properties such as high surface reactivity resulting in low corrosion resistance, poor cold formability, and limited strength at elevated temperature [1,3,21].

Besides their usage in 3C industries (computer, communication, and consumer products), Mg alloys have taken a significant part in transportation industries (automotive and aerospace) thanks to their desirable properties. Application of Mg alloys in the automotive industry mainly covers transfer case, instrument-panel beam, steering parts, gearbox housing, and engine block components. On the other hand, transmission casing, gearbox parts, auxiliary casing, and tray components are also manufactured

from Mg alloys in the aerospace industry [2,19,21]. Figure 2.1 presents various components made of Mg alloys for transportation industries.

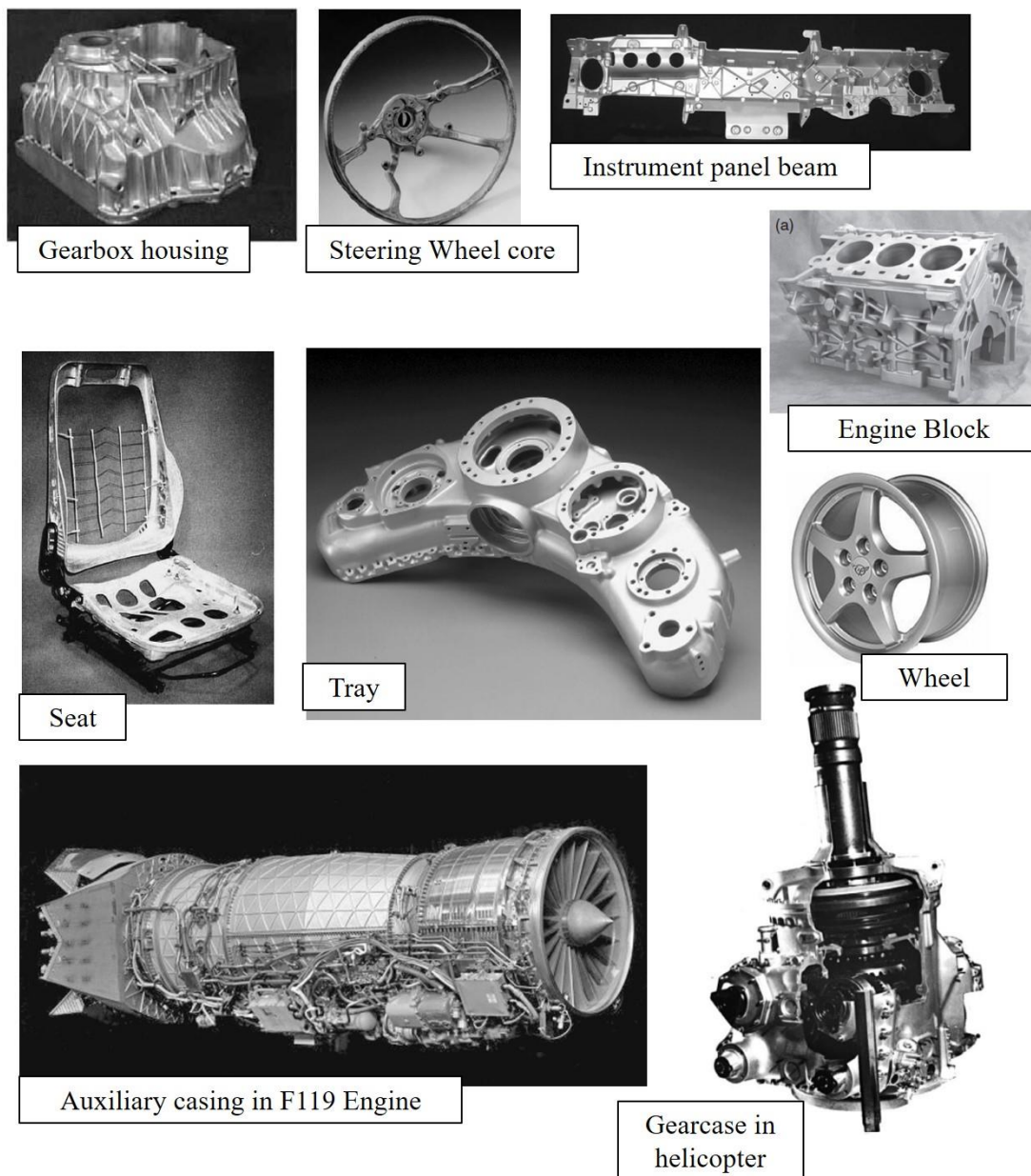


Figure 2.1: Some components made of Mg alloys in automotive and aerospace industries [2,19,22].

The physical and mechanical properties of the pure Mg is given in Table 2.1. Mg exhibits a hexagonal closed packed (HCP) crystal structure, which results in poor cold forming ability, and has the atomic diameter of 0.32 nm. The atomic size of the Mg offers an opportunity to form a solid solution with a wide range of elements having an acceptable difference in atomic size ($\pm 15\%$, according to the Hume-Rothery rules). In

this regard, many alloying elements can be used to develop several Mg alloys with enhanced properties such as high strength and creep resistance [2,22,23].

Table 2.1: Some of the important physical and mechanical properties of pure Mg [18].

Property	Value
Density (g/cm ³)	1.738
Melting Temperature (T _m , °C)	650
Heat Conductivity (W/mK)	156 (RT)
Linear Expansion Coefficient (K ⁻¹)	26×10 ⁻⁶ (RT)
Specific Electrical Conductivity (m/Ωmm ⁻²)	22.4 (RT)
Young Modulus (E, GPa)	45
Ultimate Tensile Stress (UTS, MPa)	80-180
Fracture Elongation (%)	1-12

Before mentioning the influence of the alloying elements on the properties of Mg, a universally accepted alloy designation system introduced by the American Society for Testing and Materials (ASTM) is presented in Table 2.2. According to this system, the first two letters (shown in Table 2.2) designate two major alloying elements, while two numbers following the letters indicate the average chemical composition in wt. %, for example, WE43 alloy consists of 4 wt.% yttrium (Y) and 3 wt.% rare earth (RE) elements [24].

Table 2.2: Alloy designation system introduced by ASTM [24].

Element	Designation	Element	Designation
Aluminium (Al)	A	Lithium (Li)	L
Copper (Cu)	C	Manganese (Mn)	M
Cadmium (Cd)	D	Silver (Ag)	Q
Rare earth (RE)	E	Chromium (Cr)	R
Iron (Fe)	F	Silicon (Si)	S
Thorium (Th)	H	Gadolinium (Gd)	V
Strontium (Sr)	J	Yttrium (Y)	W
Zirconium (Zr)	K	Zinc (Zn)	Z

With the aim of meeting the automotive and aerospace industries demands, different routes have been followed to develop a cast or wrought Mg alloy having high specific

strength, ductility and creep resistance [1], as shown in Figure 2.2. In this respect; some alloying elements, which are Al, Zn, Ca, Ag, cerium (Ce), gallium (Ga), nickel (Ni), Cu and Th, have been used for increasing strength and ductility while Sr, Mn, Y, and REs promote significant improvement in creep resistance. Since the formability of the Mg at ambient temperature is very limited, a certain amount of Li addition increases both ductility and cold formability. On the other hand, corrosion resistance of the Mg has been enhanced by alloying with Al, Ca, Sr, and RE elements [23].

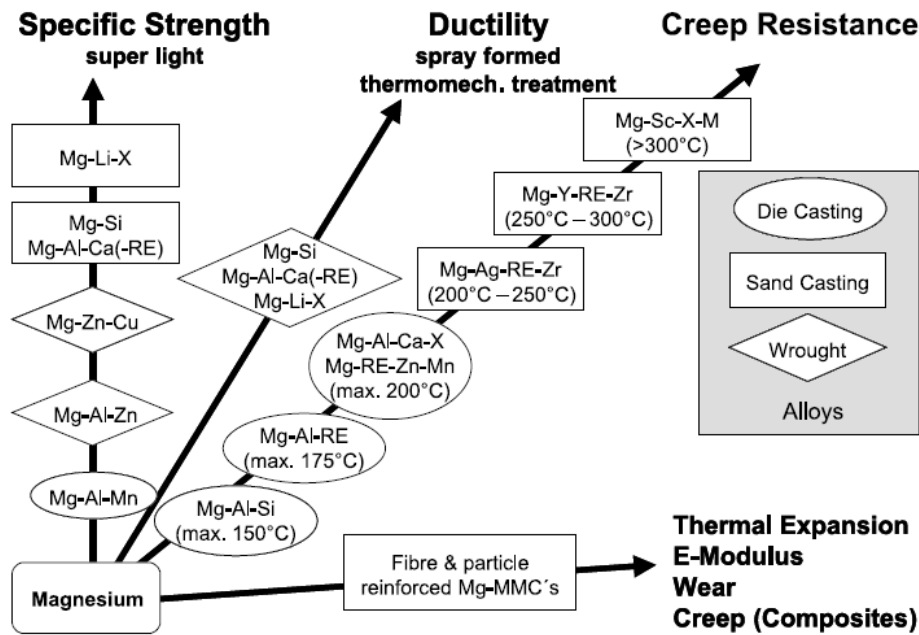


Figure 2.2: Alloy development route [2].

Although the most common Mg alloys used in the automotive industry is Al and Zn alloyed AZ series such as AZ91, their stability at the temperature in engine and transmission applications, hinders the usage of these alloys [3]. The demand for high temperature applications, where the components are subjected to 147 °C and 327 °C such as support parts near the aircraft engines and pistons of the engine blocks in the racing car [4], leads to the development of high creep resistance Mg alloys as shown in Figure 2.2.

2.1 Mg Alloys for High Temperature Applications

Although their limited slip systems restrict plastic deformation of Mg and its alloys at room temperature, increment in temperature leads additional slip systems to become activated. Due to these additional systems, Mg and its alloys have fairly low strength

at high temperatures and low melting points, resulting in low creep resistance. As mentioned in the above section, several attempts have been made by adding Zn, Mn, Si, Sr and REs to commonly used Mg-Al system in order to extend their limited usage in high temperature applications arising from its poor thermal stability ($>120\text{ }^{\circ}\text{C}$). The creep behaviour of the developed AZ91, AM (Mg-Al-Mn), AS (Mg-Al-Si), and AE (Mg-Al-Re) series alloys under a stress of 50 MPa at $150\text{ }^{\circ}\text{C}$ is given in Figure 2.3. While the developed alloys provide an improvement in creep resistance compared to the common AZ91 alloy, their properties are still far behind the aluminium alloys. Thus, new binary and ternary alloy systems have been developed by using RE elements such as Ce, La, Y, Gd, and Nd. In addition to REs, Ag, and Zn are also preferred as principal alloying elements for high temperature application [22].

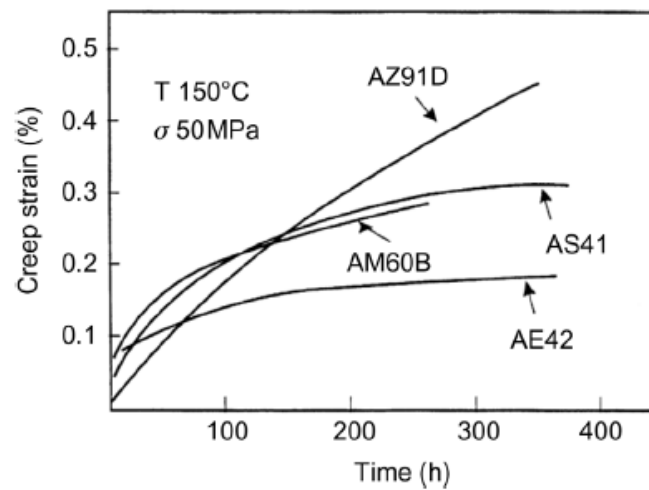


Figure 2.3: Creep curves of the commercially available Mg alloys after testing at $150\text{ }^{\circ}\text{C}$ under 50 MPa stresses [22].

In Figure 2.4, the dependence of the yield strength of various Mg alloys on temperature (Figure 2.4a) and their creep strength at $200\text{ }^{\circ}\text{C}$ (Figure 2.4b) are depicted. WE (Mg-Y-RE) series alloys exhibit higher strength up to $250\text{ }^{\circ}\text{C}$ - $300\text{ }^{\circ}\text{C}$ and higher creep resistance as compared to other series such as QE (Mg-Ag-RE), ZK (Mg-Zn-Zr), and EZ (Mg-RE-Zn). On the other hand, new alloy systems have continuously developed to obtain higher creep strength above $300\text{ }^{\circ}\text{C}$, for example, Mg-Gd and Mg-Sc systems. However, the higher costs of Gd and Sc restrict their usage in aerospace applications [22].

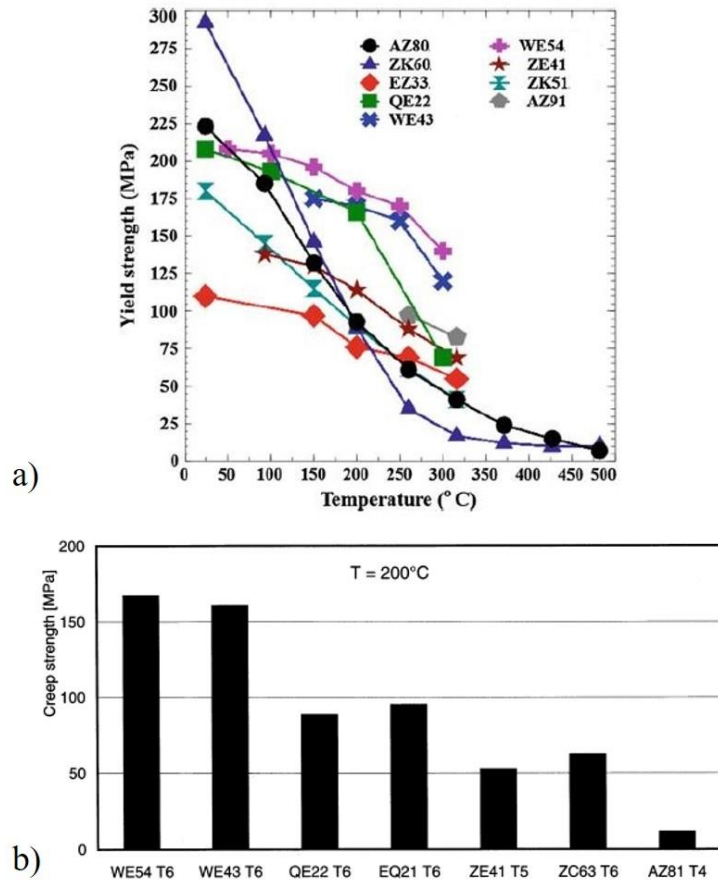


Figure 2.4: (a) Change in the yield strength of the Mg alloys with temperature [20] and (b) creep strength of Mg alloys tested at 200 °C [25].

Due to significant solute solution strengthening contribution of Y and thermally stable Mg-Y-RE precipitates, WE series alloys step forward with high strength and creep resistance up to 300 °C in addition to their good castability [4,26].

However, Mg alloys suffer from their poor corrosion resistance due to high reactivity and lack of protective film on their surface. Moreover, WE series alloys have the lowest corrosion potential among the others (Figure 2.5), making them the most active Mg alloy in sodium chloride media [27,28].

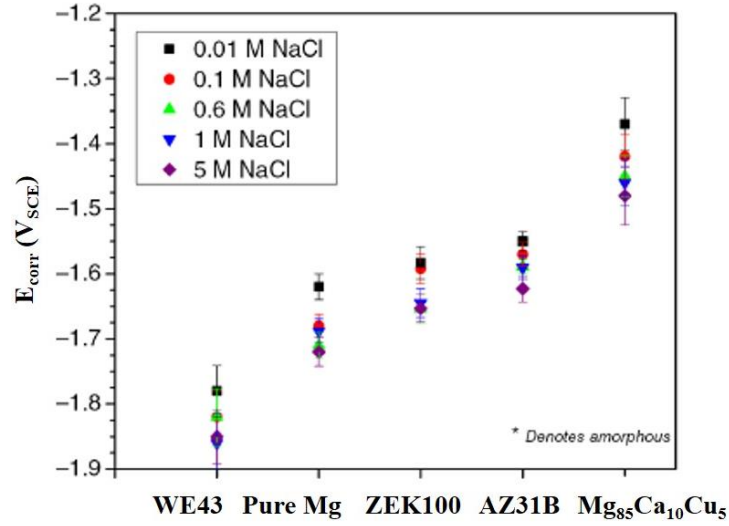


Figure 2.5: Corrosion potentials of some Mg alloys in 3.5 wt. % NaCl media [27].

On the other hand, surface deterioration by mechanical effects, namely wear, is one of the most concerning issues limiting the application of Mg and its alloys. Since Mg alloys are subjected to sliding contacts during working in engine parts or brake systems, their resistance against wear, especially at high temperatures, should be improved in order to enhance the service life of the components [29–34].

In the scope of improving corrosion and wear resistance of the Mg alloys, several surface modification/coating techniques have been employed to increase surface hardness and electrochemical stability of the Mg alloys. In this regard, micro-arc oxidation process, which is also referred as plasma electrolytic oxidation, has gained significant attention as a relatively novel coating process [35,36].



3. MICRO-ARC OXIDATION OF MAGNESIUM ALLOYS

3.1 Principles of MAO Process

The usage of Mg alloys in the automotive and aerospace industries is restricted by their insufficient corrosion and wear resistance arising from their high electrochemical activity and low mechanical strength at both room and elevated temperature. In this respect, many surface treatments, which are mainly classified as dry and wet techniques (Table 3.1), have been employed to Mg alloys to enhance their surface properties. Among the other techniques, micro-arc oxidation (MAO) is an attractive method to produce hard ceramic coatings on Mg and its alloys in an environmentally friendly and inexpensive way [5,7,37–41].

Table 3.1: Widely applied surface treatment techniques for Mg and its alloys [39].

Dry Techniques	Wet Techniques
Spray Coatings; thermal spray and cold spray	Electroplating
Laser surface cladding	Electroless plating
Physical vapour deposition (PVD)	Anodizing
Chemical vapour deposition (CVD)	Micro-Arc Oxidation (MAO)
	Sol-gel coating (silica, ceria)

As compared to other surface treatment techniques, MAO has several advantages over them, which are listed as follows.

- High metallurgical bonding between the oxide layer and metal substrate,
- No detrimental effect on the substrate mechanical properties due to negligible heat input,
- Possible to be employed on parts having a complex shape,
- Low cost and no necessity of vacuum or gas atmosphere,
- No hazardous effect on the environment due to the usage of alkaline electrolytes rather than acid-based solutions.

In MAO process, high electrical voltage (> 120 V) applied to the metallic sample, which is immersed in stainless steel tank full of an aqueous electrolyte (alkaline), triggers the formation of plasma discharge at the sample surface/electrolyte interface and results in thick and porous oxide based ceramic coatings on the surface. Generated plasma discharge leads the surface of the sample to be subjected to high instantaneous localized temperature and pressure. When electrical energy is applied, the sample acts as an anode while the stainless steel tank full of an electrolyte acts as a counter electrode (cathode). Schematic illustration of the MAO system and electrode processes that occurred during electrolysis in an aqueous electrolyte are presented in Figure 3.1 [5,37].

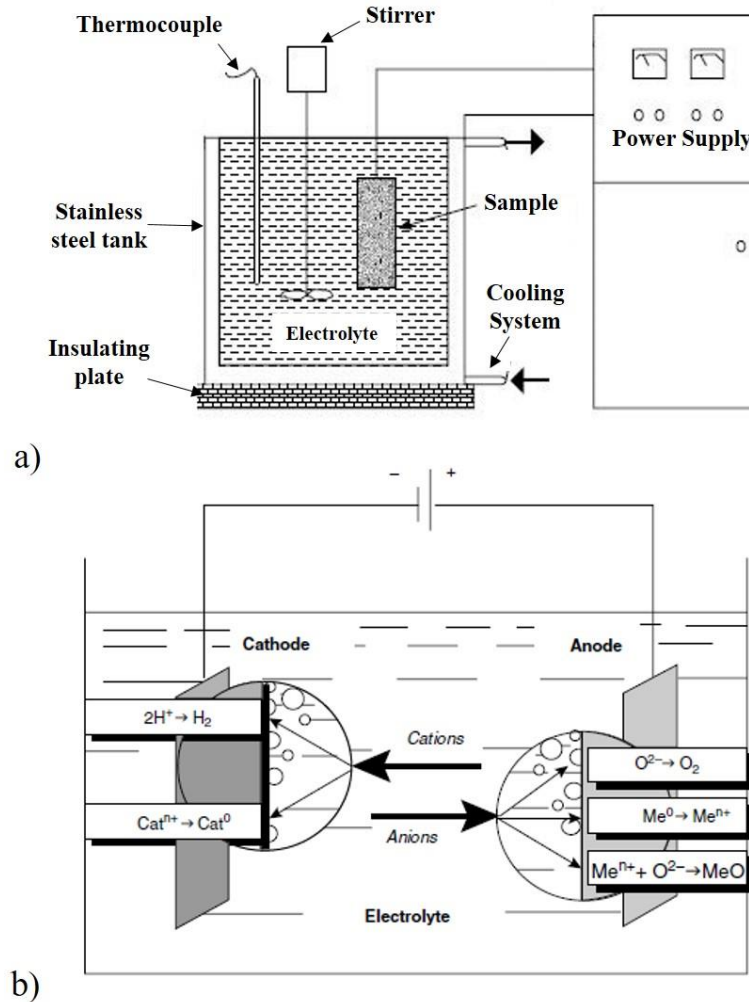


Figure 3.1: (a) Schematic illustration of MAO system [5] and (b) electrolysis cell in aqueous electrolyte [37].

During electrolysis in aqueous electrolytes, the liberation of oxygen in the gaseous state and/or oxidation of metal occurs on the surface of the anode (sample). When the

applied voltage is high enough to exceed dielectric breakdown, where the passive film is partly broken, micro discharges causing the formation of an oxide layer on the metal surface occur in MAO process. The appearance of micro-arc discharge on the surface of the Mg alloy as a function of processing time during the MAO process is given in Figure 3.2.

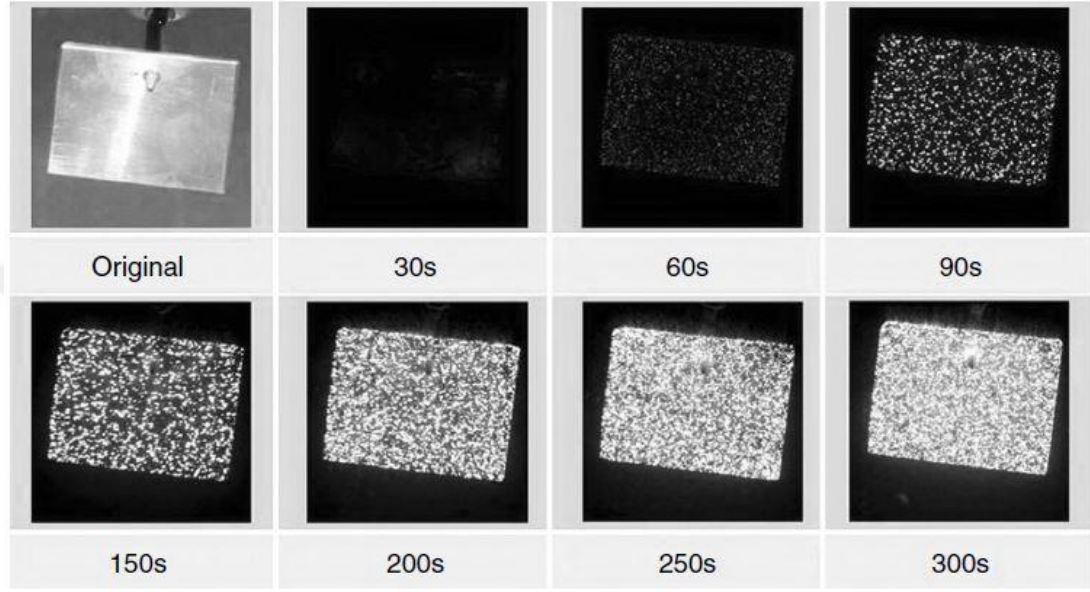
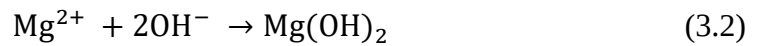


Figure 3.2: Spark formation during MAO of Mg alloys [5].

MAO process can be applied in two modes by controlling electrical parameters, i.e. constant current and constant voltage. In order to explain the coating formation mechanism on the Mg alloy substrate, voltage change during MAO process applied in the constant current mode is shown in Figure 3.3. In the voltage-time curve, four different stages can be realized as evidence of different discharge phenomenon. The passive film mainly consisted of Mg(OH)_2 and MgO is formed on the surface of the Mg alloy substrate at the first stage, as shown in the following reactions [5].



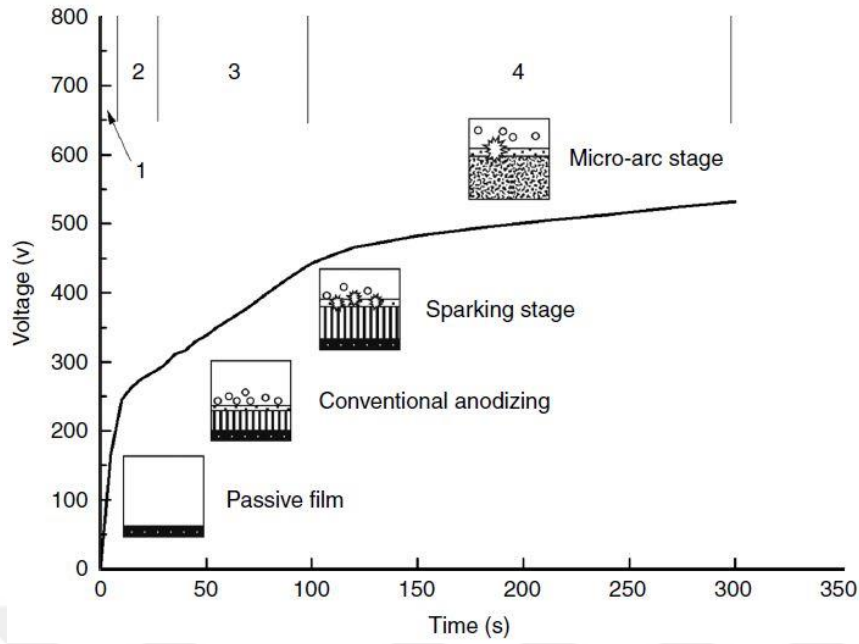


Figure 3.3: Voltage-time graph recorded during MAO process of a Mg alloy [5].

In the second stage, formed passive film breaks down after critical voltage is exceeded (breakdown voltage), and sparking occurs at the surface of the sample along with gas evolution (equations 3.4 and 3.5). Whilst the composition of the passive film can be varied with the electrolyte, breakdown voltage also depends on the composition of the electrolyte and the substrate in addition to the conductivity of the electrolyte.



While the sparks formed during the second stage of MAO process are fine, increasing voltage and time at the third stage cause an increment in the number and the size of the sparks leading to the growth of the oxide layer on the Mg alloy. During the fourth stage of the MAO process, sparks become larger and stay longer on the substrate's surface as compared to previous stages. Finally, the oxide based porous ceramic coating is generated on the Mg alloy substrate, as shown in Figure 3.4, which depicts the surface and cross-sectional SEM images of the coating [5].

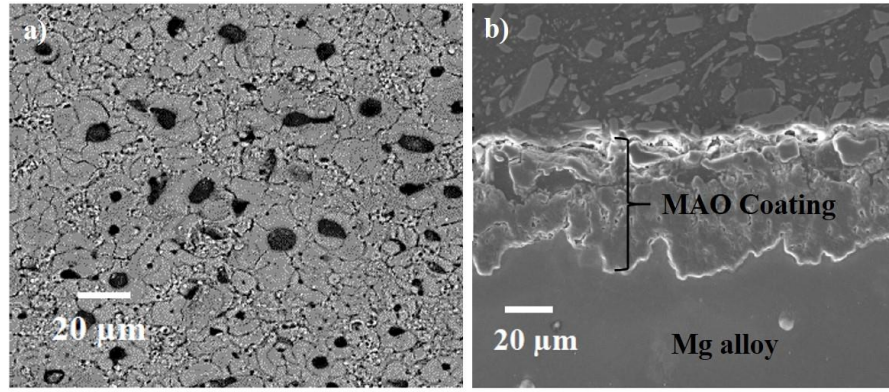


Figure 3.4: SEM images of the MAO coating produced on a Mg alloy taken from (a) surface and (b) cross-section [6].

The surface features (i.e. composition, roughness, etc.) of the MAO coatings produced on the Mg alloys are mainly controlled by the composition of the electrolyte and electrical parameters applied during MAO process along with the processing time. The research on the wear and corrosion resistant coating on Mg alloys continues with an attempt to investigate the influences of electrical parameters, types of electrolyte, and particle incorporation into the electrolyte on the properties of the coatings [7,42]. The effect of the electrical parameters (i.e. current density, duty cycle, voltage, and frequency) on the thickness and surface roughness of the MAO coatings generated on AZ31B Mg alloy in a sodium silicate-based electrolyte is shortly summarized in Table 3.2.

Table 3.2: Variation in the coating thickness and surface roughness with electrical parameters [5].

Electrical Parameters	Coating Thickness	Surface Roughness
Current density (A/dm^2) : 0.5 to 8	increase (5 to 18 μm)	increase
Voltage (V) : 250 to 450	increase (7 to 18 μm)	increase
Duty cycle : 3% to 15%	increase (8 to 21 μm)	decrease
Frequency (Hz) : 500 to 2000	increase (12 to 19 μm)	decrease

On the other hand, the influence of the electrolyte composition (i.e. silicate-, phosphate- and aluminate-based) on the structural constituents of the coating layer formed on AM series Mg alloys is also exemplified in Table 3.3.

Table 3.3: Effect of the electrolyte composition on the phase structure of the MAO coatings [5].

Electrolyte Composition	Structural Constituents of the Coating
Na_2SiO_3 (10 g/L) + KOH (1 g/L)	Magnesium oxide (MgO), Magnesium silicate (MgSiO_4)
Na_3PO_4 (10 g/L) + KOH (1 g/L)	MgO, Magnesium phosphate $\text{Mg}_3(\text{PO}_4)_2$
Na_3PO_4 (10 g/L) + NaAlO_2 (8 g/L) + KOH (1 g/L)	MgO, Magnesium aluminate (MgAl_2O_4)

3.2 Literature Review on MAO Coatings Formed on WE Series Mg Alloys

Several attempts have been done to improve corrosion and wear resistance of the high creep resistant WE series alloys by MAO process. These research studies focusing MAO coatings on WE series alloys, especially WE43, are summarized in detail below.

Firstly, Birss et al. [43] produced oxide-based coatings on the WE43 alloy in an alkaline silicate electrolyte (7 g/L KOH, 10 g/L KF, and 20 g/L Na_4SiO_4) under a range of anodizing conditions (10-30 mA/cm², 280-420 V, and 5 to 20 min). The coatings formed on the WE43 alloy consisted of MgO, Mg(OH)₂, MgF₂ and SiO₂ phases. They reported that the corrosion resistance of the WE43 alloy was enhanced by applied anodizing process, and further improvement was achieved with increasing electrical parameters (higher voltage and higher current) and time. They also stated that, increment in the thickness with increasing voltage resulted in improvement of corrosion resistance unless the formation of larger pores could be prevented.

On the other hand, Arrabal et al. [8] investigated the corrosion resistance of MAO coatings produced on WE43 and AZ91 alloys in the phosphate-based electrolyte under a constant current condition (3 A/dm²) for 40 min. The voltage-time curve recorded during MAO process and surface and cross-sectional SEM images of the MAO coating having a thickness of ~30 µm on WE43 alloy are shown in Figure 3.5. The final voltage recorded during MAO process on WE43 alloy was in the range of 520 V (Figure 3.5a). Although the surface of the MAO coating exhibited low amount of pores having small size (Figure 3.5b), the inner part of the coating contained larger cavities as compared to the outer layer (Figure 3.5c). They conducted electrochemical polarization and im-

immersion tests on the samples in 3.5 wt % sodium chloride (NaCl) media. The polarization curves of the sample and cross-sectional SEM images of the uncoated and MAO coated WE43 alloy after five days of immersion are given in Figure 3.6.

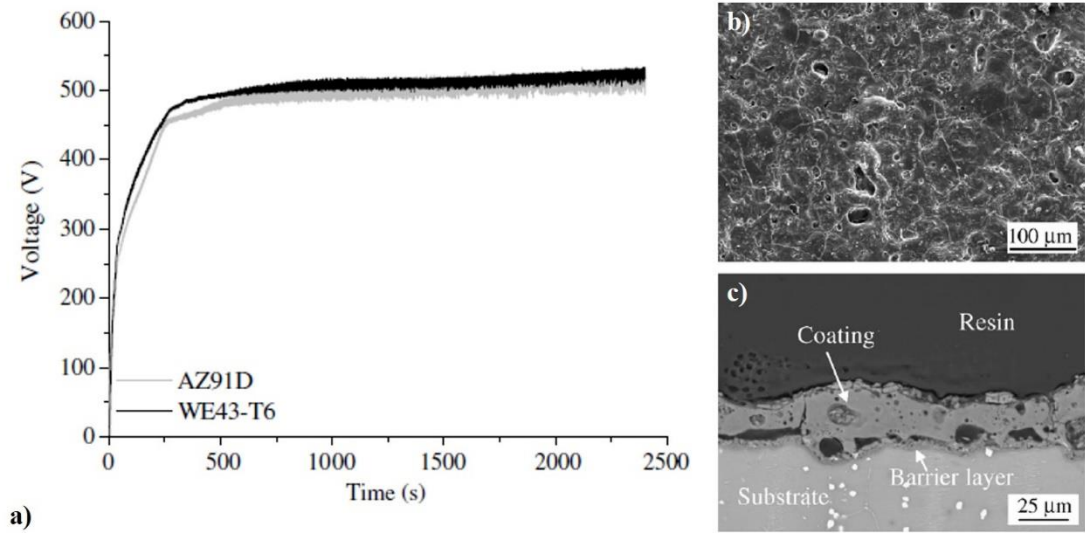


Figure 3.5: (a) Voltage-time graph recorded during MAO process and (b) surface and (c) cross-sectional SEM images of the MAO coating [8].

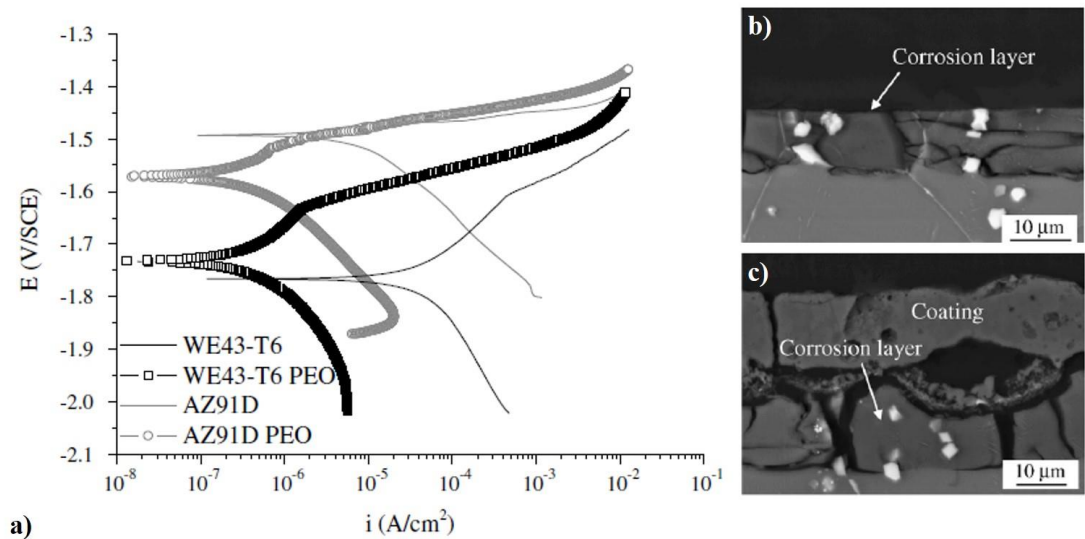


Figure 3.6: (a) Polarization curves and cross-sectional SEM images of the (b) WE43 alloy and (c) MAO coating after corrosion tests [8].

According to the potentiodynamic polarization curves (Figure 3.6a), MAO treatment successfully increased the corrosion resistance of the substrates. When the cross-sectional SEM image of the WE43 alloy is of concern (Figure 3.6b), a uniform corrosion layer with a thickness of 10 μm was visualized on the surface. Similar to the substrate, the corrosion layer with a thickness of 13 μm was also detected at the substrate/coating interface (Figure 3.6c), indicating failure of MAO coating after five days of immersion even it protected the substrate against corrosion at the earlier stage. The authors stated that the thin barrier layer and relatively high porous layer in the MAO coating could not provide sufficient resistance against corrosion [8].

Similar to their previous work Arrabal et al. [9] also studied MAO coatings prepared on a range of commercial Mg alloys including WE43 in silicate-phosphate containing electrolyte (25 mL/L Na_2SiO_3 and 15 g/L $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$) under a constant current condition (65 A/dm²) for 15 min. The MAO coating comprising MgO and Mg_2SiO_4 on WE43 alloy had a thickness of about 110 μm and a hardness of about 430 HV_{0.05}. They also reported that the corrosion rate of investigated alloys in 3.5 wt. % NaCl media was reduced 2-4 times by the application of MAO process. The thick and relatively dense inner layer could provide better corrosion resistance in NaCl media as compared to their previous study [8].

Tekin et al. [10], on the other hand, investigated electrochemical behaviour of MAO coatings on AZ31, E21 and WE43 alloys produced in silicate- and phosphate-based electrolyte (5 g/L $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$, 5 g/L $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, and 4 g/L NaOH) under constant current mode (10 A/dm²) for 12 min. They conducted potentiodynamic polarization tests in 3.5 wt. % NaCl media and reported that the MAO coating having a thickness of ~ 13 μm on WE43 alloy provided better corrosion resistance as compared to un-coated state. Additionally, Figure 3.7 depicts the cross-sectional SEM images of the MAO coated WE43 alloy before and after 24 hours of electrochemical impedance spectroscopy (EIS) test. They stated that MAO coatings produced on RE element containing substrate exhibited better corrosion resistance due to the incorporation of RE elements, particularly Nd, into the coating structure.

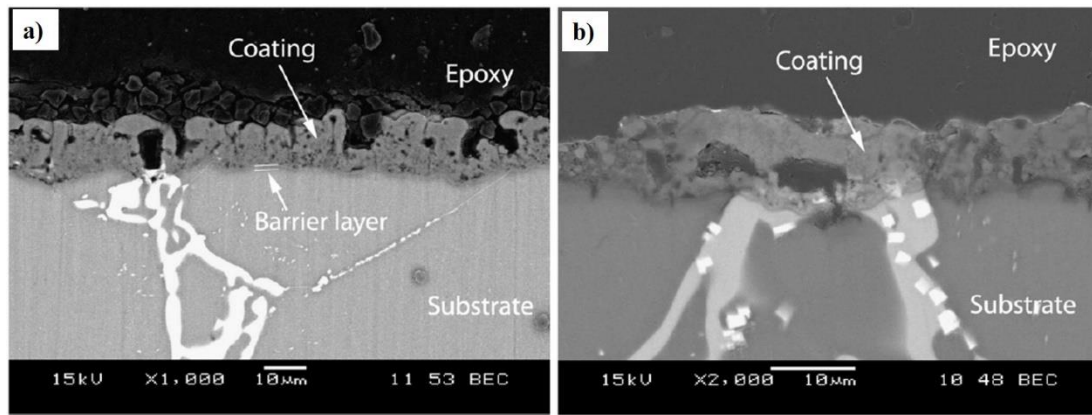


Figure 3.7: Cross-sectional SEM images of the MAO coating (a) before and (b) after corrosion tests [10].

The studies summarized above mainly focused on improving the corrosion resistance of the WE43 alloy by the MAO process to extend its usage in the automotive and aerospace industries. However, some other studies were also conducted on the MAO coating of WE43 alloy to enhance its properties for biological application [44–48]. Firstly, Liu et al. [44] investigated corrosion resistance of WE43 alloy after MAO and successive polymer coating processes by spin coating in simulated body fluid (SBF) solution. They performed MAO process in an alkaline silicate-based electrolyte (15 g/L Na_2SiO_3 and 3 g/L KOH) under constant voltage condition (350 V) for 15 min. After electrochemical corrosion tests, they reported that corrosion resistance of WE43 alloy was significantly improved by applying MAO and polymer sealing coating. On the other hand, Zhu et al. [47] investigated the effects of NaSiO_3 and EDTA- ZnNa_2 concentration in the electrolyte on the corrosion resistance of MAO coated WE43 alloy in SBF solution. The MAO coatings were prepared in 6 g/L NaOH, 5 g/L NaF, 6 g/L H_{12}Phy containing base electrolyte with various amount of NaSiO_3 (0–20 g/L) and EDTA- ZnNa_2 (0–5 g/L) additions. MAO process was conducted under constant current mode (60 mA/cm^2) for 3 min. They determined the optimum addition amount for NaSiO_3 and EDTA- ZnNa_2 as 15 g/L and 3 g/L, respectively, in order to obtain remarkable protection against corrosion in the SBF solution. Recently, Shi et al [48], fabricated selenium-containing MAO coatings on WE43 alloy in an electrolyte composed of 6 g/L NaOH, 4 g/L sodium phytate, 4 g/L $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and 4 g/L Na_2SeO_3 under constant current mode (60 mA/cm^2). They reported that Se-containing MAO coatings successfully increased the corrosion resistance WE43 alloy in Hank's solution.

Since the components used in automotive and aerospace industries were subjected to friction and wear as well, special attention should be paid to the tribological properties

of the MAO coatings produced on WE43 alloy. In this regard, Malayoğlu et al. [11] investigated the wear behaviour of the MAO coated E21 and WE43 alloys. MAO process, which was applied in silicate- and phosphate-based electrolyte (5 g/L $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$, 2 g/L $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, 3 g/L KOH, and 2 g/L KF) under constant current mode (10 A/dm^2) for 20 min, fabricated $\sim 26 \text{ }\mu\text{m}$ thick coating on the WE43 alloy. They conducted dry sliding wear tests at room temperature in the ball-on-plate configuration by applying the testing loads of 5 and 10 N against alumina ball counterface (6 mm dia.). The sliding velocity, stroke length, and total sliding distance were selected as 1.6 cm/s, 8 mm and 50 m, respectively. The MAO process successfully improved the wear resistance of the E21 and WE43 alloys, as can be seen in Table 3.4 listing wear volume loss of the samples.

Table 3.4: Wear loss data calculated for the WE43 and MAO coated WE43 samples [11].

Sample	Wear Volume Loss (mm^3)	
	5 N	10 N
WE43	0.585 ± 0.033	0.939 ± 0.03
MAOed WE43	0.012 ± 0.003	0.051 ± 0.002

They reported that both alloys and coatings exhibited similar characteristics under dry sliding wear conditions, and thus, they only presented the worn surface images for E21 alloy. The dominant wear mechanism for the Mg alloy substrate was determined as abrasive wear with grooves on the worn surface while the worn surface of the MAO coating exhibited delamination and micro-cracks as evidence of brittle fracture mechanism.

The studies investigated wear behaviour of the MAO coated WE43 alloy at room and high temperatures are limited in the open literature. Even though MAO coating enhances the corrosion and wear resistance of the Mg alloys by producing magnesium oxide based coatings, further improvement by combined application of cold spray and MAO processes was reported in the literature as a novel technique to produce alumina (Al_2O_3) based multilayer coatings on Mg alloys [16,17,49,50].

3.2.1 New approach to MAO of Mg alloys

Low hardness and thermodynamic stability of MgO as compared to Al₂O₃, which eventually result in low wear and corrosion resistance, led researchers to produce alumina layer on the Mg alloys. In this respect, some studies have been conducted using the thermal spray technique to obtain alumina coating on the Mg alloys [14,51]. However, application of the thermal spray, which generates excessive heat input on the surface of the substrate, on the Mg alloys has some detrimental effects such as oxidation, phase transformation in the substrate and high residual stress arising from high temperature gradient and thermal expansion mismatch. In order to overcome these drawbacks, a combination of cold spray and MAO process, as a new approach, yielded promising results. In this technique, firstly, a cold spray layer consisting of monolithic Al or Al matrix composites was fabricated on the Mg alloy substrate without oxidation and phase transformation in both substrate and coating layer thanks to very low process temperature of the cold spray. Then, MAO process successively applied to produce aluminium oxide layer on the surface. Hence, multilayer coating with an alumina layer on the top can be successfully fabricated without any detrimental effect on the Mg alloy substrate [17].

On the scope of producing alumina coatings on Mg alloys, Krishna et al. [16] and Tazegül et al. [17] firstly introduced a novel technique, which combines cold spray with MAO process on the AZ91 alloy. Krishna et al. [16] applied cold spray (CS) process by using commercially pure Al powders (30-45 µm dia.) with air under a pressure of 20 bar and obtained CS coating layer on AZ91 alloy with a thickness of 22 µm. Then, CSed sample was subjected to MAO process in silicate and aluminate-based electrolyte (6 g/L Na₂SiO₃, 2 g/L KOH, and 2 g/L NaAlO₂) under constant current mode (20 A/dm²) for 10 min. The coating obtained by CS and sequentially MAO process composed of MgO, MgAl₂O₄, Mg₂SiO₄, and Mg₃Al₂(SiO₄)₃ with the thickness of 28 µm. They reported that this novel technique significantly enhanced the corrosion resistance of the AZ91 alloy as compared to single application of MAO process. However, the coating produced by combining CS with MAO process did not have the characteristics of multi-layered coatings due to the consumption of the CSed Al layer. Also, the coating did not contain any form of Al₂O₃ phase.

On the other hand, Tazegül et al. [17] also produced MAO coatings on CSed Al and Al₂O₃ reinforced Al matrix composite layer on the AZ91 alloy in the aluminate-based

electrolyte (0.18 mol/L NaAlO_2 and 0.035 mol/L KOH) under constant voltage mode (400 V) for 20 min. In order to compare corrosion and wear resistance of the coatings, AZ91 alloy was also subjected to MAO process without CS deposition. Figure 3.8 depicts the surface and the cross-sectional SEM images of the multi-layered coating produced by the combined application of CS and MAO techniques. The interfaces between the substrate and CSed layer and also CSed layer and MAOed layer exhibited crack-free nature without any discontinuities. The thicknesses of the MAO coatings were measured as 22 μm for produced on the monolithic CS layer and 28 μm for that on the composite CS layer. The hardness of the CSed layer having the thickness bigger than 200 μm were measured as 57 HV and 78 HV under 25 g load for monolithic and composite layer, respectively.

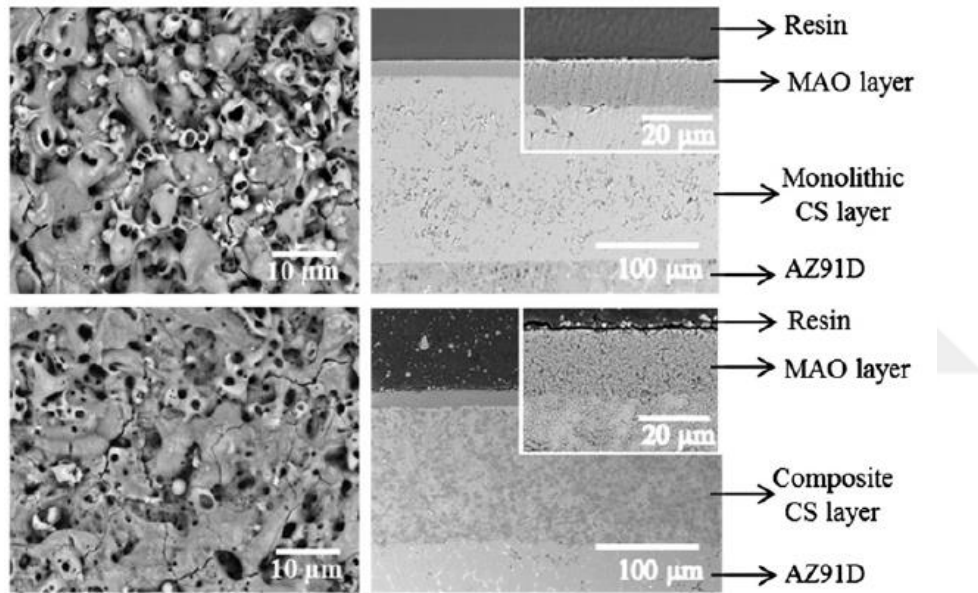


Figure 3.8: Surface and cross-sectional SEM images of the multilayer coatings [17].

MAO coatings produced on CSed layers exhibited higher hardness than that of MAO coating on AZ91 alloy due to higher hardness of alumina than magnesia. On the other hand, MAO coatings on composite CS layer had higher hardness than that on monolithic CS layer due to the higher amount of $\alpha\text{-Al}_2\text{O}_3$ in the coating. They investigated the wear behaviour of the MAO coatings and reported that MAO coating on the composite CS layer exhibited the higher wear resistance against alumina ball counterface (6 mm dia.) under sliding contact at a load of 5 N. They also conducted electrochemical polarization tests in 3.5 wt. % NaCl media and stated that the corrosion resistance of the AZ91 alloy remarkably improved by combined application of CS and MAO process, especially for the case of the coatings on the composite CS layer.

Recently, Martin et al. [49] investigated the combined application of CS and MAO process on EV31 Mg alloy and a steel substrate. They produced MAO coatings on two different monolithic Al CSed coatings having a thickness of 66 and 220 μm in silicate-based electrolyte (1 g/L KOH and 1.65 g/L Na_2SiO_3) under constant current condition (48 A/dm^2) for 8, 20 and 35 min. They reported that relatively low thickness of the CSed layer caused the formation of a porous inner layer on the Mg alloy substrate after 20 min of oxidation (Figure 3.9). Then, consuming of the CSed layer finally resulted in the delamination at the former Al/Mg interface after 35 min of oxidation. At the same time, relatively denser MAO coating was achieved on the thicker CSed layer for all oxidation times.

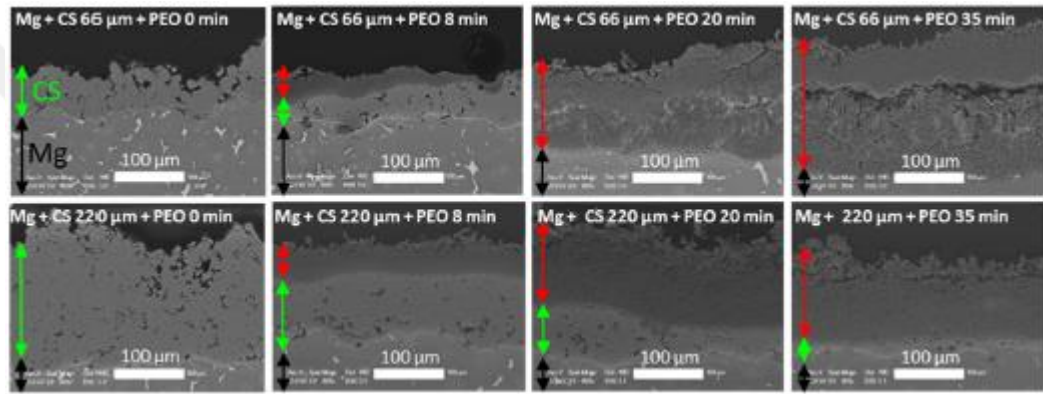


Figure 3.9: Cross-sectional SEM images of the multilayer coatings having different CS and MAO layer thicknesses [49].

With the light of the above-mentioned studies, CS and MAO processes are sequentially applied on the WE43 alloy to enhance the wear resistance of the WE43 alloy at both room and high temperature in addition to corrosion resistance via producing alumina layer on the surface.



4. EXPERIMENTAL STUDIES

In this study, WE43 alloy was subjected to a combined application of CS and MAO process to produce alumina coating on its surface, having high wear and corrosion resistance. The experimental procedure conducted during this thesis is explained briefly in the following sections.

4.1 Material and Coating Processes

4.1.1 Material

WE43 alloy was supplied from Magnesium Elektron Ltd. (Manchester, England) company in solution treated and artificially aged (T6) condition. The chemical composition of WE43 alloy is presented in Table 4.1. X-ray diffractometer (XRD), optical microscope (OM) and energy-dispersive spectrometer (EDS) equipped scanning electron microscope (SEM) were utilized in order to characterize phase structure and microstructure of the WE43 alloy. Details about XRD and SEM-EDS analyses are explained in Section 4.2.1 and 4.2.2, respectively.

Table 4.1: The chemical composition of the WE43 alloy [10,11].

Element	wt. %
Y	3.8
Nd	2.1
Zr	0.76
Fe	0.002
Cu	0.003
Other REs	<0.38
Mg	Bal.

XRD pattern of the WE43 alloy is given in Figure 4.1. In addition to Mg peaks, $\text{Mg}_{41}\text{Nd}_5$, $\text{Mg}_{14}\text{Nd}_2\text{Y}$, and Mg_{12}Nd peaks were also detected in XRD pattern of the WE43 alloy, as reported in the open literature [52–55].

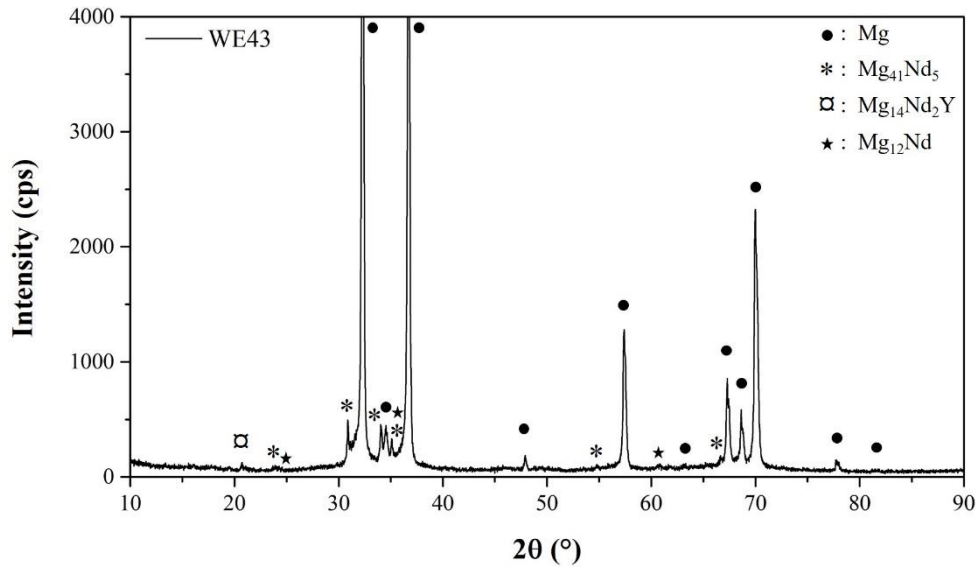


Figure 4.1: XRD pattern of the examined WE43 alloy.

OM and SEM images of the WE43 alloy is depicted in Figure 4.2, after standard metallographic specimen preparation steps (grinding, polishing, and etching with 5 wt.% nital solution). As reported in the literature, microstructure of the WE43 alloy consisted of equiaxed α -Mg grains (Figure 4.2a), rectangular-shaped Y-rich intermetallics, Zr-rich intermetallics and Nd-rich intermetallics at the grain-boundaries (Figure 4.2b) [10,28,56]. Additionally, the hardness of the WE43 alloy was measured as 94 ± 5 HV_{0.025} and 87 ± 2 HV₁. The hardness result of the WE43 alloy is in good agreement with the literature [57–59].

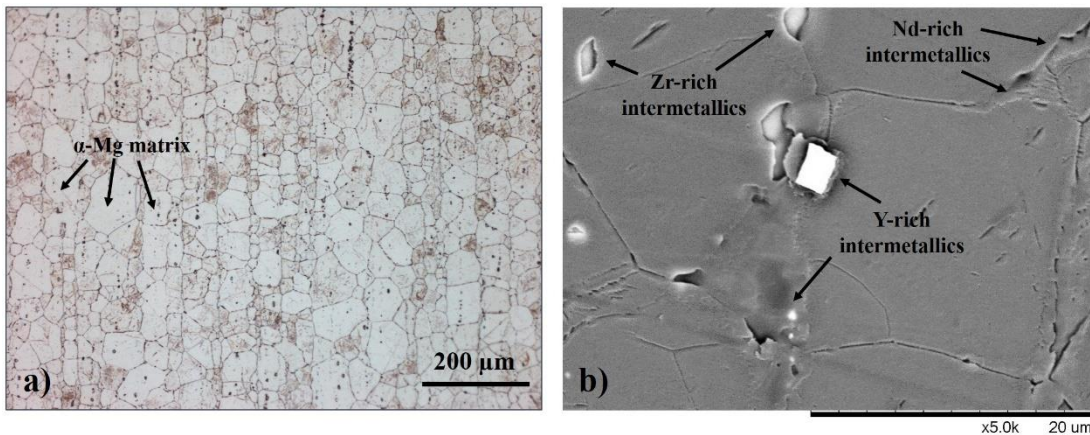


Figure 4.2: (a) OM and (b) SEM image taken from the WE43 alloy after etching.

4.1.2 Cold spray coating

Cold gas dynamic spraying (CGDS), shortly known as cold spray (CS), was applied to produce Al₂O₃ particle reinforced Al matrix composite layer on the surface of WE43 alloy. The reason for the selection of composite CS layer is to obtain a coating layer

having higher hardness and wear resistance as compared to the monolithic Al layer, which is finally resulted in better properties in the oxidized layer as reported by Tazegül et al. [17]. CS coatings on WE43 alloy was produced in a company (Dymet Soğuk Kaynak Teknolojileri) located in İzmir by using commercially available Dymet K-10-01 (Al+60 wt.% Al₂O₃) powders. As can be seen in Figure 4.3, Dymet K-10-01 powders consisted of spherical Al particles (50 ± 10 µm) and irregular Al₂O₃ particles (~25 µm) [60].

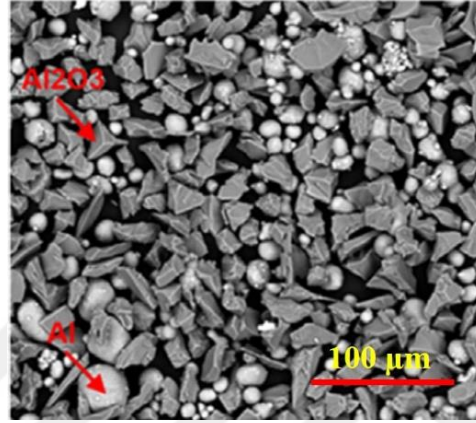


Figure 4.3: Commercial Dymet K-10-01 (Al+60 wt.% Al₂O₃) powder mixing used in CS process [60].

Figure 4.4 presents XRD pattern of the CSed coating produced on the WE43 alloy. On the XRD pattern, two different phases of the alumina were identified as α -Al₂O₃ and γ -Al₂O₃ in addition to Al peaks. The peaks of stainless steel (AISI 304L grade) were also detected on the XRD pattern of CSed coating, indicating partial material transfer from cold spray nozzle to deposit powders during spraying due to abrasive effect of alumina particles. Cross-sectional back-scattered electron (BSE) SEM image of the CSed coating given in Figure 4.5 shows that the coating thickness was about 300 µm (Figure 4.5a). Good bonding characteristic between the CSed layer and WE43 alloy interface was observed without any cracks or pores (Figure 4.5b).

Additionally, the hardness of the CSed coating was measured as 102 ± 17 HV_{0.025}. The hardness results were in good agreement with the open literature [61,62]. The sample only coated with Al/Al₂O₃ composite CSed layer on WE43 alloy will be referred as “WE43+CS” hereafter.

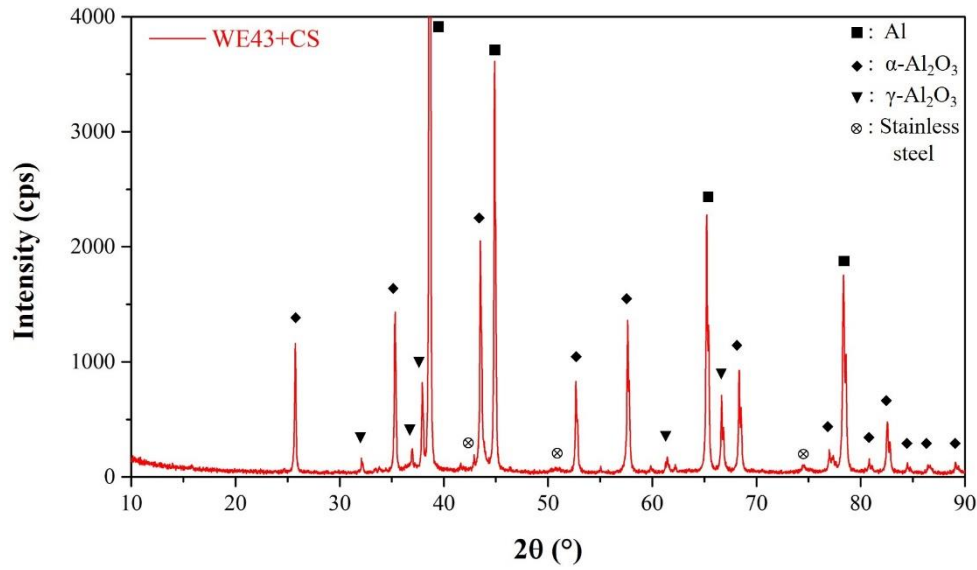


Figure 4.4: XRD pattern of the WE43+CS sample.

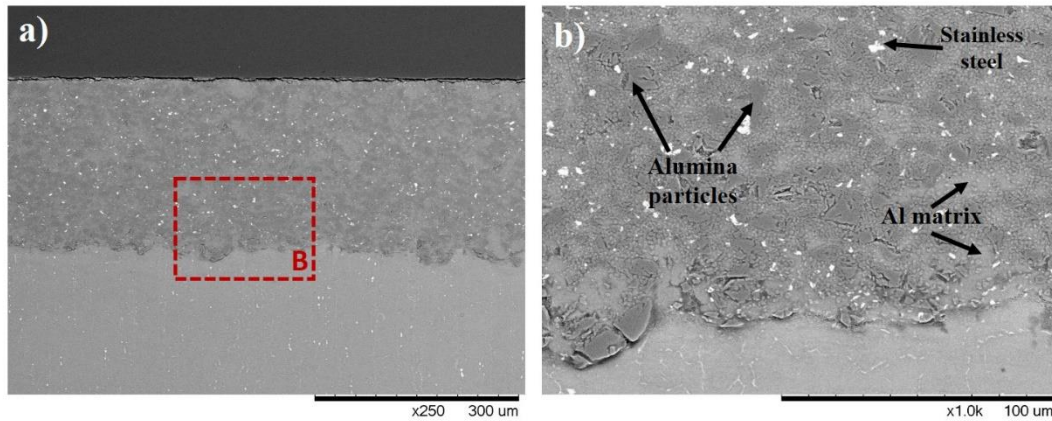


Figure 4.5: (a) Cross-sectional SEM image of the WE43+CS sample and (b) high magnification SEM image taken from the region B shown in (a).

The elemental composition of the Al matrix, alumina particles, and bright particles at the microstructure were determined by the EDS analysis conducted at the cross-section of the CSed layer (Figure 4.5b). Results of the EDS analysis, shown in Figure 4.6, revealed that the bright phase consisted of Fe, Ni, and Cr. This observation can be accompanied by the presence of the stainless steel peaks on the XRD pattern (Figure 4.4).

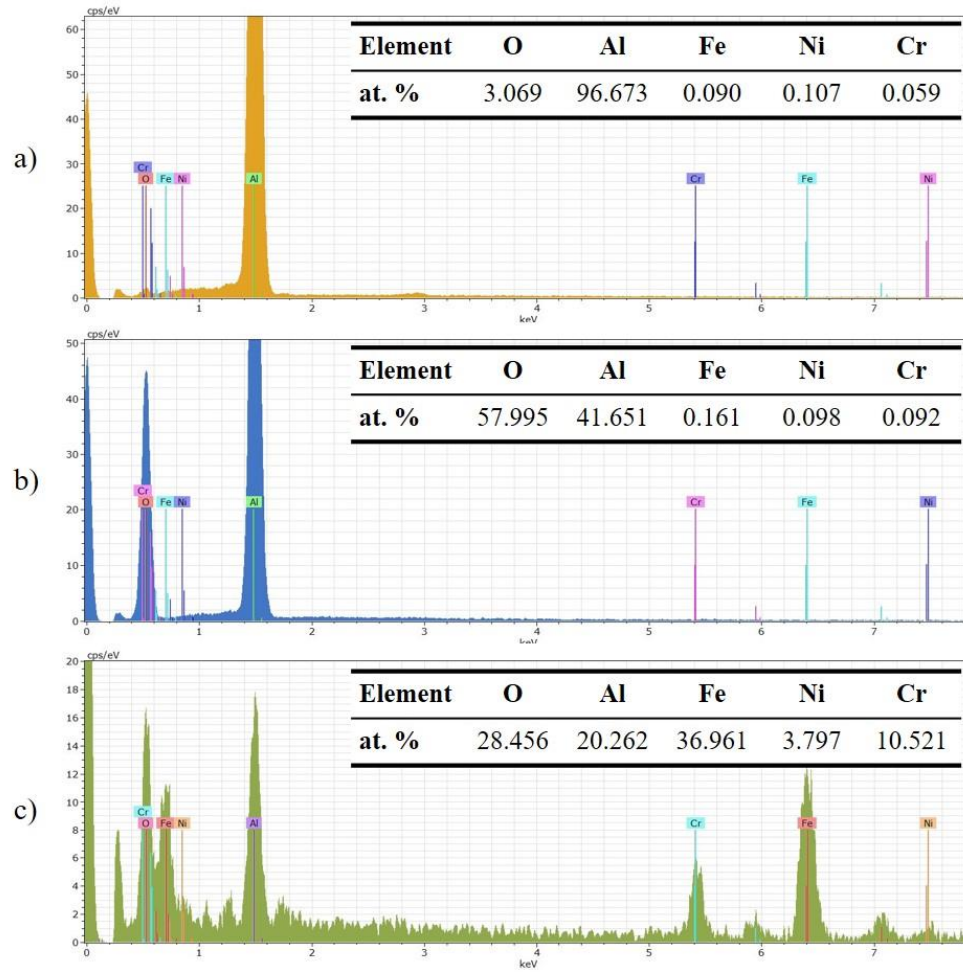


Figure 4.6: Results of the EDS analysis conducted on the (a) Al matrix, (b) alumina particles, and (c) bright particles (Stainless steel) at the BSE-SEM image of the WE43+CS sample shown in Figure 4.5b.

4.1.3 Micro-arc oxidation coating

Samples were cut from bare and CSed WE43 alloy with dimensions of 20 mm in width, 20 mm in length and 6 mm in thickness. Before MAO process, samples were ground 2500 grit with SiC sandpapers and rinsed with distilled water and ethanol. In order to oxidize only Al/Al₂O₃ coated surface of the CSed sample, samples were moulded in epoxy resin. WE43 alloy (bare) was also moulded to operate MAO process on the samples having equal surface area. MAO unit utilizing bi-polar pulsed direct current (DC) is presented in Figure 4.7 along with an image showing the spark formation on the sample during MAO process for an example. The principles of the MAO process were explained in Section 3.1.



Figure 4.7: MAO unit and an example for spark formation on the sample during the process.

MAO process was applied under constant voltage condition (voltage control mode) in aluminate-based electrolyte composed of 10 g/L NaAlO_2 and 2 g/L KOH in distilled water. During MAO process the electrolyte temperature was kept below 25 °C by an external water cooling system to regulate chemical reaction rate by preventing excessive heating of electrolytes. Electrical parameters conducted during MAO process are given in Table 4.2. While the electrolyte composition remained stable for both samples (bare and CSed WE43), electrical parameters were slightly changed to obtain identical thickness for each coating. After MAO process, samples were rinsed in distilled water. MAO coating on the WE43 alloy (monolayer) and CSed WE43 alloy (multilayer) will be referred as WE43+MAO and WE43+CS+MAO, respectively, hereafter.

Table 4.2: Process parameters for WE43+MAO and WE43+CS+MAO samples.

Parameter	WE43+MAO	WE43+CS+MAO
Positive Voltage	440 V	480 V
Negative Voltage	70 V	80 V
Duration	5 min	8 min

4.2 Structural Characterization of the MAO Coatings

4.2.1 XRD analysis

In order to determine the phase composition of the coatings, an X-ray diffractometer (XRD, GBC MMA 027) device was used with Cu-K_α radiation. XRD analyses were

conducted at 2 Theta (θ) range between 10-90 ° with a step of 0.02 ° and a scan speed of 1°/min. Bare WE43 alloy and WE43+CS samples were also subjected to XRD analysis (Figure 4.1 and Figure 4.4, respectively).

4.2.2 SEM/EDS analysis

The surface morphology of the coatings was investigated by using scanning electron microscope (SEM, Hitachi TM-1000). Cross-section of the coatings was also investigated by using a SEM (JEOL 6060) equipped with energy-dispersive spectrometer (EDS) after standard metallographic specimen preparation procedure, including grinding with SiC papers and polishing with colloidal silica (0.05 μm). High magnification secondary electron (SE) images and elemental mapping analysis of the coatings were done by using EDS (Quantax 800) equipped SEM (Zeiss Merlin Gemini II). Additionally, the porosity of the MAOed samples was calculated by using ImageJ analysing software.

4.2.3 Micro-hardness measurements

The hardness measurements were conducted on the well-polished cross-section of the examined samples via using Vickers micro-hardness tester (Wilson Tukon 1102). 25 g load was applied by Vickers indenter during the test. At least 10 measurements were conducted for each sample, and results were presented as an average value with standard deviation.

4.3 Electrochemical Corrosion Tests

The electrochemical corrosion tests of the examined samples were conducted by using the potentiodynamic polarization module of a potentiostat (Gamry Reference 600) at room temperature in a media containing 3.5 wt.% NaCl solution. The standard three-electrode flat cell setup with saturated calomel electrode ($\text{Hg}/\text{Hg}_2\text{Cl}_2$, SCE) as a reference electrode, a platinum mesh as a counter electrode, and the sample as a working electrode was used for polarization tests, as can be seen in Figure 4.8. The samples were ground and gently polished prior to the electrochemical polarization tests. Before beginning the polarization test, the open circuit potential (OCP) of the sample was stabilized for 30 min. The potential scan was the initiated from -0.25 V (vs. OCP) and increased with a rate of 0.2 mV/s until the current density reached 5 mA/cm^2 in the

external circuit between counter electrode and the sample. The surface area of the samples exposed to NaCl solution was assumed as about 1 cm².

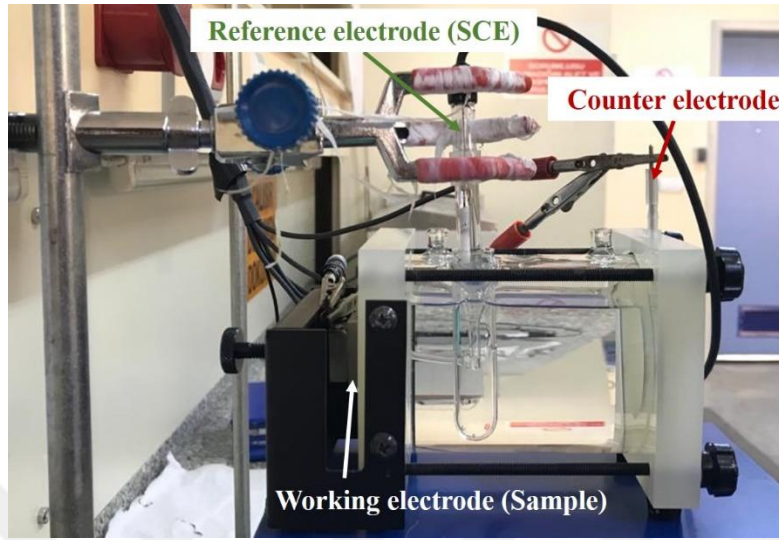


Figure 4.8: Standard three electrode corrosion flat cell setup used in this study for polarization tests.

After polarization tests, corrosion potential (E_{corr}), current density (I_{corr}), anodic and cathodic Tafel constants (β_a and β_c) for the examined samples were determined from polarization curves by Tafel extrapolation method. Additionally, polarization resistance (R_p) of the examined samples was calculated using the Stern-Geary relationship as given in equation 4.1[63].

$$R_p = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c) i_{\text{corr}}} \quad (4.1)$$

4.4 Wear Tests

Samples were gently ground with SiC paper to 2500 grit size prior to wear tests. The wear behaviour of the samples was examined under the dry sliding condition in two different testing configurations. Firstly, a ball-on-plate reciprocating tribometer (TriboTech Oscillating Tribotester) was used to investigate the effect of the testing load on the wear behaviour of the samples. Then, influence of the testing temperature on the wear performance of the samples was also examined by using unidirectional ball-on-disc tribometer (CSM-High Temperature). The wear test parameters for both configurations are listed in Table 4.3. After wear tests, wear track formed on the surface of the examined samples was examined via 2-D stylus type surface profilometer (Veeco Dektak 6M) in order to calculate the specific wear rate of the samples, as shown in the

equation 4.2. In this equation, volume loss can be calculated by multiplying wear track area measured from 2-D profiles with wear track length for reciprocating wear tests. On the other hand, wear track area is multiplied with the wear track circumference to calculate volume loss of the sample for ball-on-disc wear tests.

Table 4.3: Process parameters for reciprocating ball-on-plate and unidirectional ball-on-disc wear tests.

Parameter	Reciprocating	Ball-on-disc
Counterface	Alumina ball (6 mm in dia.)	Alumina ball (6 mm in dia.)
Sliding Velocity	6 mm/s	20 mm/s
Total Sliding Distance	100 m	50 m
Stroke (Wear Track Length)	2 mm	-
Wear Track Diameter	-	5 mm
Testing Load	1 and 4 N	2 N
Testing Temperature	25 °C	25, 250, 320 °C

$$\text{Specific Wear Rate (mm}^3\text{/Nm)} = \frac{\text{Volume loss (mm}^3\text{)}}{\text{Load(N)} \times \text{Sliding Distance (m)}} \quad (4.2)$$

Additionally, the worn surface of the samples was investigated by SEM (Hitachi TM-1000), while an optical microscope (OM, Leica DM750M) was used for the investigation of the contact surface of the alumina ball counterface.



5. RESULTS AND DISCUSSION

5.1 Structure of the MAO Coatings

Structural characterization of the MAO coatings produced on the WE43 (WE43+MAO) and CSed WE43 alloy (WE43+CS+MAO) was performed by using XRD and SEM/EDS analyses. The results of these investigations are given below.

5.1.1 MAO coating fabricated on the WE43 alloy

XRD pattern of the WE43+MAO sample is presented in Figure 5.1. MgO and MgAl₂O₄ peaks were realized on the XRD pattern in addition to the Mg peaks, belonging to the substrate due to penetration of X-rays through the porous coating layer. The spinel MgAl₂O₄ phase formation was also reported in the literature when aluminate-based electrolyte was used in the MAO process [36,64].

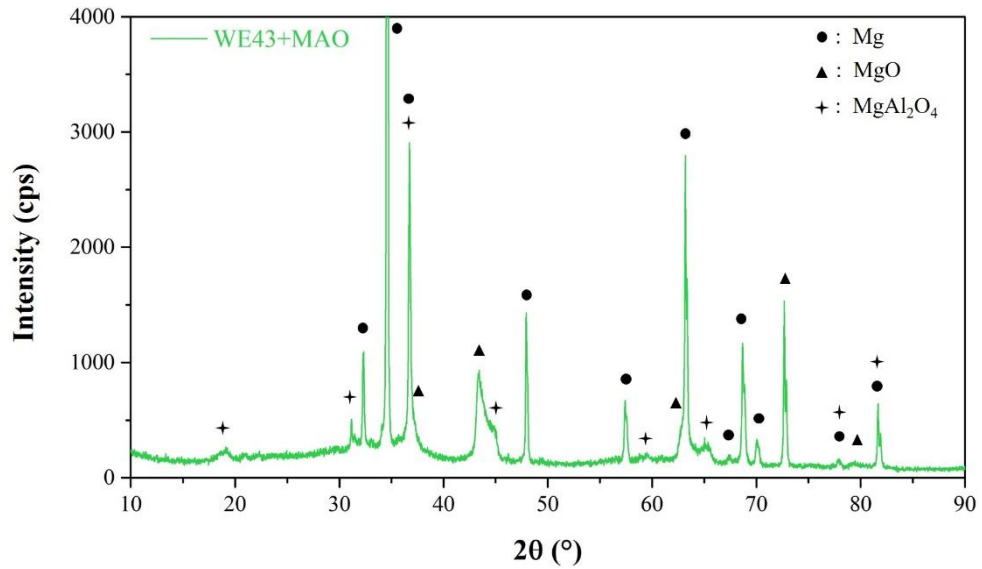


Figure 5.1: XRD pattern of the WE43+MAO sample.

Surface and cross-sectional SEM images of the WE43+MAO sample at low and high magnifications are shown in Figure 5.2. The surface of the WE43+MAO samples exhibited porous structure as typical characteristics of the MAO coatings. The porosity on the surface of the WE43+MAO sample was calculated as ~ 4.25 %. On the other

hand, micro-crack network was visualized on the surface (Figure 5.2a and b) mainly due to thermal stresses arising from heating and cooling cycles during MAO process. When the cross-section of the WE43+MAO sample is of concern (Figure 5.2c), it can be clearly seen that the pores and discharge channels were get through the inner parts of the coating layer from the surface. In addition, relatively bigger pores in size were observed at the cross-section of the coating as compared to the surface. It should be noted that the coating thickness, which is not uniform throughout the surface, was measured as $15.9 \pm 3 \mu\text{m}$. Additionally, the interface between coating and the WE43 alloy exhibited good bonding characteristics without any defects such as delamination or pores. At the high magnification SE-SEM image taken from the cross-section of the WE43+MAO sample (Figure 5.2d), A, B, and C type discharges were detected as schematically illustrated by Hussein and Northwood [6] in Figure 5.3.

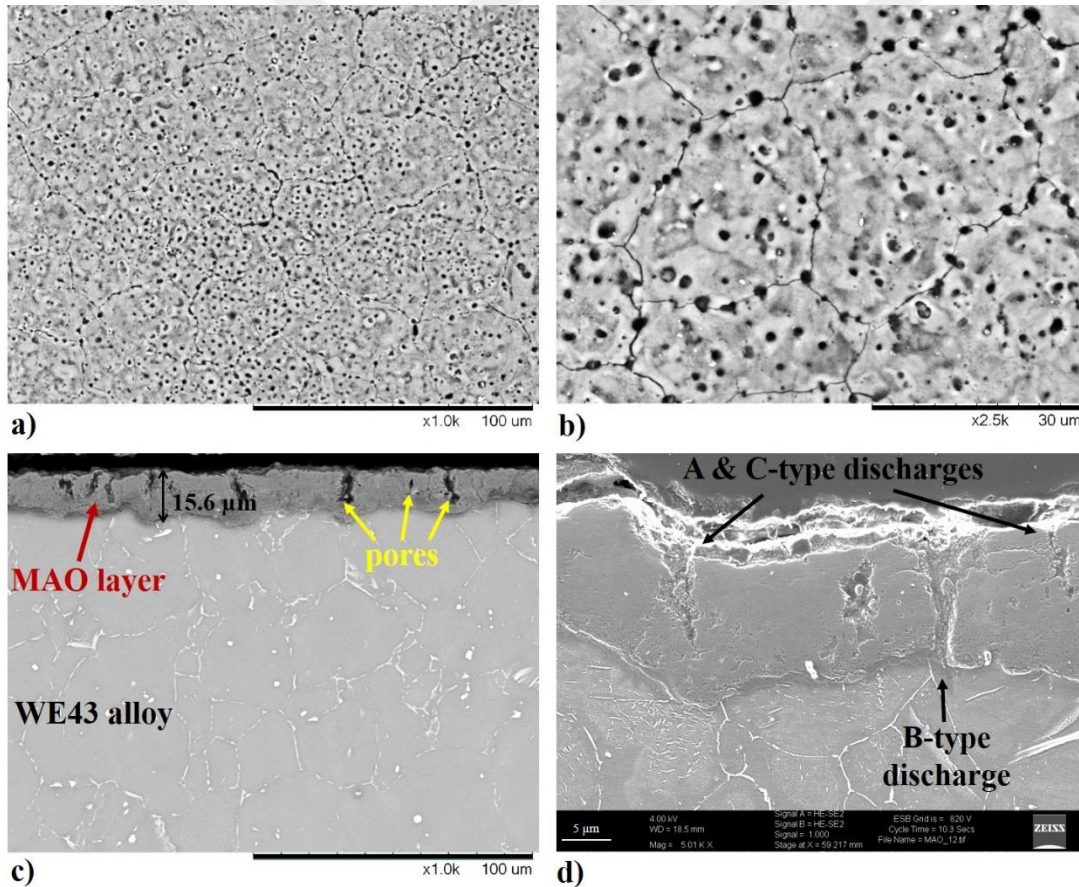


Figure 5.2: SEM images taken from the (a,b) surface and (c,d) cross-section of the WE43+MAO sample.

It is reported in the literature that discharge formation occurred when the voltage exceeded the critical threshold [7]. B-type discharges were indicated as the strongest one and they reached to the substrate while A and C types were weaker discharges occurred

at and/or just beneath the surface. The B-type discharges may result in the deterioration of the coating layer with the formation of bigger pores in size. It is also stated that discharges, which are high in the number and not too violent, are desired to obtain more uniform and thicker coating.

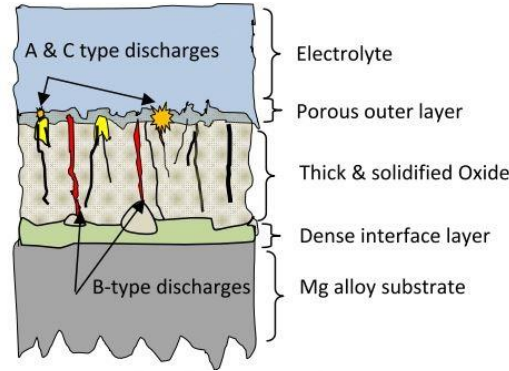


Figure 5.3: Coating structure and discharge types formed after MAO process on Mg alloy [6].

Results of the elemental mapping analysis conducted on the cross-section of the WE43+MAO sample for Mg, O, Na, Al, and Zr are given in Figure 5.4. At first glance, it is noticed that MAO layer on the WE43 alloy's surface consisted of two different regions, namely outer and inner layers. When mapping image for Al is of concern, more intense Al at the outer layer was detected as compared to inner layer. Additionally, the presence of the Mg was more apparently visualized at the inner layer than the outer. In order to reveal the elemental composition of the outer and inner layers, EDS analysis was also conducted the regions marked as O and I in Figure 5.4. Results of the EDS analysis conducted at the regions O and I, which are listed in Table 5.1, confirmed that the outer layer contained more Al and Na than the inner layer.

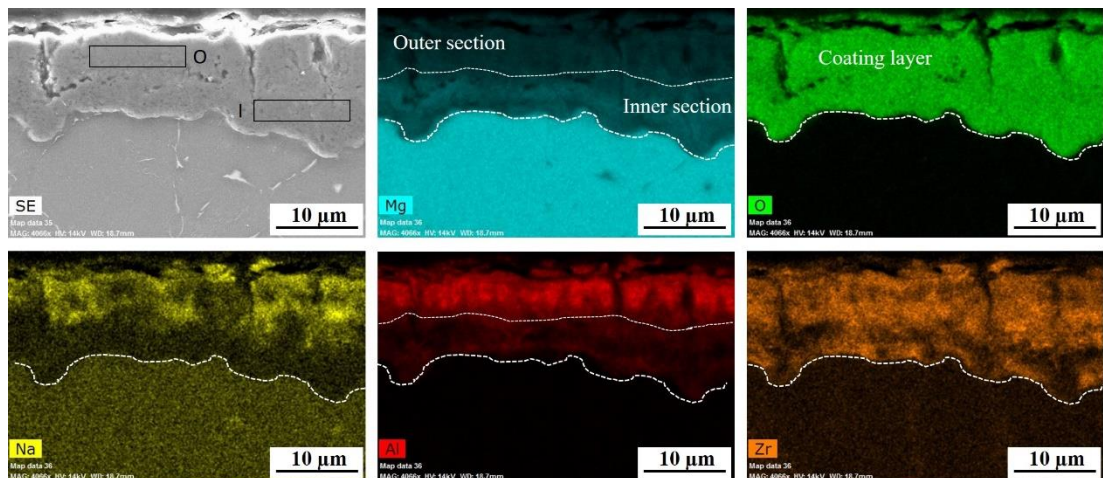
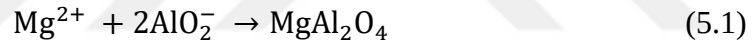


Figure 5.4: Elemental mapping analysis of the WE43+MAO sample showing the presence of Mg, O, Na, Al, and Zr.

Table 5.1: Results of the EDS analysis conducted in the Regions O and I of the cross-section of the WE43+MAO sample.

Element	Outer Layer (O) (at. %)	Inner Layer (I) (at. %)
Mg	21.35	39.12
O	61.88	56.53
Al	14.26	3.50
Y	0.63	0.31
Nd	0.11	0.09
Na	1.60	0.31
K	0.17	0.13

Results of the EDS analysis and elemental mapping suggested that MgAl_2O_4 as a spinel phase of the MgO and Al_2O_3 was formed on the outer layer of the MAO coating produced in an aluminate-based electrolyte. This observation can also be accompanied with the results of the XRD analysis (Figure 5.1). The formation of the MgAl_2O_4 phase during MAO process can be explained by equation 5.1, as reported in the open literature.



On the other hand, the hardness of the WE43+MAO sample was measured as $311 \pm 74 \text{ HV}_{0.025}$ from the mid-section of the coating layer. In the literature, the hardness of the MAO coatings on the Mg and its alloys was reported to vary in 200-1000 HV depending on the substrate, electrolyte, and particle incorporation [38,64]. While Arrabal et al. reported that the hardness of the MAO coating produced on the WE43 alloy was about $430 \text{ HV}_{0.05}$ [9], the coating they produced was remarkably thicker and denser as compared to that of produced in this study. It is suggested that relatively lower hardness of the WE43+MAO sample could be related to the presence of coarse pores in its structure.

5.1.2 MAO coating fabricated on the CSed WE43 alloy

XRD pattern of the WE43+CS+MAO sample is given in Figure 5.5. In addition to Al peaks belonging to the underlying CSed layer, alumina peaks consisting of $\alpha\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$ phases were detected on the XRD pattern, as a typical characteristic of

the MAO coatings produced on Al and its alloys [6,65,66]. It should be noted that the peaks of α - Al_2O_3 phase had more intensity than that of the peaks of γ - Al_2O_3 .

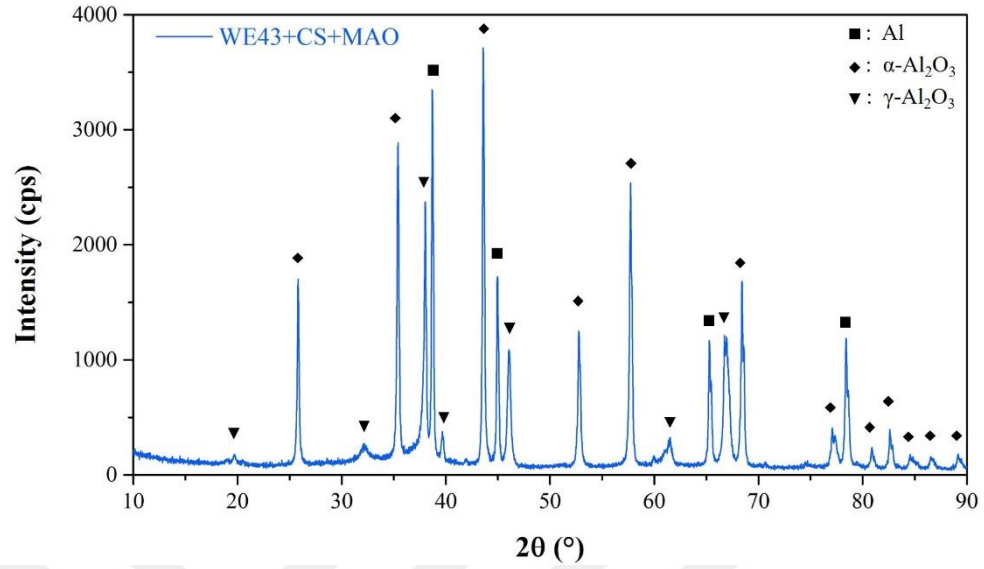
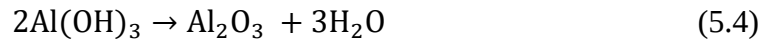
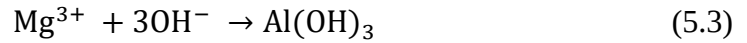


Figure 5.5: XRD pattern of the WE43+CS+MAO sample.

The formation mechanism of MAO coating on Al and its alloys can be explained with the reactions taken place during MAO process, as given in the following equations 5.2-5.4.



While γ - Al_2O_3 formed at the earlier stage of MAO process due to its lower critical free energy for nucleation than that of α - Al_2O_3 , the transformation from γ - Al_2O_3 to α - Al_2O_3 took place at the later stages of MAO process as a result of high temperature and pressure generated by micro-discharges [66].

Figure 5.6 presents low and high magnification SEM images taken from the surface and cross-section of the WE43+CS+MAO sample. The surface of the WE43+CS+MAO sample was in porous nature similar to the WE43+MAO sample. However, the surface porosity of the WE43+CS+MAO sample was lower (3.13 %) as compared to that of the WE43+MAO sample. Additionally, the micro-cracks were hardly detected on the surface of the WE43+CS+MAO sample (Figure 5.6b). In addition to its low surface porosity, cross-section of the WE43+CS+MAO sample shows

that the coating layer was more uniform and denser than the WE43+MAO sample (Figure 5.6c). On the other hand, the interface of the MAOed layer and CSed composite layer was hardly recognized, indicating excellent bonding between alumina containing oxide layer and alumina reinforced Al matrix composite layer (Figure 5.6d). The thickness of the coating was measured as $19.1 \pm 1 \mu\text{m}$. When the high magnification SE-SEM image is of concern (Figure 5.6d), uniformly distributed sub-micron sized ($< 1 \mu\text{m}$) pores were detected without any types of discharge channels and bigger pores like observed in the WE43+MAO sample (Figure 5.2d).

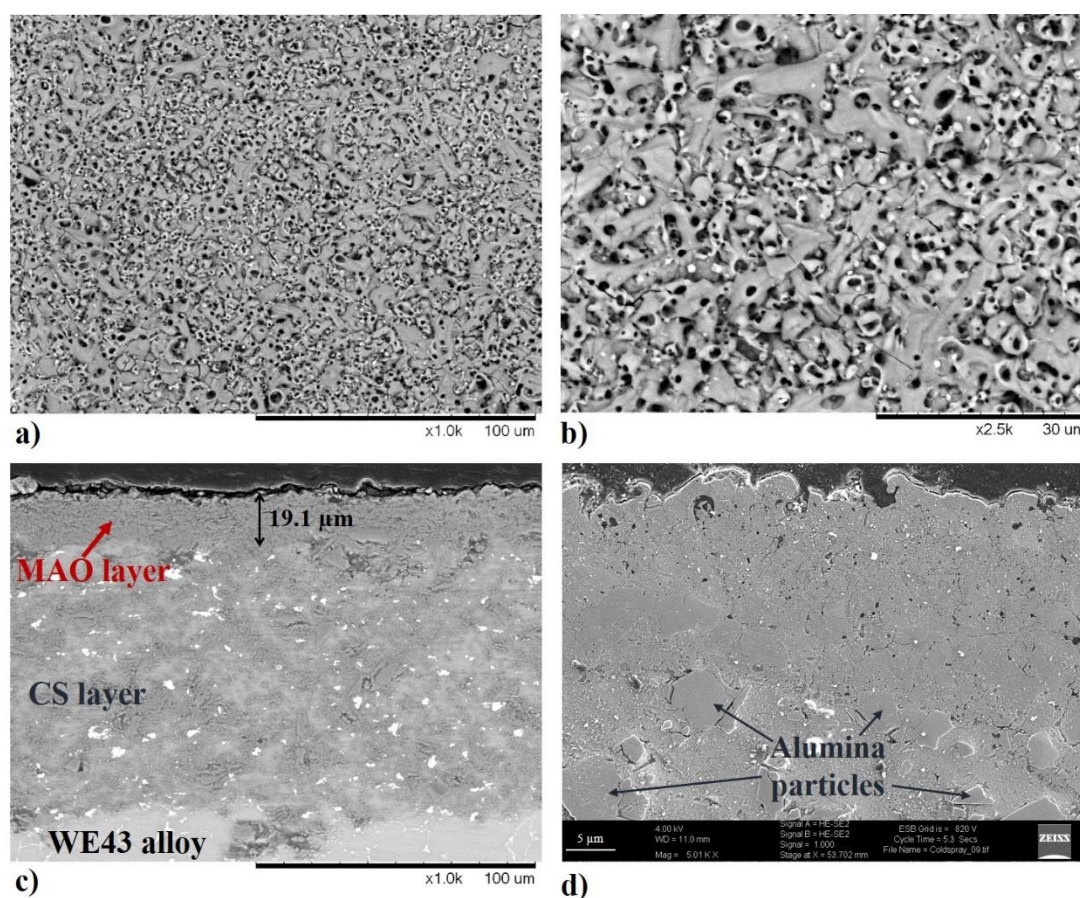


Figure 5.6: SEM images taken from the (a,b) surface and (c,d) cross-section of the WE43+CS+MAO sample.

Elemental mapping analysis images conducted at the cross-section of the WE43+CS+MAO sample are presented in Figure 5.7 for Al, O, Fe, Cr, and Mg elements. While alumina particles were clearly detected at the CSed layer beneath the oxidized coating in elemental mapping images of Al and O, the presence of stainless steel particles was also confirmed by the elemental mapping images of Fe and Cr. MAO layer on the WE43+CS+MAO sample exhibited uniform and dense characteris-

tics without any discontinuities. Additionally, no difference in the elemental composition, which results in distinguishing coatings as inner and outer layer, was observed in the WE43+CS+MAO sample.

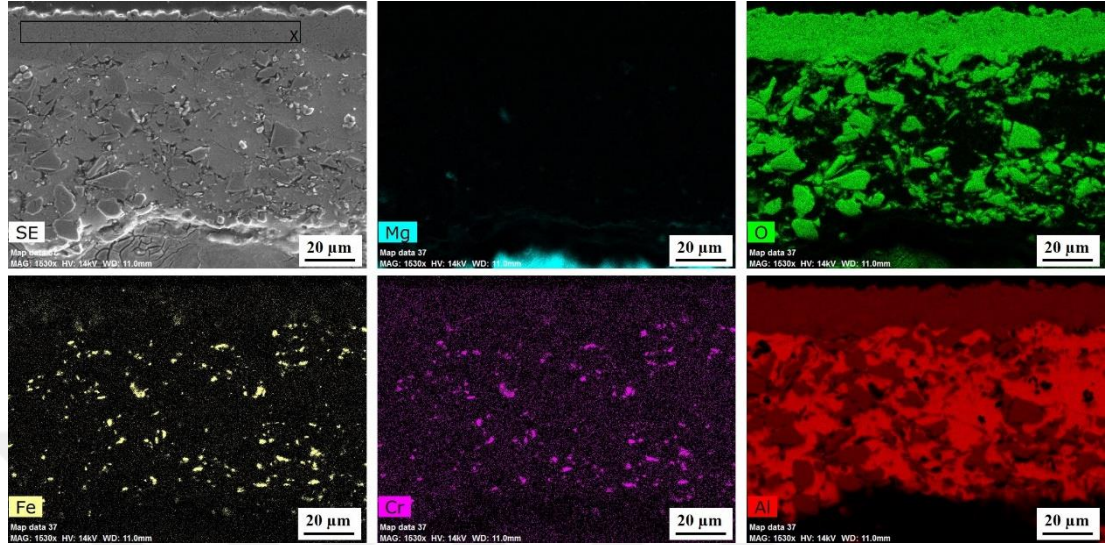


Figure 5.7: Elemental mapping analysis of the WE43+CS+MAO sample showing the presence of Al, O, Fe, Cr, and Mg.

In order to reveal the elemental composition of the MAO coating on the WE43+CS+MAO sample, EDS analysis was conducted in the region X shown in Figure 5.7. According to the EDS analysis results listed in Table 5.2, the MAO coating produced on the CSed composite layer consisted of ~ 59.2 at. % O and ~ 39.3 at. % Al, which is almost the exact stoichiometry of Al_2O_3 (60 at. % O and 40 at. % Al).

Table 5.2: Results of the EDS analysis conducted in Region X of the cross-section of the WE43+CS+MAO sample.

Element	Region X (at. %)
O	59.175
Al	39.278
Mg	0.633
Fe	0.342
Na	0.340
K	0.035
Ni	0.117
Cr	0.077

The hardness of the WE43+CS+MAO sample was measured as $1129 \pm 102 \text{ HV}_{0.025}$ from the cross-section and middle of the coating layer. The result of the hardness measurements for the WE43+CS+MAO sample is in agreement with the literature for MAO coatings on Al and its alloys. More specifically, Tazegül et al. [17] also reported that the hardness of the MAO coating produced on 20 vol. % alumina reinforced Al matrix composite CSed layer was in the range of 500 to 1500 $\text{HV}_{0.025}$ from the surface to the MAO/CS interface. When the middle section of the coating is of concern, the coating hardness was measured as 1200-1300 $\text{HV}_{0.025}$, which indicates similar hardness measurements found in this study. They also reported that MAO coatings produced on the composite CSed layer exhibited higher hardness value as compared to that of the monolithic CSed layer. Although the amount of alumina particle reinforcement in the CSed layer was higher in WE43+CS+MAO sample as compared to that of Tazegül et al., coatings exhibited similar hardness values mainly due to higher MAO processing time (20 min) which in turn resulted in thicker and denser coatings in the study of Tazegül et al. [17].

Considering the higher thickness and lower porosity of WE43+CS+MAO coating as compared to WE43+MAO sample, it is suggested that the formation of stronger discharges (especially B-type) caused generation of more porous coating layer for WE43+MAO sample. In addition to its porous nature, presence of the magnesia, having a lower hardness than that of alumina [12,13], on the surface WE43+MAO sample resulted in remarkably lower hardness than that of WE43+CS+MAO sample.

5.2 Electrochemical Corrosion Behaviour

Figure 5.8 presents the potentiodynamic polarization curves for the examined samples immersed in 3.5 wt. % NaCl media. After using the Tafel extrapolation method, anodic (β_a) and cathodic (β_c) Tafel constants, corrosion current density (I_{corr}), and corrosion potential (E_{corr}) of the examined samples were determined as listed in Table 5.3. Also, polarization resistance (R_p) of the WE43 alloy, WE43+CS, WE43+MAO, and WE43+CS+MAO samples calculated by using the Stern-Geary equation are given in Table 5.3.

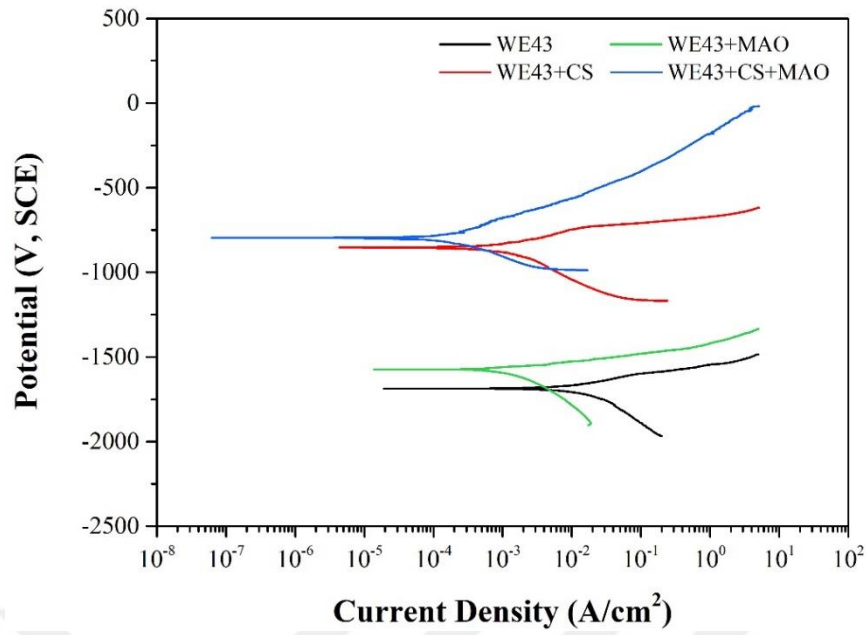


Figure 5.8: Potentiodynamic polarization curves for the examined samples tested in 3.5 wt. % NaCl solution.

When the corrosion potentials of the examined samples are of concern, almost two times higher values were observed for WE43+CS and WE43+CS+MAO samples as compared to WE43 and WE43+MAO samples, mainly due to the higher stability of the Al and alumina than that of Mg and magnesia. On the other hand, the corrosion current density of the WE43 alloy was remarkably decreased by application of MAO process (WE43+MAO). At the same time, the WE43+CS+MAO sample exhibited lowest corrosion current density owing to the presence of alumina coating on its surface. Although significant increment in polarization resistance of WE43 alloy was achieved in the WE43+MAO sample by the application of MAO process due to the formation of a stable ceramic layer on its surface, the polarization resistance of the WE43+CS+MAO sample was 73 times higher than that of WE43 alloy.

Table 5.3: Results of the potentiodynamic polarization tests conducted on the examined samples in 3.5 wt. % NaCl solution.

Sample	E_{corr} (V _{SCE})	I_{corr} (A/cm ²)	β_a (V _{SCE} / decade)	β_c (V _{SCE} / decade)	R_p (Ω /cm ²)
WE43	-1.69	1.61×10^{-5}	0.1219	0.2408	2182.7
WE43+CS	-0.854	1.09×10^{-6}	0.1080	0.1883	27341.5
WE43+MAO	-1.57	1.23×10^{-6}	0.0485	0.2126	13941.2
WE43+CS+MAO	-0.797	2.59×10^{-7}	0.1905	0.1895	159267.4

On the other hand, the potentiodynamic polarization behaviour of the WE43+CS sample was matched well with the findings of the study conducted by Tao et al., who investigated the corrosion behaviour of CSed 50 wt.% alumina particle reinforced Al matrix composite coatings on AZ91 alloy in 3.5 wt. % NaCl media [67]. They reported that the application of CS could provide remarkable improvement in corrosion resistance of the AZ91 alloy. Similarly, the WE43+CS sample exhibited better resistance against corrosion in 3.5 wt.% NaCl media with more lower current density and higher corrosion potential. Additionally, the corrosion performance of the WE43+MAO sample was worse than WE43+CS sample due to limited protection ability of the porous oxide layer on the surface.

WE43+CS+MAO sample exhibited better corrosion resistance as compared to the WE43+MAO sample due to the bigger pores and thinner coating layer of the WE43+MAO sample than that of WE43+CS+MAO sample. It was also reported by Arrabal et al. that the coating produced on WE3 alloy showed limited corrosion protection due to the porous inner layer in its structure [8]. This observation is in agreement with the findings of the present study. Furthermore, alumina layer having high stability on the surface of the WE43+CS+MAO also provided remarkably higher protection against corrosion as compared to the magnesia containing WE43+MAO sample, as similarly stated by Tazegül et al. [17].

Results of the potentiodynamic polarization tests conducted in 3.5 wt.% NaCl media revealed that the presence of the alumina layer on the surface of the WE43 was more beneficial to protect the surface against corrosion rather than the magnesia layer.

5.3 Wear Behaviour

The wear performance of MAO coatings produced on WE43 and CSed WE43 alloy was determined by investigating the effects of testing load and testing temperature. In order to compare the wear resistance of the MAO coatings, WE43 and WE43+CS samples were also subjected to the wear tests along with WE43+MAO and WE43+CS+MAO samples. Results of the wear tests conducted on the examined sample to determine their wear behaviour under the effect of testing load and testing temperature are presented in the following sections.

5.3.1 Effect of the testing load

Figure 5.9 shows the variation in friction coefficient with sliding distance recorded during the wear testing at room temperature under the load of 1 and 4 N for the examined samples. At first glance, the lowest friction coefficient values were recorded for the WE43+CS+MAO sample under both testing condition.

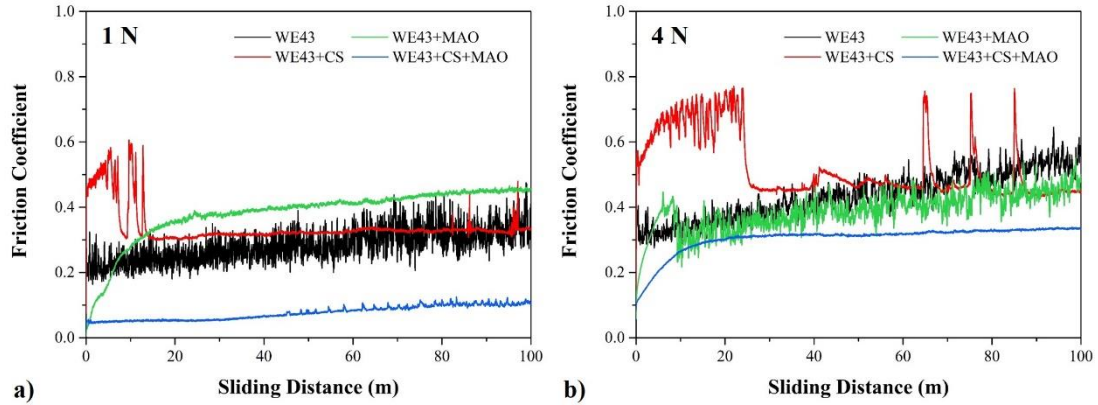


Figure 5.9: Friction curves of the examined samples tested at the load of (a) 1 N and (b) 4 N.

The friction curve of the WE43 alloy for both testing loads exhibited fluctuation as an evidence of the stick-slip phenomenon [68]. Additionally, the friction coefficient value for the WE43 sample increased with increasing testing load. On the other hand, the friction curve of the WE43+CS sample tested at 1 N also fluctuated after running-in, and became stable at the certain sliding distance. At the higher testing load (4 N), the WE43+CS sample's friction curve also stabilized after a long time from running-in. While the friction curve of WE43+CS sample exhibited smooth appearance after a certain sliding distance at 1 N, some sudden changes in the friction coefficient were observed when tested at 4 N. It is suggested that smoothening in the friction curve of the WE43+CS alloy could be related to the formation of the tribo-chemical layer on the contact surface. When the testing load increased, some local detachments might be taken place in that tribo-layer, which can be seen as a sudden increment in the friction curve of the WE43+CS sample tested at 4 N (Figure 5.9b). Increment in the testing load also led to an increase in the friction coefficient of the WE43+CS sample.

The friction curve of the WE43+MAO sample exhibited smooth appearance when tested at the load of 1 N, while steady-state friction was realized at the sliding distance of about 20 m after running-in. On the other hand, smooth appearance of the friction curve recorded during testing at 4 N was changed at the sliding distance of about 10 m

after running-in and the friction curve started fluctuating similar to WE43 substrate. This observation can be associated with the removal of the coating which in turn resulting in metal/ceramic (substrate/counterface) contact. Although the friction curves of the WE43+CS+MAO sample displayed smooth appearances under both testing loads due to ceramic/ceramic sliding contact, friction coefficient remarkably increased with increasing testing load to 4 N.

2-D profiles of the wear tracks formed on the examined samples' contact surface of after testing at 1 and 4 N are given in Figure 5.10. The depth of the wear track formed on the WE43 sample was the highest for both testing conditions while WE43+CS+MAO sample had the smallest wear track depth. Even though WE43+MAO sample exhibited almost identical wear track profile with WE43+CS+MAO sample after testing at 1 N (Figure 5.10a), depth of the wear track was measured as about 258 μm after testing at 4 N indicating the coating layer ($\sim 15 \mu\text{m}$) on its surface was exceeded during testing (Figure 5.10b). In order to make a quantitative comparison in the wear resistance of the examined samples, specific wear rates calculated from the 2-D profiles of the samples tested at the load of 1 and 4 N are listed in Table 5.4.

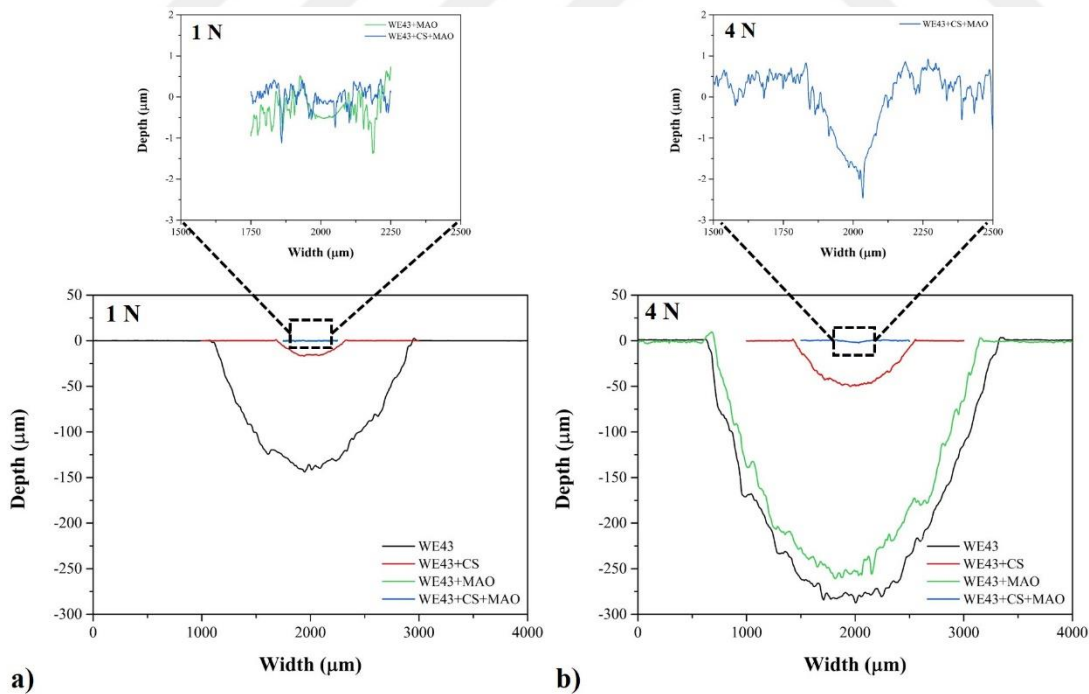


Figure 5.10: 2-D profiles taken from the wear tracks of the examined samples tested at the load of (a) 1 N and (b) 4 N.

Table 5.4: Calculated specific wear rates and the max. depth of the wear tracks of the examined samples tested at 1 and 4 N.

Sample	Specific Wear Rate ($\times 10^{-7}$ mm ³ /Nm)		Max. Depth of the Wear Track (μ m)	
	1 N	4 N	1 N	4 N
WE43	34405.9 $\pm$ 639	26004.8 $\pm$ 978	~ 142	~ 287
WE43+CS	1398.5 $\pm$ 67	1875.9 $\pm$ 33	~ 17	~ 49
WE43+MAO	9.9 $\pm$ 2.8	22048.1 $\pm$ 1200	~ 0.5	~ 258
WE43+CS+MAO	2.6 $\pm$ 0.6	12.7 $\pm$ 0.5	~ 0.2	~ 2

In the case of WE43 sample, the specific wear rate was found significantly high due to the lower wear resistance of Mg alloys arising from their low hardness and crystal structure (HCP). The specific wear rate of the WE43 alloy was remarkably decreased by the application of alumina reinforced Al composite layer on its surface via CS technique. In this respect, specific wear rate of the WE43+CS sample was 25 times and 15 times lower than that WE43 sample at the testing load of 1 N and 4 N, respectively. Furthermore, MAO application led to a significant decrease (~3500 times) in the wear rate, especially for the case of testing at 1 N. While the WE43+MAO sample exhibited a competitive wear rate with WE43+CS+MAO sample under the testing load of 1 N, an increase in the testing load caused a drastic increment in the wear rate of the WE43+MAO sample. For both testing loads, the WE43+CS+MAO sample exhibited the lowest specific wear rate owing to its highest surface hardness arising from its compact ceramic nature.

In order to determine the wear mechanism, worn surface of the examined samples tested at the load of 1 N was investigated. SEM images taken from the samples' worn surfaces at low (X60) and high (X1000) magnifications are presented in Figure 5.11. Furthermore, OM images showing the wear scars formed on the counterface's contact surface used in testing at 1 N are also given in Figure 5.12. When the WE43 Mg alloy is of concern, grooves, flakes and some products of tribo-chemical reactions were detected on the worn surface. Detection of the flaking and the delaminated regions indicated that, the contact surface of the WE43 alloy was subjected to severe plastic deformation by the ploughing action of alumina counterface, which was also realized as grooves on the worn surface [69]. Additionally, the darkening of the contact surface of the counterface slid on the WE43 alloy at the testing load of 1 N was realized as an indication of the material transfer from WE43 alloy to alumina counterface [70]. In

light of these observations, the operative wear mechanism of the WE43 alloy was identified as plastic deformation and adhesive wear with the evidence of flaking and material transfer along with the stick-slip phenomenon that occurred on the friction curve (Figure 5.9a).

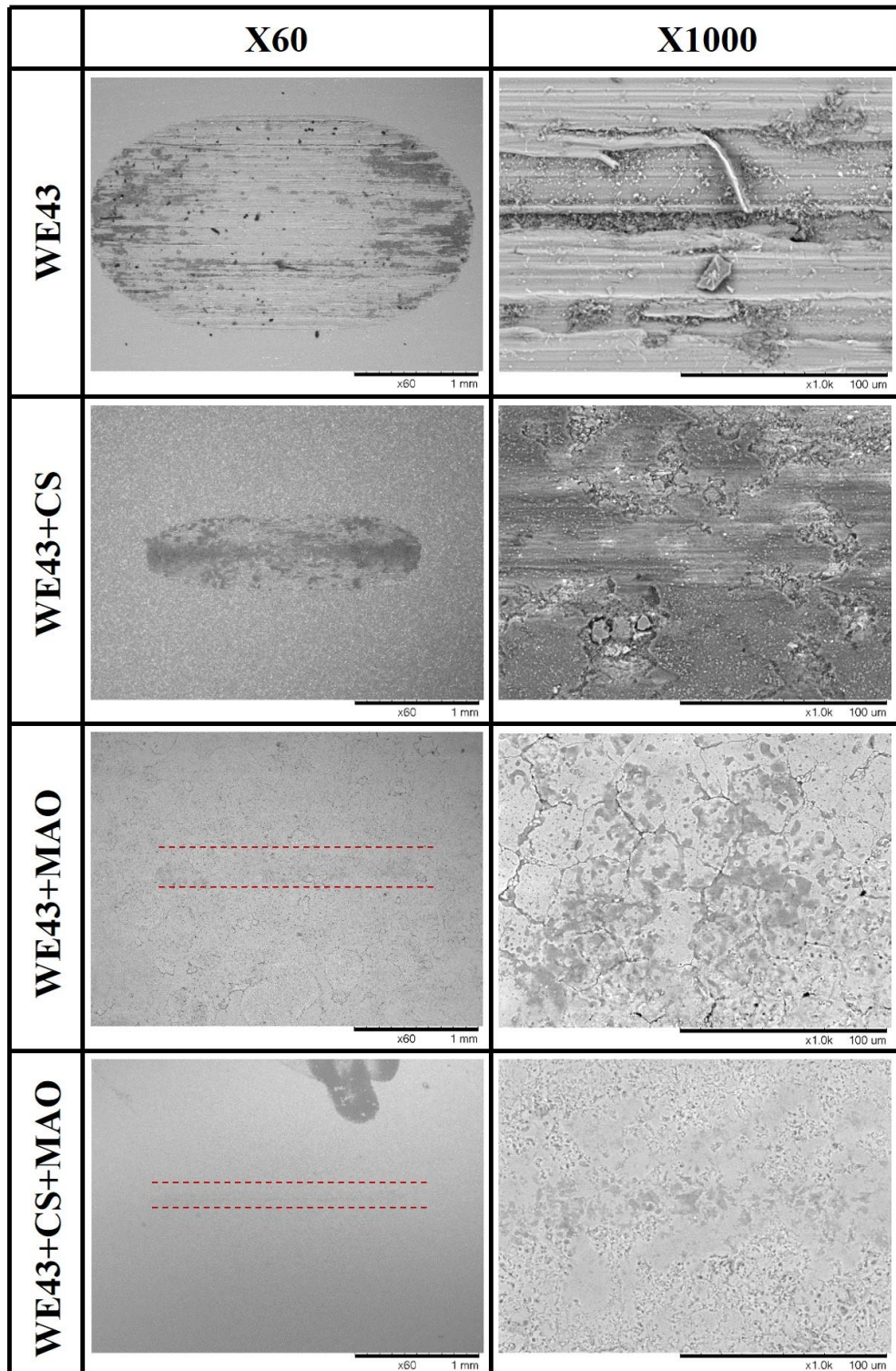


Figure 5.11: Worn surface SEM images of the examined samples tested at the load of 1 N.

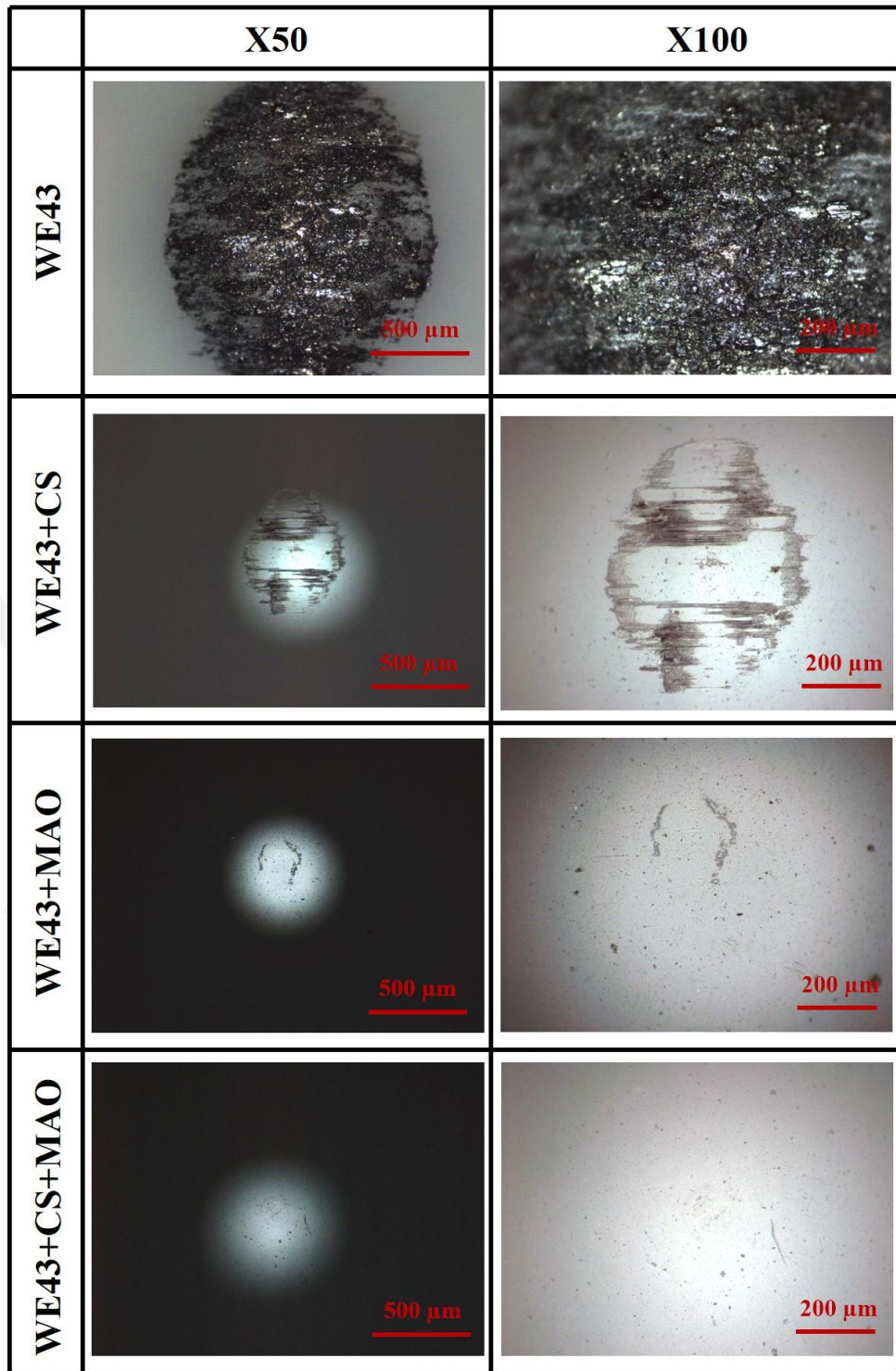


Figure 5.12: OM images of the wear scars formed on the alumina ball counterfaces used in wear testing of the examined samples at a load of 1 N.

On the other hand, worn surface of the WE43+CS sample was fully covered with dark tribo-chemical layer, which was reported as tribo-oxides in the open literature [71,72]. This observation was in good agreement with a sharp decrease in the friction curve of the WE43+CS sample after running-in (Figure 5.9a) due to the lubricious effect of the

formed tribo-oxide layer. Although no detachment of alumina particles from Al matrix was observed, partial delamination was detected on the worn surface of the WE43+CS sample along with micro-grooves. The contact surface of the counterface used in the testing of WE43+CS sample at 1 N was partially covered with the darker layer, especially at the edges of the wear scar. The dominant wear mechanism under the testing load of 1 N was determined as oxidative wear and delamination for the WE43+CS sample.

In the case of MAOed samples, wear track formed on the contact surface of MAOed samples were hardly recognized and remarkably narrower than that of WE43 and WE43+CS samples similarly observed in the 2-D profiles of wear tracks (Figure 5.10a). On the worn surfaces of MAOed samples, only polishing was realized without any detachment and/or delamination. Unlike the WE43+CS+MAO sample, micro-cracks network was detected on the contact surface of WE43+MAO sample. However, the surface of the WE43+MAO sample had already exhibited network like micro-cracks before the wear tests (Figure 5.2b). Thus, it is suggested that sliding motion of the alumina counterface could play a role in propagation of the existent cracks. When the counterfaces used in the testing of the MAOed samples are of concern, wear scar formed on the contact surface was also hardly recognized and no evidence of material transfer was realized.

SEM images at low (X60) and high (X1000) magnifications taken from the worn surfaces of the examined samples are depicted in Figure 5.13. In contrast, OM images of the wear scars formed on the contact surface of the alumina ball used in wear tests at 4 N are given in Figure 5.14. It is noticed that worn surface of the WE3 sample tested at 4 N and contact surface of the alumina ball slid on the WE43 sample exhibited similar characteristics with that of the WE43 sample tested at 1 N. This observation indicated that the dominant wear mechanism for WE43 alloy (plastic deformation and adhesive wear) did not shift with increasing testing load. Similar to the WE43 alloy, the contact surface of the alumina ball and the worn surface of the WE43+CS sample tested at 4 N displayed identical features with that of tested at 1 N. However, covering of the contact surface with tribo-oxide layer and delamination were more dominant for the WE43+CS sample tested at 4 N. Thus, the operative wear mechanism of the WE43+CS sample under the testing load of 4 N was similarly determined as oxidative wear and delamination.

On the other hand, increase in the testing load resulted in the complete removal of the MAO layer on the surface of WE43+MAO sample as can be evidently seen on the contact surface of the WE43+MAO sample tested at 4 N. At high magnification SEM images, the contact surface of the WE43+MAO sample exhibited grooves and flakes in similar to the WE43 substrate, as an evidence of severe plastic deformation by the ploughing action of alumina ball. This observation is in good agreement with the friction curve indicating ceramic/metal contact (Figure 5.1b) and 2-D profile (Figure 5.2b) of the WE43+MAO sample tested at 4 N. In addition, the contact surface of the counterface used in the testing of WE43+CS sample was covered with darker layer as an indication of material transfer. After wear testing at 4 N, the dominant wear mechanism of the WE43+MAO sample was shifted from polishing to plastic deformation and adhesive wear by the complete removal of the MAO coating from the surface.

Unlike to WE43+MAO sample, the worn surface of the WE43+CS+MAO sample tested at 1 N exhibited identical characteristics with that of tested at 1 N. Additionally, the contact surface of the alumina ball slid on the WE43+CS+MAO sample had smooth appearance without any sign of the material transfer. Although increasing the testing load to 4 N made the wear track of the WE43+CS+MAO sample more apparent, no remarkable difference in the wear mechanism was revealed.

Application of CSed composite layer on the WE43 alloy successfully improved its wear resistance while providing ceramic/composite contact rather than ceramic metal contact, which dominated plastic deformation and adhesion. On the other hand, MAO coatings producing porous oxide layer on the surface drastically decreased the wear loss of the WE43 alloy under the testing load of 1 N due to the oxide layer's higher hardness and stability. The lower wear resistance of the WE43 alloy and WE43+CS sample tested at 1 N than MAOed samples can be related to their lower hardness. However, the WE43+MAO sample exhibited almost similar wear behaviour of the WE43 substrate under the testing load of 4 N, indicating that MAO coating could not protect the surface against high contact stresses. Unlike the WE43+MAO sample, the MAO coating on the CSed WE43 alloy containing alumina provided sufficient resistance against wear even under the high contact stresses. This observation can be correlated with the higher hardness of the alumina than magnesia.

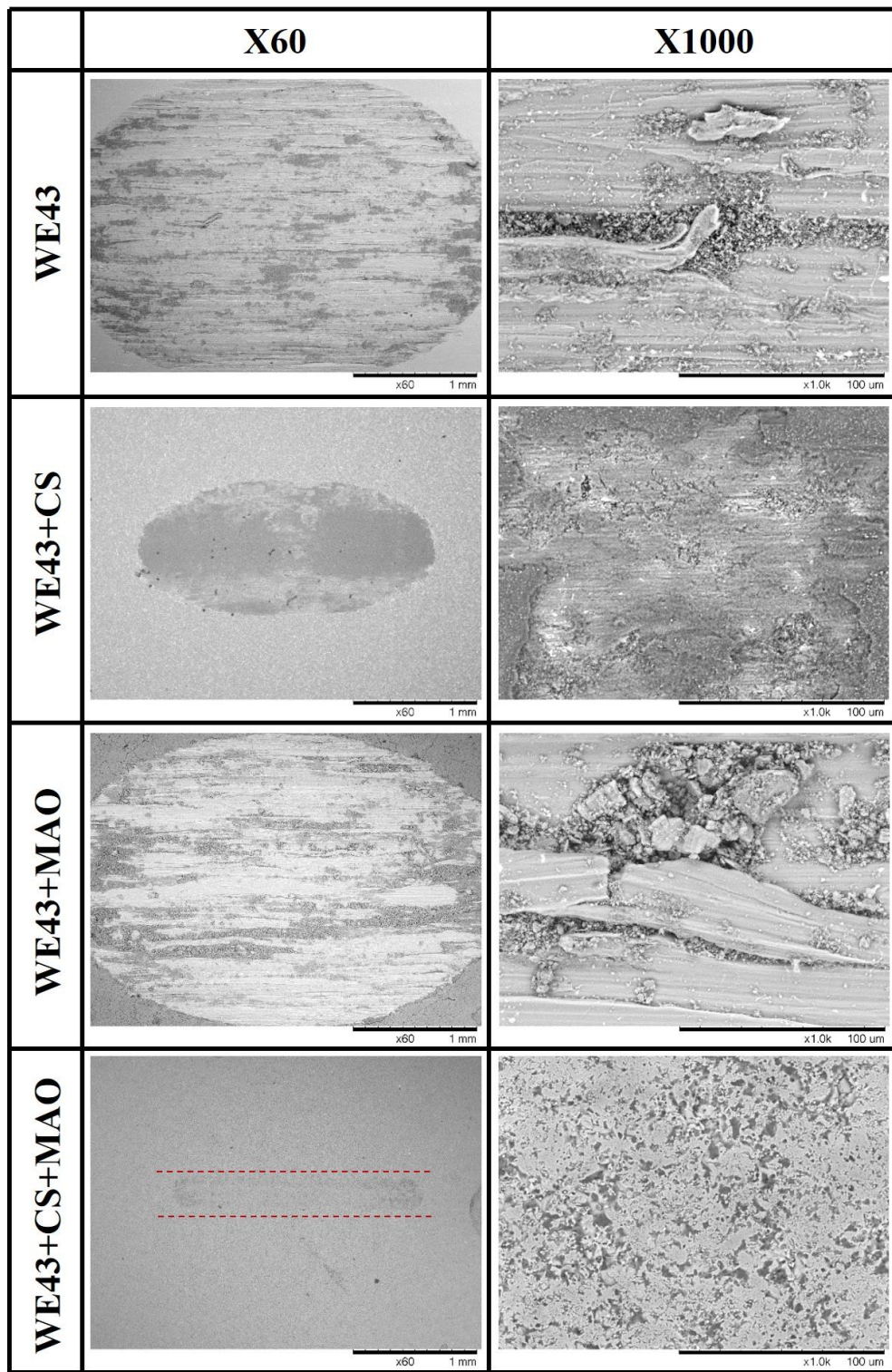


Figure 5.13: Worn surface SEM images of the examined samples tested at the load of 4 N.

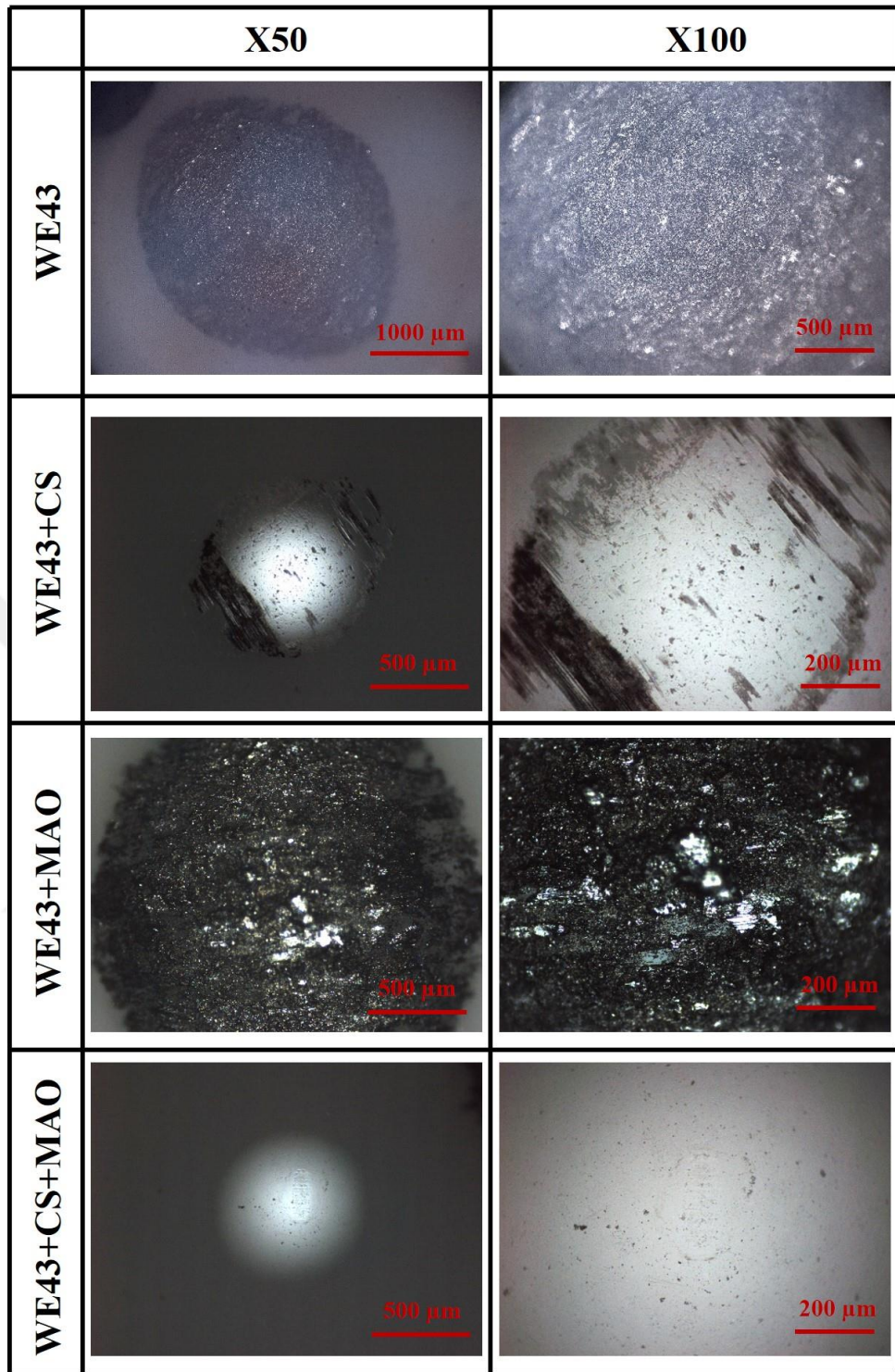


Figure 5.14: OM images of the wear scars formed on the alumina ball counterfaces used in wear testing of the examined samples at a load of 4 N.

With the aim of understanding the effect of the contact stresses on the wear behaviour and determining the depth of the maximum shear stress beneath the surface, calculations were made for the examined samples tested at the load of 1 and 4 N according to

the Hertz contact mechanics theory [73]. Details about calculation and elastic properties of the materials [74–77] are given in Appendix A. The calculated contact stresses and depth of the maximum shear stress exposing beneath the surface are listed in Table 5.5. When the WE43+MAO sample is of concern, the depth of shear stress beneath the surface during wear testing at 4 N was calculated as 17 μm , which is above the thickness of the coating ($\sim 15 \mu\text{m}$). This observation can explain why the complete removal of the WE43+MAO sample after wear testing under the load of 4 N.

Table 5.5: Results of the contact stress and depth of the maximum shear stress calculations for the examined samples tested at 1 and 4 N.

Sample	Contact Stress (MPa)		Depth of the Max. Shear Stress (μm)		Coating Thickness (μm)
	1 N	4 N	1 N	4 N	
WE43	336.6	534.3	18	28	-
WE43+CS	740.9	1176	12	19	~ 300
WE43+MAO	785.7	1247.3	11	17	~ 16
WE43+CS+MAO	887.8	1409.2	11	17	~ 19

5.3.2 Effect of the testing temperature

The variation in friction coefficient with sliding distance recorded during ball-on-disc wear tests of the samples under the load of 2 N at the temperature of 25 °C, 250 °C, and 320 °C is shown in Figure 5.15. At first glance, the WE43 alloy's friction curve for both testing temperatures exhibited fluctuation as evidence of the stick-slip phenomenon similar to the reciprocating wear tests. Also, it should be noticed that increase in the testing temperature did not affect the friction coefficient of the WE43 alloy. On the other hand, the WE43+CS sample exhibited the highest friction coefficient for all testing conditions. More specifically, friction curve of the WE43+CS sample sharply increased after running-in and then became stable when tested at 25 °C (Figure 5.15a) similarly in the case of reciprocating wear tests (Figure 5.9). However, the friction curve of the WE43+CS sample tested at high temperatures (250 and 320 °C) fluctuated roughly and increased with sliding distance. Apart from WE43 and WE43+CS samples, MAOed samples exhibited smooth appearances, as an indication of ceramic/ceramic contact, when tested at 25 °C. When the monolayer WE43+MAO sample is of concern, increase in the testing temperature led the friction curve to fluctuate roughly

after sliding distance of about 5 m. This observation suggested that metal/ceramic contact occurred on the contact surface of the WE43+MAO sample tested at 250 °C due to the removal of the MAO layer. Unlike the WE43+MAO sample, the multilayer WE43+CS+MAO sample displayed a smooth friction curve for all testing temperatures.

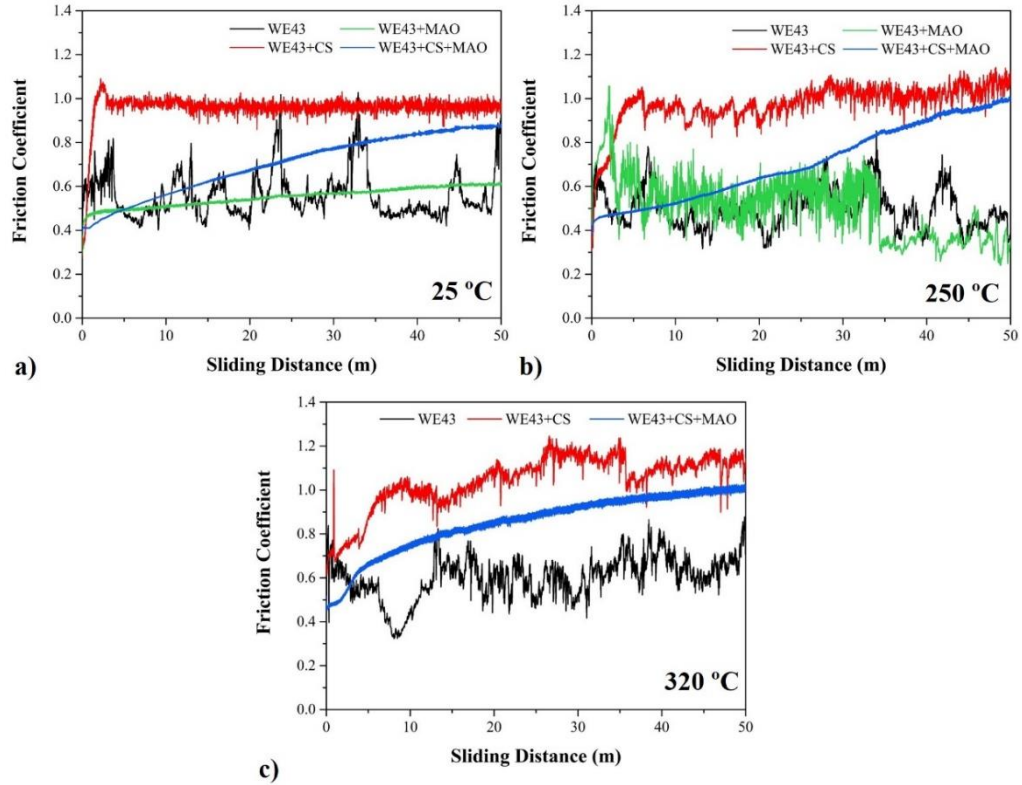


Figure 5.15: Friction curves of the samples tested at (a) 25 °C, (b) 250 °C, and (c) 320 °C.

2-D profiles of the wear tracks formed on the contact surface of the samples after testing at the temperature of 25 °C, 250 °C and 320 °C are depicted in Figure 5.16. The average depth of the wear track formed on the WE43+CS+MAO sample was the lowest for both testing conditions. When the 2-D profiles of the samples tested at 25 °C are of concern (Figure 5.16a), the WE43+MAO sample exhibited almost identical wear track profiles with the WE43+CS+MAO sample. However, increase in the testing temperature to 250 °C resulted in a dramatic increase in the depth of the wear track of the WE43+MAO sample to ~50 μm . Thus, the WE43+MAO sample exhibited an almost similar 2-D profile with WE43 substrate as evidence of complete removal of the coating layer having a thickness of ~15 μm .

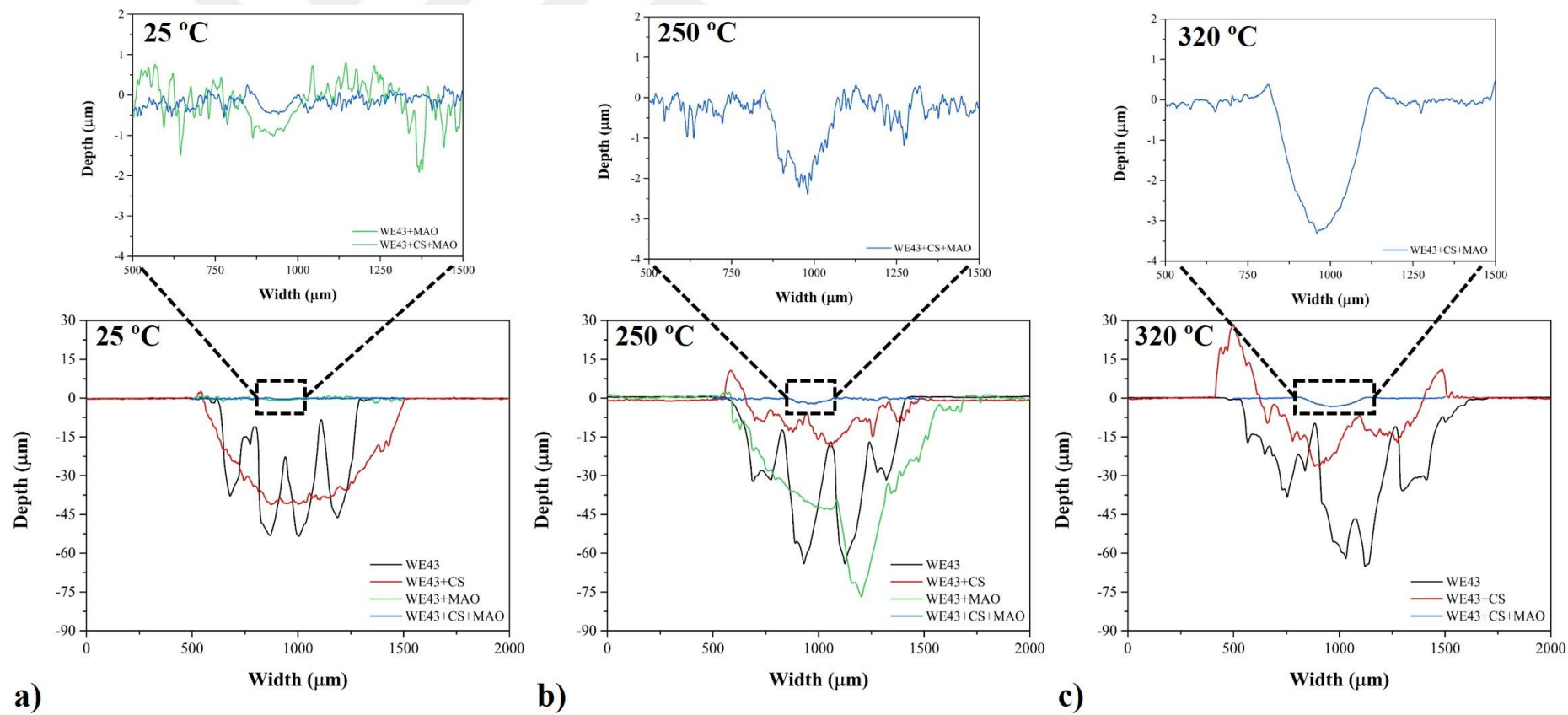


Figure 5.16: 2-D profiles taken from the wear tracks of the examined samples tested at (a) 25 °C, (b) 250 °C, and (c) 320 °C.

On the other hand, increase in the testing temperature to 320 °C only caused a slight increment in the wear track depth of the WE43+CS+MAO sample, and wear track became more evident with increasing temperature. It should be noted that because of the complete removal of the coating layer from the surface of the WE43+MAO sample after testing at 250 °C, WE43+MAO sample did not be tested at the higher temperature (320 °C). Among the other samples, 2-D profiles of the WE43+CS sample tested at high temperatures show rough appearance, and pile-ups at the borders of the wear tracks were realized. This observation can be related to oxidation and plastic deformation.

The specific wear rate of the samples tested at 25 °C, 250 °C, and 320 °C are listed in Table 5.6 to make a quantitative comparison. First of all, it can be seen that specific wear rate of the WE43 alloy tested under the load of 2 N increased with testing temperature. Nevertheless, no remarkable change was realized, indicating that the operative wear mechanism of WE43 alloy was not shifted with increasing temperature to 320 °C. While the specific wear rate of the WE43+CS sample was almost identical to WE43 alloy at room temperature, an increase in the testing temperature led 4 times decrement in the specific wear rate of the WE43+CS sample. It is suggested that this dramatic decrease could be related with heavy oxidation on the contact surface.

Table 5.6: Calculated specific wear rates of the examined samples tested at 25 °C, 250 °C, and 320 °C.

Sample	Specific Wear Rate ($\times 10^{-7}$ mm ³ /Nm)		
	25 °C	250 °C	320 °C
WE43	32279.4 $\pm$ 926	41296.7 $\pm$ 761	39369.7 $\pm$ 6843
WE43+CS	38542.1 $\pm$ 7001	10543.6 $\pm$ 596	14045.1 $\pm$ 2677
WE43+MAO	160.4 $\pm$ 53	49641.2 $\pm$ 7007	Not-tested
WE43+CS+MAO	75.2 $\pm$ 31	448.8 $\pm$ 62	895.9 $\pm$ 115

Although MAOed samples tested at 25 °C showed nearly similar specific wear rate results, the specific wear rate of the WE43+MAO sample drastically increased about 300 times with increasing testing temperature to 250 °C. This observation can be accompanied by complete removal of the coating layer as visualized in the friction curve

and 2-D profiles of the WE43+MAO sample (Figure 5.15b and Figure 5.16b, respectively). When WE43+CS+MAO sample is considered, the lowest specific wear rate was measured for all testing conditions. More specifically, the WE43+CS+MAO sample exhibited 44 times lower specific wear rate as compared to WE43 alloy substrate when tested at the temperature of 320 °C. From this point of view, the WE43+CS+MAO sample having the multilayer coating structure shows the best performance under dry sliding condition at high temperatures. Similar to reciprocating wear test results, ball-on-disc wear tests also confirmed that multilayer coating having a hard and dense alumina layer on its surface could successfully protect WE43 alloy against wear up to 320 °C. In comparison, the porous and relatively soft magnesia based monolayer coating failed at 250 °C.

Worn surface BSE-SEM images at X150, X1000, and X2500 magnifications taken from the WE43 alloy are presented in Figure 5.17 after wear testing at 25 °C, 250 °C and 320 °C. On the contact surface of the WE43 alloy tested at 25 °C, grooves and flakes formed by the ploughing action of the alumina ball were detected as evidence of heavy plastic deformation. On the other hand, similar to the reciprocating wear tests, the counterface's contact surface was covered with a darker layer indicating material transfer from WE43 alloy to alumina ball. An increase in the testing temperature resulted in the formation of wider grooves on the contact surface of the WE43 alloy. This observation suggested that plastic deformation took place easily with the aid of additional slip systems triggered by temperature increase. At higher magnification SEM images, delaminated regions were also realized for both testing conditions. Similar to the reciprocating wear tests, the operative wear mechanism of the WE43 alloy was identified as plastic deformation and adhesive wear with the shreds of evidence of flaking and material transfer in addition to the stick-slip phenomenon occurred on the friction curve (Figure 5.15). Even though plastic deformation became more dominant at the higher temperature, increment in the testing temperature to 320 °C had no effect on the shifting of the wear mechanism which was confirmed by the specific wear rate results (Table 5.6) and the friction curves (Figure 5.15).

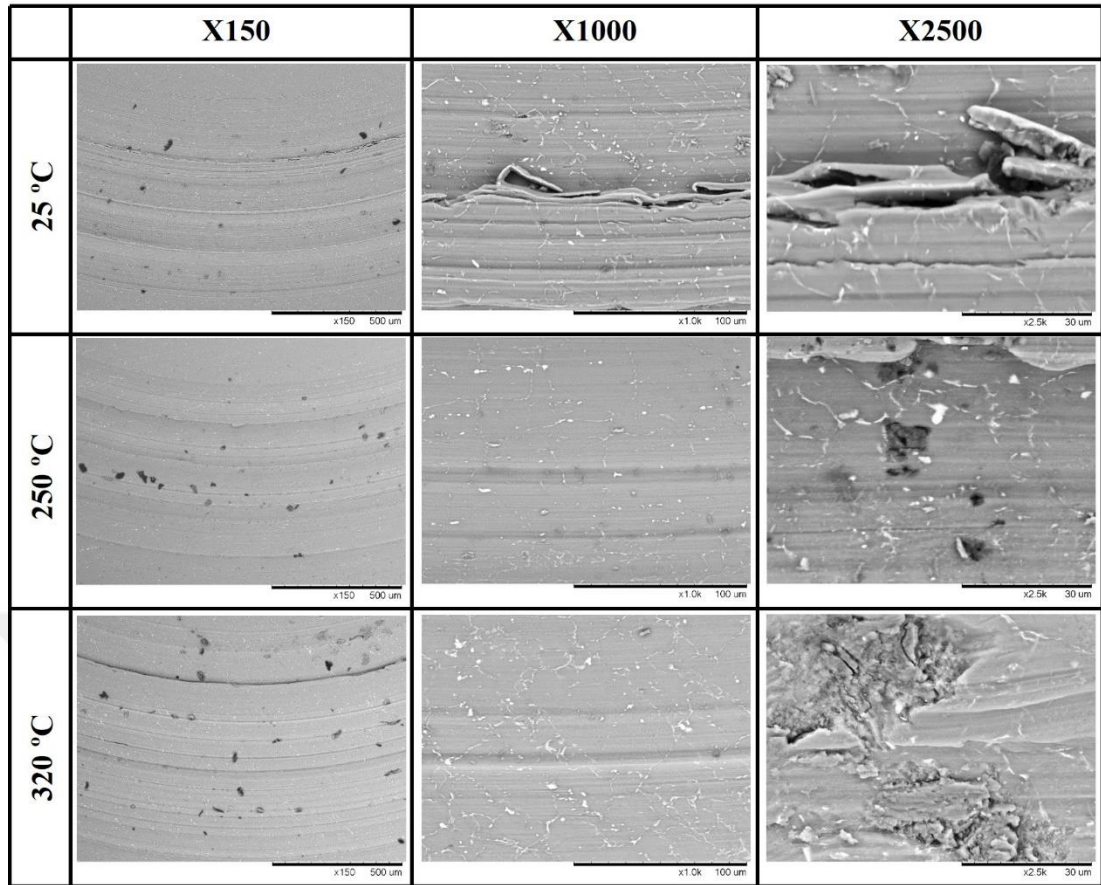


Figure 5.17: BSE-SEM images taken from the worn surface of the WE43 sample after wear testing at 25 °C, 250 °C, and 320 °C.

SEM images at X150, X1000, and X2500 magnifications taken from the worn surfaces of WE43+CS sample tested at 25 °C, 250 °C, and 320 °C are given in Figure 5.18. When the low magnification images are of concern, it is clearly seen that the contact surfaces of the WE43+CS samples were covered with a darker layer (tribo-oxide layer) for all conditions. Also, the tribo-oxide layer became thicker and denser with increasing testing temperature, possibly due to the high reaction rate triggered with temperature. On the other hand, the tribo-oxide layer accumulation at the borders of the wear tracks of WE43+CS sample tested at 250 and 320 °C was realized. This observation can be associated with 2-D profiles of the wear tracks (Figure 5.16b and c). While the tribo-oxides at the wear track of the WE43+CS sample tested at 250 °C seemed to be dense and adherent, some detachment of this layer was detected on the worn surface of the WE43+CS sample tested at 320 °C. After testing at 25 °C, only fine grooves and stable tribo-layer was realized on the worn surface of the WE43+MAO sample. Additionally, no detachment of alumina particles from the matrix and no cracking of the alumina particles were visualized. However, increasing temperature resulted in the

delamination on the contact surface of the WE43+CS sample, especially for the sample tested at 320 °C. This observation can be associated with heavy plastic deformation and also accompanied by friction curves, and 2-D profiles of the sample tested at 250 °C and 320 °C. Apart from heavy plastic deformation, cracking of the alumina particles was also realized along with the hole formation at the particle/matrix interface. When the wear rate results are of concern, it is interestingly seen that the wear rate of the WE43+CS sample decreased dramatically with increasing the testing temperature to 250 °C. This observation is related to the formation of the tribo-oxide layer on the contact surface as confirmed by SEM images. This result is also in good agreement with previous studies reported by Wilson and Alpas [78]. They stated that after a certain temperature, which corresponds to flow stress decrease, operative wear mechanism of Al alloys and Al matrix composites under dry sliding conditions transformed from mild wear to severe wear. Moreover, this transformation temperature could be increased with the ceramic particle addition. From their study, 20 vol. % Al_2O_3 reinforced 6061 Al alloy matrix composite showed mild to severe wear transition at 300 °C. In the present study, although the increase in the testing temperature from 250 °C to 320 °C resulted in a slight increment in the wear rate, more tests should be conducted at higher temperatures (>320 °C) to determine the critical temperature. But, from this point of view, if we consider the high magnification SEM images, slight traces of severe wear such as delamination was realized at the contact surface of the WE43+CS sample tested at 320 °C. Thus the operative wear mechanism of the WE43+CS sample was determined as mild wear with oxidation up to 250 °C. At 320 °C, the wear mechanism was identified as mild to severe wear transition.

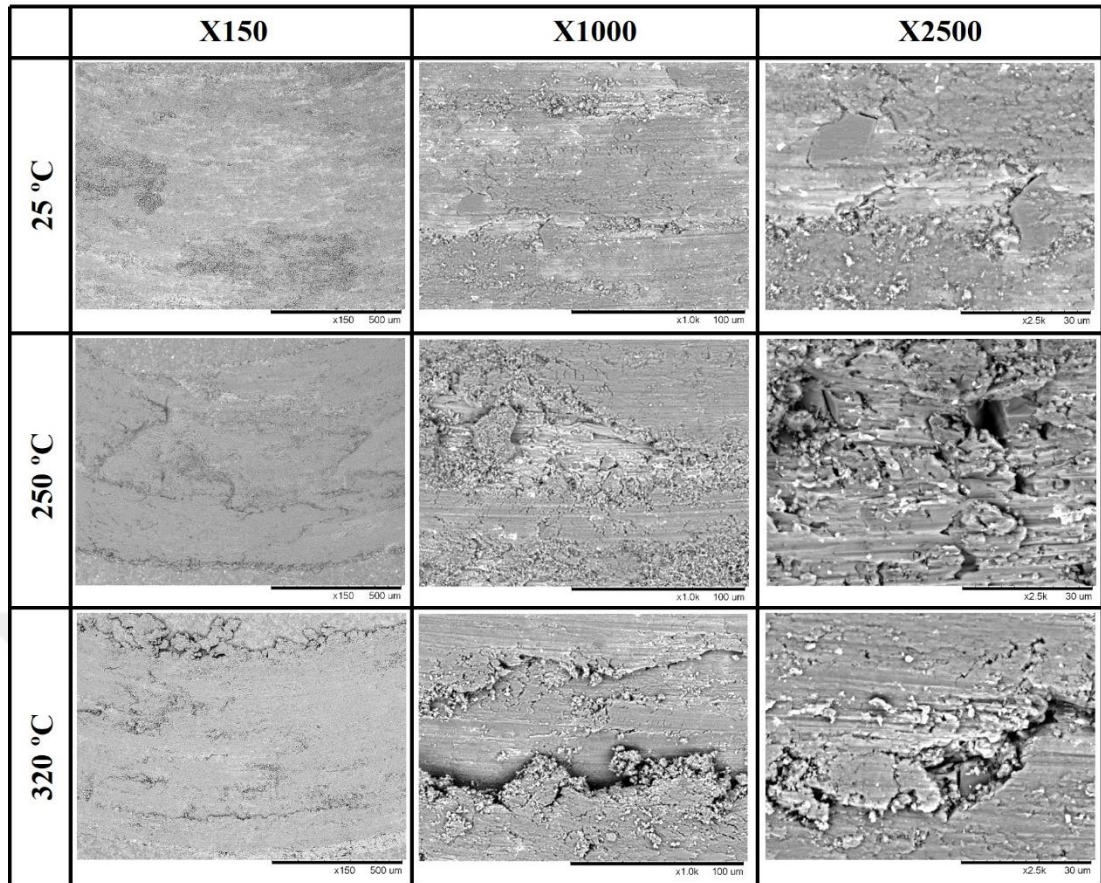


Figure 5.18: Worn surface SEM images of the WE43+CS sample tested at the temperature of 25 °C, 250 °C, and 320 °C.

On the one hand, contact surface BSE- SEM images of the WE43+MAO sample tested at 25 °C and 250 °C are presented in Figure 5.19. The worn surface of the WE43+MAO sample tested at 25 °C exhibited similar characteristics with the sample tested by reciprocating tribometer. Thus, polishing the contact surface by the sliding motion of alumina counterface was visualized along with few micro-cracks as a typical characteristic of ceramic/ceramic contact. However, the wear track formed on the contact surface of the WE43+MAO sample tested at 250 °C seemed brighter than the un-worn surface, indicating metal surface was exposed to sliding contact after complete removal of the MAO coating. Abrasive grooves, flakes, and delaminated regions at the worn surface also demonstrated that metal/ceramic contact was established after complete removal of the MAO coating, which can also be accompanied by friction curve (Figure 5.15b) and 2-D profile of the wear track (Figure 5.16b).

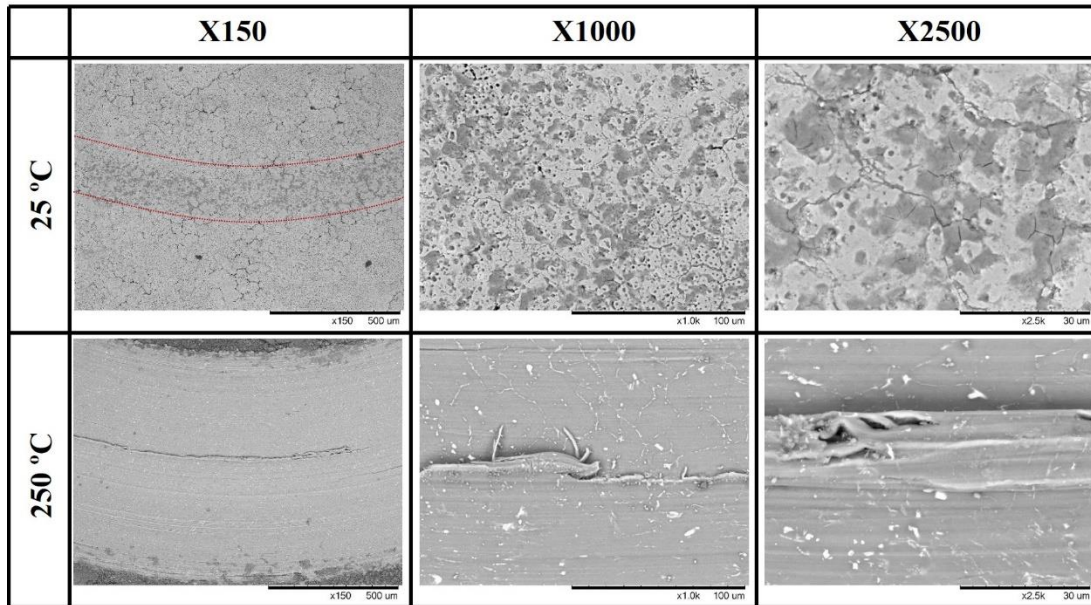


Figure 5.19: Worn surface SEM images of the WE43+MAO sample tested at the temperature of 25 °C and 250 °C.

Figure 5.20 shows SEM images at X150, X1000, and X2500 magnifications taken from the worn surface of the WE43+CS+MAO sample tested at 25 °C, 250 °C, and 320 °C. When the low magnification SEM images taken from the contact surface are of concern, it was difficult to notice the wear track of the sample tested at 25 °C and wear track became more evident with increasing testing temperature. At higher magnification SEM images of the sample tested at 25 °C, only polishing of the contact surface was realized. At the same time, micro cracks were detected at the borders of the wear tracks of the sample tested at high temperatures. It should be notified that the amount of the micro-cracks was higher at the contact surface of the sample tested at 320 °C than that of 250 °C. Although micro-cracks were appeared on the edges of the wear tracks (as marked in Figure 5.20 with dashed lines), no spallation or delamination was detected on the contact surface of the sample tested at high temperatures. Considering cracks, which are formed at the edges of the wear tracks, it should be recognized that this type of cracks generated during sliding contact could be referred as chevron type tensile cracks. This type cracks formed at the contact surface when the hard indenter slides on the surface under the normal load due to the tensile stresses generated on the surface. It is also interestingly noticed that these cracks were not formed on the worn surface when the sample tested at room temperature even in the higher testing load (reciprocating test, 4 N). It is suggested that the underlying layer of the coating

softened with increasing testing temperature and could not provide sufficient resistance for the coating layer, which in turn resulted in the formation of the tensile cracks at the surroundings of the contact surface.

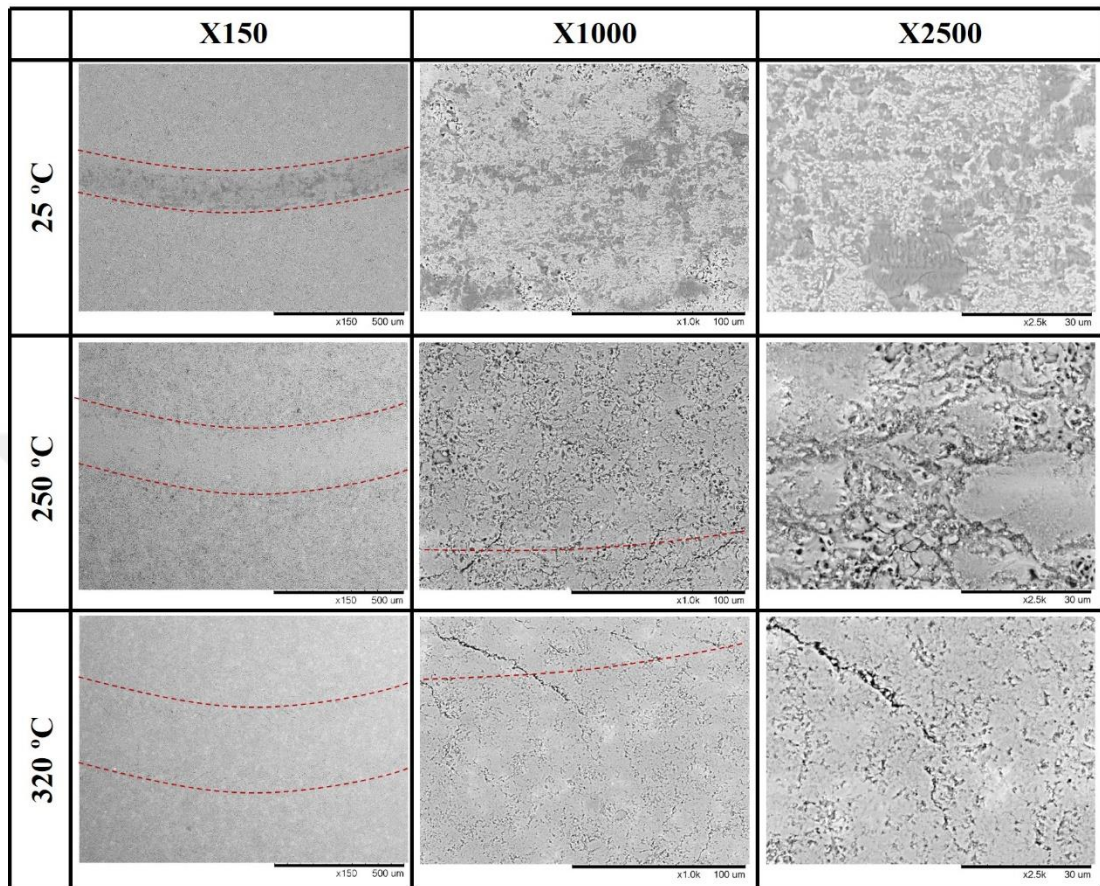


Figure 5.20: Worn surface SEM images of the WE43+CS+MAO sample tested at the temperature of 25 °C, 250 °C, and 320 °C



6. CONCLUSIONS

In this study, corrosion resistance, room and high temperature wear behaviour of bare WE43 alloy, CSed WE43 alloy, monolayer magnesium oxide-based, and multilayer aluminium oxide-based MAO coated WE43 alloy were investigated. On the basis of the findings of these examinations, conclusions can be summarized as follows.

- MAO process was successfully applied on the WE43 and CSed WE43 alloy, and eventually “monolayer” magnesium oxide-based ($\sim 16\ \mu\text{m}$) and “multilayer” aluminium oxide-based ($\sim 19\ \mu\text{m}$) coatings were obtained. WE43+MAO sample contained magnesium oxide and magnesium aluminate phases on its surface, while the outermost surface of the WE43+CS+MAO sample consisted of alpha- and gamma-alumina phases. The average hardness of the MAO coatings was measured as $311\ \text{HV}_{0.025}$ and $1129\ \text{HV}_{0.025}$ for WE43+MAO and WE43+CS+MAO sample, respectively. It should be noted that lower hardness of the magnesium oxide than that of aluminium oxide along with its porous nature played a crucial role in the lower hardness of the WE43+MAO sample.
- MAO coated and CSed samples yielded remarkably higher corrosion resistance than that of bare WE43 alloy in 3.5 wt. % NaCl media. But, WE43+CS+MAO sample exhibited the highest corrosion resistance owing to higher chemical stability of the alumina than magnesia and the dense nature of the multilayer coating along with good interfacial bonding with the underlying CSed layer. The lower compactness of the magnesium oxide and its higher porosity could result in the lower corrosion resistance of the WE43+MAO sample as compared to the WE43+CS+MAO sample.
- Room temperature dry sliding wear tests under the load of 1 N revealed that wear resistance of the WE43 alloy was significantly improved by both individual and combined application of CS and MAO processes. However, WE43+CS+MAO sample exhibited the highest wear resistance up to the load of 4 N. In contrast, WE43+MAO sample could not protect the surface of WE43 alloy against wear at 4 N. The operative wear mechanism of the WE43 alloy

was determined as plastic deformation dominated adhesive wear while the oxidative wear was dominant for the WE43+CS sample. On the other hand, the WE43+MAO sample exhibited a brittle fracture mechanism under dry sliding condition while the only polishing effect of the counterface was detected for the WE43+CS+MAO sample. The lower wear resistance and durability of the WE43+MAO sample as compared to the WE43+CS sample can be related with its lower hardness and higher porosity.

- According to the results of high temperature wear tests, the WE43+CS+MAO sample showed the highest wear resistance up to 320 °C at 2 N under dry sliding condition, whilst the WE43+MAO sample failed when tested at 250 °C. Apart from the higher hardness of the WE43+CS+MAO sample, the multilayer structure of the coating could play a critical role in lowering thermal expansion coefficient differences between coating and substrate and improving load carrying capacity as compared to the monolayer coating.

REFERENCES

- [1] **Mordike, B. L., and Ebert, T.** (2001). Magnesium Properties - applications - potential, *Materials Science and Engineering A*, 302, 37–45.
- [2] **Friedrich, H. E., Mordike B. L.** (2006). *Magnesium Technology: Metallurgy, Design Data, Applications*. Springer.
- [3] **King, J. F.** (2007). Magnesium: commodity or exotic?, *Materials Science and Technology*, 23, 1–14.
- [4] **Wu, L., and Yang, Z.** (2015). Oxidation behaviour of Mg-2.1Gd-1.1Y-0.82Zn-0.11Zr alloy at high temperatures, *Journal of Alloys and Compounds*, 626, 194–202.
- [5] **Jiang, B. L., and Ge Y. F.** (2013). Micro-arc oxidation (MAO) to improve the corrosion resistance of magnesium (Mg) alloys. In G. L. Song (Ed.), *Corrosion Prevention of Magnesium Alloy* (pp. 163–196), Oxford: Woodhead Publishing.
- [6] **Hussein, R. O., and Northwood, D. O.** (2014). Production of Anti-Corrosion Coatings on Light Alloys (Al, Mg, Ti) by Plasma-Electrolytic Oxidation (PEO). In M. Aliofkhazraei (Ed.), *Developments in Corrosion Protection* (pp 201-239), Intechopen.
- [7] **Dou, J., Chen, Y., Yu, H., Chen, C.** (2017). Research status of magnesium alloys by micro-arc oxidation: a review, *Surface Engineering*, 33, 731–738.
- [8] **Arrabal, R., Matykina, E., Viejo, F., Skeldon, P., Thompson G. E.** (2008). Corrosion resistance of WE43 and AZ91D magnesium alloys with phosphate PEO coatings, *Corrosion Science*, 50, 1744–1752.
- [9] **Arrabal, R., Matykina, E., Hashimoto, T., Skeldon, P., Thompson G. E.** (2009). Characterization of AC PEO coatings on magnesium alloys, *Surface and Coatings Technology*, 203, 2207–2220.
- [10] **Tekin, K. C., Malayoğlu, U., Shrestha, S.** (2013) Electrochemical behavior of plasma electrolytic oxide coatings on rare earth element containing Mg alloys, *Surface and Coatings Technology*, 236, 540–549.
- [11] **Malayoğlu, U., and Tekin, K. C.** (2017). Wear behaviour of plasma electrolytic oxide coatings on E21 and WE43 Mg alloys, *Surface Engineering*, 31 (7), 526-533.
- [12] **Loubet, J. L., Georges, J. M., Machesini, O., Meille, G.** (1984). Vickers indentation curves of magnesium oxide (MgO), *Journal of Tribology and Transactions ASME*, 106, 43–48.
- [13] **Nie, X., Meletis, E. I., Jiang, J. C., Leyland, A., Yerokhin, A. L., Matthews, A.** (2002). Abrasive wear/corrosion properties and TEM analysis of Al₂O₃ coatings fabricated using plasma electrolysis, *Surface and Coatings Technology*, 149 245–251.
- [14] **Thirumalaikumarasamy, D., Shanmugam, K., Balasubramanian, V.** (2014). Corrosion performance of atmospheric plasma sprayed alumina coatings on AZ31B magnesium alloy under immersion environment, *Journal of Asian Ceramic Society*, 2, 403–415

- [15] **Kumar, S., Kumar, A., Kumar, D., Jain, J.** (2017). Thermally sprayed alumina and ceria-doped-alumina coatings on AZ91 Mg alloy, *Surface and Coatings Technology*, 332, 533–541.
- [16] **Krishna, L. R., Poshal, G., Jyothirmayi, A., Sundararajan, G.** (2013). Compositionally modulated CGDS + MAO duplex coatings for corrosion protection of AZ91 magnesium alloy, *Journal of Alloys and Compounds*, 578, 355–361.
- [17] **Tazegül, O., Muhaffel, F., Meydanoğlu, O., Baydoğan, M., Kayalı, E. S., Cimenoglu, H.** (2014). Wear and corrosion characteristics of novel alumina coatings produced by micro arc oxidation on AZ91D magnesium alloy, *Surface and Coatings Technology*, 258, 168–173.
- [18] **Kainer, K. U.** (Ed.). (2003) *Magnesium – Alloys and Technology*, John Wiley & Sons.
- [19] **Luo, A. A.** (2013). Applications: Aerospace, automotive and other structural applications of magnesium, In M. O Pekgülyüz, K. U. Kainer, A. A. Kaya *Fundamentals of Magnesium Alloy Metallurgy* (pp. 266-316), Oxford : Woodhead Publishing Limited.
- [20] **Prabhu, T. R., Vedantam, S., Singh, V.** (2017). Magnesium Alloys, In N. E Prasad, and R. J. H. Wanhill (Eds.) *Aerospace Materials and Material Technologies* (Vol. 1. Vol. 1 Aerospace Materials p. 586.), Singapore : Springer Nature.
- [21] **Czerwinski, F.** (2014). Controlling the ignition and flammability of magnesium for aerospace applications, *Corrosion Science*, 86, 1–16.
- [22] **Polmear, I., Stjohn, D., Nie, J., Qian, M.** (2017). Magnesium alloys, In *Light Alloys: Metallurgy of the Light Metals* (5th ed.), Oxford, UK: Butterworth-Heinemann.
- [23] **Pekgülyüz, M.** (2013). Alloying behavior of magnesium and alloy design, In M. O Pekgülyüz, K. U. Kainer, A. A. Kaya (Eds.) *Fundamentals of Magnesium Alloy Metallurgy* (pp. 152-196), Oxford : Woodhead Publishing Limited.
- [24] **ASTM** (2018). *Standard Practice for Codification of Unalloyed Magnesium and Magnesium – Alloys, Cast and Wrought* (ASTM B951-11).
- [25] **Mordike, B. L.** (2002). Creep-resistant magnesium alloys, *Materials Science and Engineering A*, 324, 103–112.
- [26] **Kang, Y. H., Yan, H., Chen, R. S.** (2015) Effects of heat treatment on the precipitates and mechanical properties of sand-cast Mg-4Y-2.3Nd-1Gd-0.6Zr magnesium alloy, *Materials Science and Engineering A*, 645, 361–368.
- [27] **Cain, T., Bland, L. G., Birbilis, N., Scully, J. R.** (2014) A compilation of corrosion potentials for magnesium alloys, *Corrosion*, 70 (10), 1043–1051.
- [28] **Chu, P., and Marquis, E. A.** (2015). Linking the microstructure of a heat-treated WE43 Mg alloy with its corrosion behavior, *Corrosion Science*, 101, 94–104.
- [29] **Chen, H., and Alpas A. T.** (2000). Sliding wear map for the magnesium alloy Mg-9Al-0.9Zn (AZ91), *Wear*, 246, 106–116.
- [30] **An, J., Li, R. G., Lu, Y., Chen, C. M., Xu, Y., Chen, X., Wang, L. M.** (2008). Dry sliding wear behavior of magnesium alloys, *Wear*, 265, 97–104.
- [31] **Barylski, A., Kupka, M., Anio, K., Rak, J.** (2017), The effect of precipitation hardening on the structure and mechanical and tribological properties of magnesium alloy WE54, *Vacuum*, 139, 77–86.

- [32] **Xie, Z., Guo, F., Huang, X., Li, K., Chen, Q., Chen, Y.** (2020). Understanding the anti-wear mechanism of SiCp / WE43 magnesium matrix composite, *Vacuum*, 172, 109049.
- [33] **Li, C., Feng, X., Fan, X., Yu, X., Yin, Z., Kannan, M. B., Chen, X., Guan, S., Zhang, X., Zeng, R.** (2019). Corrosion and wear resistance of micro-arc oxidation composite coatings on magnesium alloy AZ31 — The influence of inclusions of carbon spheres, *Advanced Engineering Materials*, 21 (9), 1–16.
- [34] **Jie, J., and Huan, L.** (2017). Friction and wear behavior of micro arc oxidation coatings on magnesium alloy at high temperature, *Rare Metal Materials and Engineering*, 46, 1202–1206.
- [35] **Blawert, C., Sah, S. P., Scharnagl, N., Kannan, M. B.** (2015). Plasma electrolytic oxidation/micro-arc oxidation of magnesium and its alloys, In T. S. N. S. Narayanan, I. S. Park and M. H. Lee (Eds.) *Surface Modification of Magnesium and its Alloys for Biomedical Applications* (vol. 2 Modification and Coating Techniques, pp. 193–234), Oxford : Woodhead Publishing Limited.
- [36] **Muhaffel, F. and Çimenoglu, H.** (2019). Development of corrosion and wear resistant micro-arc oxidation coating on a magnesium alloy, *Surface and Coatings Technology*, 357, 822–832.
- [37] **Yerokhin, A. L., Nie, X., Leyland, A., Matthews, A., Dowey, S. J.** (1999) Plasma electrolysis for surface engineering, *Surface and Coatings Technology*, 122, 73–93.
- [38] **Qingbiao, L., Liang, J., Wang, Q.** (2013). Plasma Electrolytic Oxidation Coatings on Lightweight Metals, In M. Aliofkhazraei (Ed.) *Modern Surface Engineering Treatments* (pp.75–99), Intechopen.
- [39] **Salman, S. A., and Okido, M.** (2013). Anodization of magnesium (Mg) alloys to improve corrosion resistance, In G. L. Song (Ed.), *Corrosion Prevention of Magnesium Alloy* (pp. 197–231), Oxford: Woodhead Publishing.
- [40] **Song, G. L., and Shi, Z.** (2013). Anodization and corrosion of magnesium (Mg) alloys, In G. L. Song (Ed.), *Corrosion Prevention of Magnesium Alloy* (pp. 232–281), Oxford: Woodhead Publishing.
- [41] **Darband, G. B., Aliofkhazraei, M., Hamghalam, P., Valizade, N.** (2017). Plasma electrolytic oxidation of magnesium and its alloys : Mechanism , properties and applications, *Journal of Magnesium and Alloys*, 5, 74–132.
- [42] **Lu, X., Mohedano, M., Blawert, C., Matykina, E., Arrabal, R., Kainer, K. U., Zheludkevich, M. L.** (2016). Plasma electrolytic oxidation coatings with particle additions – A review, *Surface and Coatings Technology*, 307, 1165–1182.
- [43] **Birss, V., Xia, S., Yue, R., Rateick, R. G.** (2004), Characterization of Oxide Films Formed on Mg-Based WE43 Alloy Using AC/DC Anodization in Silicate Solutions, *Journal of Electrochemical Society*, 151(1), B1–B10.
- [44] **Liu, P., Pan, X., Yang, W., Cai, K., Chen, Y.** (2012). Improved anticorrosion of magnesium alloy via layer-by-layer self-assembly technique combined with micro-arc oxidation, *Materials Letters*, 75, 118–121.

- [45] **Imwinkelried, T., Beck, S., Iizuka, T., Schaller, B.** (2013). Effect of a plasmaelectrolytic coating on the strength retention of in vivo and in vitro degraded magnesium implants, *Acta Biomateriala*, 9, 8643–8649.
- [46] **Kröger, N., Kopp, A., Staudt, M., Rusu, M., Schuh, A.** (2018). Hemocompatibility of plasma electrolytic oxidation (PEO) coated Mg-RE and Mg-Zn-Ca alloys for vascular scaffold applications, *Materials Science and Engineering C*, 92, 819–826.
- [47] **Zhu, Y., Zhang, S., Zhao, R., Lou, J., Zhang, R., Huan, X.** (2018). Influences of Na₂SiO₃ and EDTA-ZnNa₂ concentration on properties of zinc-containing coatings on WE43 magnesium alloys, *Surface and Coatings Technology*, 356, 108–122.
- [48] **Shi, X., Zhu, Y., Zhang, S., Zhao, R., Zhang, R., Chen, L., Zhang, R.** (2020). Characteristics of selenium-containing coatings on WE43 magnesium alloy by micro-arc oxidation, *Materials Letters*, 261, 126944.
- [49] **Martin, J., Akoda, K., Ntomprougkidis, V., Ferry, O., Maizeray, A., Bastien, A., Brenot, P., Ezo, G., Henrion, G.** (2020). Duplex surface treatment of metallic alloys combining cold-spray and plasma electrolytic oxidation technologies, *Surface and Coatings Technology*, 392, 125756.
- [50] **Rao, Y., Wang, Q., Oka, D., Seshadri, C.** (2020). On the PEO treatment of cold sprayed 7075 aluminum alloy and its effects on mechanical, corrosion and dry sliding wear performances thereof, *Surface and Coatings Technology*, 83, 125271.
- [51] **Kumar, S., and Kumar, D.** (2018). Role of CeO₂ doping on tribological behavior of Al₂O₃ coated AZ91 alloy, *Surface and Coatings Technology*, 349, 462–469.
- [52] **Rzychoń, T., and Kielbus, A.** (2007). Microstructure of WE43 casting magnesium alloy, *Journal of Achievements in Materials and Manufacturing Engineering*, 21, 31–34.
- [53] **Mengucci, P., Barucca, G., Riontino, G., Lussana, D. Massazza, M. Ferragut, R., Aly, E. H.** (2008). Structure evolution of a WE43 Mg alloy submitted to different thermal treatments, *Materials Science and Engineering A*, 479, 37–44.
- [54] **Kang, Y. H., Wu, D., Chen, R. S., Han, E. S.** (2014). Microstructures and mechanical properties of the age hardened Mg-4.2Y-2.5Nd-1Gd-0.6Zr (WE43) microalloyed with Zn, *Journal of Magnesium and Alloys*, 2, 109–115.
- [55] **Li, H., Lv, F., Liang, X., Qi, Y., Zhu, Z., Zhang, Z.** (2016). Effect of heat treatment on microstructures and mechanical properties of a cast Mg-Y-Nd-Zr alloy, *Materials Science and Engineering A*, 667, 409–416.
- [56] **Xiang, C., Gupta, N., Coelho, P., Cho, K.** (2018). Effect of microstructure on tensile and compressive behavior of WE43 alloy in as cast and heat treated conditions, *Materials Science and Engineering A*, 710, 74–85.
- [57] **Ninlachart, J., Karmiol, Z., Chidambaram, D., Raja, K. S.** (2017). Effect of heat treatment conditions on the passivation behavior of WE43C Mg-Y-Nd alloy in chloride containing alkaline environments, *Journal of Magnesium and Alloys*, 5, 147–165.
- [58] **Kang, Y. H., Wang, X. X., Zhang, N., Yan, H., Chen, R. S.** (2017). Effect of initial temper on the creep behavior of precipitation-hardened WE43 alloy, *Materials Science and Engineering A*, 689, 419–426.

- [59] **Bhattacharyya, J. J., Wang, F., McQuade, P. J., Agnew, S. R.** (2017). Deformation and fracture behavior of Mg alloy, WE43, after various aging heat treatments, *Materials Science and Engineering A*, 705, 79–88.
- [60] **Winnicki, M., Małachowska, A., Piwowarczyk, T., Rutkowska-Gorczyca, M., Ambroziak, A.** (2016). The bond strength of Al + Al₂O₃ cermet coatings deposited by low-pressure cold spraying, *Archives of Civil and Mechanical Engineering*, 16, 743–752.
- [61] **Spencer, K., Fabijanic, D. M., Zhang, M. X.** (2009). The use of Al-Al₂O₃ cold spray coatings to improve the surface properties of magnesium alloys, *Surface and Coatings Technology*, 204, 336–344.
- [62] **Wang, Q., Spencer, K., Birbilis, N., Zhang, M. X.** (2010). The influence of ceramic particles on bond strength of cold spray composite coatings on AZ91 alloy substrate, *Surface and Coatings Technology*, 205, 50–56.
- [63] **Stern, M., and Geary, A. L.** (1957) Electrochemical Polarization: I. A theoretical analysis of the shape of polarization curves, *Journal of Electrochemical Society*, 104, 743–752.
- [64] **Wang, Y., Wei, D., Yu, J., Di, S.** (2014). Effects of Al₂O₃ nano-additive on performance of micro-arc oxidation coatings formed on AZ91D Mg alloy, *Journal of Materials Science and Technology*, 30, 984–990.
- [65] **Hsu, C. H., Teng, H. P., Lu, F. H.** (2011), Effects of addition of Al(NO₃)₃ to electrolytes on alumina coatings by plasma electrolytic oxidation, *Surface and Coatings Technology*, 205, 3677–3682.
- [66] **Arrabal, R., Moledano, M., Matykina, E., Pardo, A., Mingo, B., Merino, M. C.** (2015). Characterization and wear behaviour of PEO coatings on 6082-T6 aluminium alloy with incorporated α -Al₂O₃ particles, *Surface and Coatings Technology*, 269, 64–73.
- [67] **Tao, Y., Xiong, T., Sun, C., Jin, H., Du, H., Li, T.** (2009). Effect of α -Al₂O₃ on the properties of cold sprayed Al/ α -Al₂O₃ composite coatings on AZ91D magnesium alloy, *Applied Surface Science*, 256, 261–266.
- [68] **Bhushan, B.** (2000). *Modern Tribology Handbook* (vol. 1 Principles of Tribology), New York : CRC Press.
- [69] **Hutchings, I., and Shipway, P.** (2017). *Tribology: Friction and wear of engineering materials* (2nd ed.), Oxford : Butterworth-Heinemann.
- [70] **Muhaffel, F., Kaba, M., Cempura, G., Derin, B., Kruk, A., Atar, E., Çimenoglu, H.** (2019). Influence of alumina and zirconia incorporations on the structure and wear resistance of titania-based MAO coatings, *Surface and Coatings Technology*, 377, 124900.
- [71] **Pitchuka, S. B., Boesl, B., Zhang, C., Lahiri, D., Nieto, A., Sundararajan, G., Agarwal, A.** (2014). Dry sliding wear behavior of cold sprayed aluminum amorphous/nanocrystalline alloy coatings, *Surface and Coatings Technology*, 238, 118–125.
- [72] **Kumar, S., Reddy, S. K., Joshi, S. V.** (2017). Microstructure and performance of cold sprayed Al-SiC composite coatings with high fraction of particulates, *Surface and Coatings Technology*, 318, 62–71.
- [73] **Fischer-Cripps, A. C.** (2006). *Introduction to Contact Mechanics* (2nd ed.), New York : Springer.
- [74] **Auerkari, P.** (1996). Mechanical and physical properties of engineering alumina ceramics, Technical Research Centre of Finland, VTT Tiedotteita - Meddelanden - Research Notes.

- [75] **Url-1** <<http://www.matweb.com/search/DataSheet.aspx?MatGUID=5e37f01d3e7348b7a1fc020246668e64&ckck=1>>, date retrieved 21.05.2020.
- [76] **Url-2** <<http://www.matweb.com/search/DataSheet.aspx?MatGUID=4b8a8c13cf354fc5893a40cf8eca022c>>, date retrieved 21.05.2020.
- [77] **Url-3** <<http://www.matweb.com/search/DataSheet.aspx?MatGUID=0cd1edf33ac145ee93a0aa6fc666c0e0>>, date retrieved 21.05.2020.
- [78] **Wilson, S., and Alpas, A. T.,** (1996). Effect of temperature on the sliding wear performance of Al alloys and Al matrix composites, *Wear*, 196, 270–278.



APPENDICES

APPENDIX A: Hertzian Contact Stress Calculation



APPENDIX A

The contact pressure between the matting surface was calculated using Hertzian sphere-plane contact theory. In this theory, the contact area has been calculated using following equation (Equation A.1), where P is load, R is indenter radius and E^* is combined elastic modulus of indenter and material. Equation A.2 also represents the formula for calculating the combined elastic modulus.

$$a^3 = \frac{3PR}{4E^*} \quad (\text{Equation A.1})$$

$$\frac{1}{E^*} = \frac{(1-\nu^2)}{E} + \frac{(1-\nu'^2)}{E'} \quad (\text{Equation A.2})$$

After the above equations, the mean contact pressure at the contact area can be found as below (Equation A.3);

$$p_m = \frac{P}{\pi a^2} = \left[\frac{4E^*}{3\pi} \right] \frac{a}{R} \quad (\text{Equation A.3})$$

For the above mentioned calculations, sphere is selected as alumina ball counterface while the examined samples were selected as plane. In order to reveal the volume fraction of the alumina particles distributed in the Al matrix, WE43+CS sample was investigated by ImageJ analyzing program. After image analyzing, the cross-section of the WE43+CS sample can be seen in the right image of the Figure A.1, which presents an example of the image analyzing process. In this figure, alumina particles can be realized as blue color while the matrix is colored with gray. According to the volume fraction measurements, average amount of the alumina particles in the Al matrix was found as 49 %.

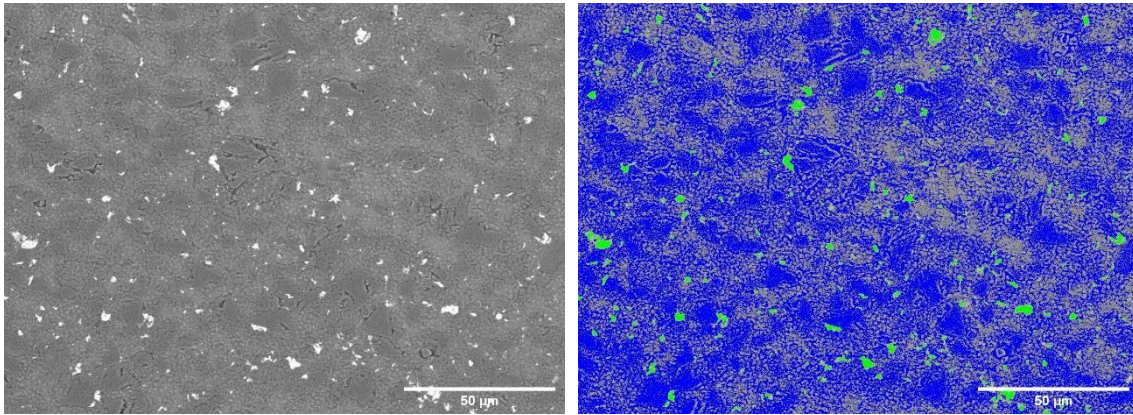


Figure A.1: An example of the volume fraction analysis of the WE43+CS sample.

In Table A.1, elastic properties of the pure Al, WE43 Mg alloy, alumina and magnesia are presented along with the WE43+CS sample, which was calculated from the rule of mixture.

Table A.2: Elastic properties of the materials.

Material	E (GPa)	Poisson Ratio
Mg (WE43)	44.2	0.27
Al	68	0.36
Al ₂ O ₃	340	0.24
(CS) Al + 49 vol.% Al ₂ O ₃	202.1	0.301
MgO	249	0.18



CIRRICULUM VITAE



Name- Surname : Mertcan KABA
Place and Date of Birth : Bursa – 11.10.1994
E-mail : mertcankaba@itu.edu.tr

EDUCATION:

- **BSc:** 2017, Dokuz Eylül University, Metallurgical and Materials Engineering

PROFESSIONAL EXPERIENCES AND REWARDS

- Research Assistant at ITU, Department of Metallurgical and Materials Engineering (2019-)

PUBLICATIONS, PRESENTATIONS AND PATENTS ON THE THESIS:

- **Kaba, M., Muhaffel, F., Malayoğlu, U., Çimenoglu, H.** 2019: Improving Wear Resistance of WE43 Magnesium Alloy by Combination of Cold Spray and Micro Arc Oxidation Technique, The International Conference on Materials Science, Machine and Automotive Engineerings and Technology, April 10-12, 2018 İzmir, Turkey.

OTHER PUBLICATIONS, PRESENTATIONS AND PATENTS:

- **Kaba, M., Donmez, A., Cukur, A., Kurban, A. F., Cubuklusu, H. E., Birol, Y.** 2018. AlSi5Mg0.3 Alloy for the manufacture of automotive wheels, *International Journal of Metalcasting*, 12(3), 614-624.
- **Muhaffel, F., Kaba, M., Cempura, G., Derin, B., Kruk, A., Atar, E., Cimenoglu, H.** 2019. Influence of alumina and zirconia incorporations on the structure and wear resistance of titania-based MAO coatings, *Surface and Coatings Technology*, 377, 124900.
- **Kaba, M., Altay, M., Çimenoglu, H.** 2020. An Investigation on the Longitudinal Cracking of Electric Resistance Welded Steel Pipes, *Journal of Failure Analysis and Prevention*, 20, 657-662.

