

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

**THERMAL OXIDATION OF TITANIUM-BASED COLD SPRAY
COATINGS FOR BIOLOGICAL AND WEAR-RELATED APPLICATIONS**



Ph.D. THESIS

Doğukan ÇETİNER

Department of Metallurgical and Materials Engineering

Metallurgical and Materials Engineering Programme

JUNE 2022

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(506142414)**

Department of Metallurgical and Materials Engineering

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**Thesis Advisor: Prof. Dr. Hüseyin ÇİMENÖĞLU
Thesis Co-Advisor: Prof. Dr. Erdem ATAR**

JUNE 2022

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

**BİYOLOJİK VE AŞINMAYA YÖNELİK UYGULAMALAR İÇİN SOĞUK
DİNAMİK GAZ PÜSKÜRTME TEKNİĞİ İLE ÜRETİLMİŞ TİTANYUM
BAZLI KAPLAMALARIN TERMAL OKSİDASYONU**

DOKTORA TEZİ

**Doğukan ÇETİNER
(506142414)**

Metalurji ve Malzeme Mühendisliği Anabilim Dalı

Metalurji ve Malzeme Mühendisliği Programı

**Tez Danışmanı: Prof. Dr. Hüseyin ÇİMENÖĞLU
Tez Eş Danışmanı: Prof. Dr. Erdem ATAR**

HAZİRAN 2022

Doğukan ÇETİNER, a Ph.D. student of ITU Graduate School student ID 506142414, successfully defended the thesis entitled “THERMAL OXIDATION OF TITANIUM-BASED COLD SPRAY COATINGS FOR BIOLOGICAL AND WEAR-RELATED APPLICATIONS”, 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**
İstanbul Technical University

Thesis Co-Advisor : **Prof. Dr. Erdem ATAR**
Gebze Technical University

Juri Members : **Prof. Dr. Mustafa Lutfi ÖVEÇOĞLU**
İstanbul Technical University

Prof. Dr. Murat BAYDOĞAN
İstanbul Technical University

Doç. Dr. İpek AKIN KARADAYI
İstanbul Technical University

Dr. Öğr. Üyesi Hakan YILMAZER
Yıldız Technical University

Dr. Amir MOTALLEBZADEH
Koç University

Date of Submission : 28 April 2022

Date of Defence : 01 June 2022





To My Family,



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Doğukan ÇETİNER
(Engineer)



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THERMAL OXIDATION OF TITANIUM-BASED COLD SPRAY COATINGS FOR BIOLOGICAL AND WEAR-RELATED APPLICATIONS

SUMMARY

The combination of strength, toughness and ductility makes metallic materials more preferable for engineering applications than ceramics and polymers. But the surface properties of metallic materials are insufficient for some of these applications. Thus, surface modification of metallic materials enables the keeping bulk properties with better surface facilities.

In this thesis, the aim is the surface modification of metallic materials (Co-Cr alloy and 316L stainless steel) via cold gas dynamic spraying (CS) system. CS enables the spraying of feedstock powders to the substrate with supersonic velocities. The collision of powders with the substrate leads to plastic deformation of powders and generates the coating formation over the substrate. Via the CS process, it is possible to deposit metallic, ceramic, polymer and composite coatings on different kinds of substrates. The application of the CS process on metallic materials generally purposes to improve the wear, corrosion and biological performance of these materials. In the scope of the thesis, the surface modification of Co-Cr alloy and S316L Stainless steel handled by Titanium-based CS coatings.

With the native oxide film forming on the Titanium and its alloys, these metals show high corrosion resistance and biocompatibility. Nevertheless, the thickness of the native oxide film is approximately 10nm and bad at wear applications. Thus, there is a need for a second treatment to make the oxide film more mechanically and chemically more stable. Thermal oxidation (TO) is a very cheap and practical method for Titanium-based materials' surface modification. TO enables the formation of relatively thick and protective oxide layers on Titanium-based materials. In the scope of the thesis, the feasibility of TO on CS'ed Titanium-based coatings is examined. Microstructural and mechanical characterisation and biological tests carried on the coatings manufactured the sequential application of CS and TO processes.

In the first section of the thesis, the feedstock was prepared by 92wt.% Titanium and 8wt.% Aluminium deposited on the ASTM F75 Co-Cr alloy via CS process. After that, TO applied these coatings at 600°C for 60h in the air atmosphere. The heating and cooling rate was kept very slow to minimise thermal stresses during the TO step. The results of microstructural examinations after the TO process proved that the outermost surface of the Titanium-based coating was covered by oxide film with a thickness of 3µm. The phase analysis showed that the oxide layer consists of the Rutile phase of TiO₂ and a minor amount of Al₂O₃. The coating showed better wear performance than the Co-Cr alloy during the wear tests conducted under 4N in dry sliding conditions. Furthermore, the bioactivity test conducted in simulated body fluid for 28 days proved that the bioactivity of the coating is way better than the Co-Cr substrate.

In the second study of the thesis, the same feedstock and substrate as the first study were used. As a difference from the first study, the microstructural changes in the inner

section of the coating were evaluated, and mechanical characterisation was done in more detail. During microstructural examinations, it was proved that the enrichment of Titanium with Oxygen took place beneath the oxide layer during the TO process. Furthermore, the reaction between neighbouring Titanium and Aluminium particles led to Ti-Al intermetallic at the inner coating section. All these reactions occurred during the TO process, making the section beneath the oxide layer harder than the deposited structure. The adhesion tests conducted under compression and shear loads proved that the oxide layer is well-adherent to the coating. The hardness of the oxide layer was measured as 1200HV via with depth-sensing method. At reciprocating wear tests conducted under 1-2-3N in dry and serum conditions, the coating produced by sequential application of CS and TO yielded higher wear resistance than the untreated Co-Cr substrate.

In the third section of the thesis, a work was initiated to examine the role of Zinc addition to the feedstock on the wear performance of the coating. For this purpose, CS feedstock was modified with different amounts of Zinc powders (2.5-5-10 wt.%). The microstructural examinations conducted on CS'ed coatings demonstrated that increment in zinc amount causes a decrement in the deposition efficiency during the CS process. The Zinc Oxide (ZnO) phase was detected along with TiO₂ and Al₂O₃ during the phase analyses conducted after the TO process. The accumulation of zinc particles in the different parts of the coating is also observed during the microstructural examinations. These sections of the coating are called "Zinc-rich regions". The phase change during/after the TO process was simulated by FactSage software for Zinc-rich and Zinc-poor regions. The main phase for zinc-reach regions after the TO process was simulated as ZnO, while the Zinc-poor regions were simulated as TiO₂, consistent with the XRD results. The wear tests conducted under 3N load in dry sliding conditions show that the coefficient of friction (COF) value can be decreased to 0.12 by adding 5wt.% Zinc to the feedstock.

In the final section of the thesis, the feedstock is reinforced with Silver to improve the biological performance of the coating. Silver is a well-known antibacterial metallic agent for biological applications. The feedstock prepared with 5wt.% Silver reinforcement was successfully deposited on 316L stainless steel via the CS process. The phase analysis conducted after the TO process proved that Silver still standing on the metallic form. Microstructural examinations have been shown that the Silver was not distributed homogenously around the coating. For mechanical evaluation, wear tests were applied under 1N load in dry and serum conditions to both coating and 316L substrate. The coating produced via sequential application of the CS and TO process yielded superior performance in both dry and serum conditions compared to the 316L substrate. Bioactivity tests proved that the coating was more bioactive than 316L stainless steel. The antibacterial efficiency of the coating was verified by the disc diffusion type test against *Staphylococcus aureus* (S. aureus) bacteria, and the antibacterial characteristics of the coating were supported by the release test of Silver ions. In this scope, the coating fabricated with 5wt.% reinforced feedstock could be a choice not only for the in-vivo applications but also the in-vitro applications where the hygiene of touch surfaces is essential such as door handles, touch plates, bed rails, and call buttons the hospitals.

In summary, with the combination of CS and TO processes, it is possible to modify surfaces of the metallic materials with Titanium-based coatings. The outermost surface of the coating is covered by an oxide layer mainly consisting of the Rutile form of TiO₂. The hardness of the oxide layer is approximately 1300HV, and this layer is well-

adherent to the coating. The tests conducted under different loads and in different conditions showed that the coatings yielded superior wear performance than the Co-Cr and 316L substrates. Furthermore, the bioactivity and antibacterial tests results indicate that these coatings can also be used in biological applications.





BİYOLOJİK VE AŞINMAYA YÖNELİK UYGULAMALAR İÇİN SOĞUK DİNAMİK GAZ PÜSKÜRTME TEKNİĞİ İLE ÜRETİLMİŞ TİTANYUM BAZLI KAPLAMALARIN TERMAL OKSİDASYONU

ÖZET

Metalik malzemelerden beklentiler farklı olmakla beraber genel olarak mukavemet, tokluk ve süneklik gibi kütsel özelliklerin kombinasyonu açısından seramik ve polimere nazaran daha cazip mühendislik malzemeleridir. Ancak bazı mühendislik uygulamalarında metalik malzemelerin yüzey özellikleri yetersiz kalmaktadır. Böyle durumlarda metalik malzemelerin mukavemet, tokluk ve süneklik gibi kütsel özellikleri korunarak yüzey özelliklerini geliştirmek için çeşitli yüzey modifikasyon tekniklerinin uygulanmasına gerek duyulmaktadır. Bu yüzey modifikasyon tekniklerine örnek olarak termal spray ve fiziksel buhar biriktirme verilebilir.

Bu tez çalışmasında 1980’li yılında geliştirilen Soğuk Dinamik Gaz Püskürtme (SDGP) yöntemi kullanılarak metalik altlıkların (Co-Cr alaşımı ve paslanmaz çelik) yüzey özelliklerinin geliştirilmesi amaçlanmıştır. SDGP yöntemi kaplanmak istenen tozların altlık malzeme yüzeyine yüksek hızlarda püskürtülmesi ve altlık malzemeye çarpan tozların plastik deformasyonu sonucu kaplama oluşması esasına dayanır. Sistem özelliklerine bağlı olarak bu yöntem ile metalik, seramik, polimer ve kompozit tozların malzeme yüzeylerinde biriktirilmesi mümkündür. SDGP yöntemi ile metalik malzemelerin yüzeyinde aşınma ve korozyon yüksek, insan vücudu ile biyoloji olarak daha uyumlu kaplamalar üretilebilmektedir. Tez çalışmasında bu tip uygulamalar için sıkça tercih edilen titanyum esaslı kaplamalar Co-Cr ve paslanmaz çelik altlıklar üzerinde biriktirilmiştir.

Titanyum esaslı alaşımlar yüzeylerinde doğal şartlarda oluşan oksit tabakası sayesinde korozyon direnci ve biyo-uyumluluk sergilemekle birlikte düşük aşınma direncine sahiptir. Titanyum metali üzerindeki bu oksit tabakasını mekanik ve kimyasal açıdan daha kararlı hale getirmek için ikincil bir işlem yapılması gerekmektedir. Termal oksidasyon (TO) titanyum ve alaşımların dış yüzeyinde nispeten kalın ve koruyucu titanyum oksit tabakası oluşturan basit ve pratik bir yöntemdir. Bu tez kapsamında Co-Cr ve 316L paslanmaz çelik altlıklar üzerinde SDGP tekniği ile biriktirilmiş titanyum esaslı kaplamalara TO işlemi uygulanarak en dış yüzeyinde Titanyum dioksit (TiO_2) tabakası oluşturulmuştur. Daha sonra iki adımlı (SDGP + TO) üretim yöntemiyle elde edilen kaplamanın karakterizasyonu yapılmış, mekanik ve biyolojik davranışları incelenmiştir.

Tez kapsamında yapılan çalışmaların birinci bölümünde ASTM F75 Kobalt-Krom (Co-Cr) alaşımı üzerine kütlece %92 Titanyum ve %8 Alüminyum içeren toz bileşimi SGDP yöntemi ile başarılı bir şekilde kaplanmıştır. Üretilen kaplamalara ikincil işlem olarak 600°C’de 60 saat TO uygulanmıştır. TO sırasında ısıl gerilmeler dolayısı ile meydana gelebilecek olumsuz durumlar kontrollü bir şekilde ısıtma ve soğutma ile minimize edilmeye çalışılmıştır. TO işlemi sonrası yapılan mikro yapısal incelemelerde yüzeyin en dış kısmında yaklaşık 3µm kalınlığında bir oksit tabakası

oluştugu görülmüştür. Faz analizinde bu oksit tabakasının TiO_2 (Rutil) yoğunluklu olduğu ve az miktarda Al_2O_3 içerdiği tespit edilmiştir. Kuru aşınma koşullarında 4N yük altında alümina bilye karşıt malzeme ile yapılan aşınma testlerinde iki adımlı proses ile üretilen kaplamanın aşınma direncinin Co-Cr altlık malzemeye ile kıyaslandığında çok daha iyi olduğu tespit edilmiştir. Biyoaktivite testi sürecinde yapay vücut sıvısı içerisinde 28 gün bekletilen TO kaplama ve Co-Cr altlık malzemenin yüzeyleri incelendiğinde TO kaplamanın Co-Cr altlık malzemeye göre daha biyo aktif davranış gösterdiği gözlemlenmiştir.

Tez kapsamında gerçekleştirilen çalışmaların ikinci bölümünde ilk bölümde kullanılan toz bileşimi ve üretim parametreleri tekrarlanarak Co-Cr altlık malzeme üzerinde kaplamalar üretilmiştir. Bu çalışmada TO işlemi sonrası kaplamanın iç bölümlerinde meydana gelen metalürjik değişimlere ışık tutulmasının yanı sıra kaplamanın detaylı mekanik karakterizasyonu da gerçekleştirilmiştir. TO sonucu kaplama yüzeyinde oluşan oksit tabakası altına da oksijen difüzyonun gerçekleştiği, bu kısımda titanyum kaplamanın oksijence zenginleştiği tespit edilmiştir. Ayrıca kaplama içerisinden yapılan faz analizlerinde komşu titanyum ve alüminyum partikülleri arasında meydana gelen reaksiyonlar sonucu içyapıda Ti-Al intermetaliklerinin olduğu belirlenmiştir. Kaplamanın iç kısımlarında Titanyumun oksijence zenginleşmesi ve Ti-Al intermetaliklerinin oluşumunun oksit tabakası altında kalan kısımda TO işlemi öncesine göre 4-5 katlık bir sertlik artışına yol açtığı görülmüştür. Oksit tabakası üzerinde yapılan yapışma deneylerinde, bu tabakanın kaplamaya çok iyi bir şekilde tutunmuş olduğu ve farklı yükleme koşullarında (kayma tipi ve basma tipi) bile bütünlüğünü koruduğu tespit edilmiştir. Oksit tabakasının sertliği derinli hassasiyetli olarak yaklaşık 1300 HV ölçülmüştür. Serum (%9'luk NaCl çözeltisi) içerisinde 1-2-3 N yük altında alümina karşıt malzeme ile yapılan aşınma deneylerinde üretilen kaplamaların sadece kuru ortamda değil, serum ortamında da Co-Cr altlık malzemeye göre daha iyi performans gösterildiği gözlemlenmiştir.

Tez kapsamında yapılan çalışmaların üçüncü bölümünde tribolojik uygulamalar için sürtünme katsayısı düşük kaplamalar üretmek hedeflenmiştir. Bu amaç doğrultusunda SDGP toz bileşimine titanyum ve alüminyumun yanı sıra farklı oranlarda (titanyum azaltılarak kütlece %2,5-5-10) çinko ilavesi yapılmıştır. SDGP prosesi üretilen kaplamalar mikro yapısal olarak incelendiğinde çinko ilavesi miktarı arttıkça kaplama verimliliğinde düşüş meydana geldiği gözlemlenmiştir. $600^{\circ}C$ 'de 60 saat gerçekleştirilen TO işleminde sonra yapılan faz analizlerinde yapıda TiO_2 ve Al_2O_3 'nın yanı sıra çinko-oksit (ZnO) fazı da tespit edilmiştir. TO sonrası yapılan mikro-yapısal incelemelerde ise çinko ağırlıklı yapıların kaplamanın bazı bölgelerinde yoğunlaştığı dikkat çekmiştir. Bu bölgelerin ve çinkonun daha az bulunduğu bölgelerin TO sırasında/sonrasında faz değişimlerini simüle etmek için FactSage programı kullanılmıştır. Simülasyon işleminde çinko ağırlıklı bölgelerde TO sonrası ağırlıklı faz ZnO iken diğer bölgelerde TiO_2 oluşumu rapor edilmiştir. SDGP ve TO işlemlerinin sıralı uygulanması sonucu üretilen kaplamalara 3N yük altında kuru ortamda alümina bilyeye karşı yapılan aşınma deneylerinde kütlece %5 çinko içeren kaplamalarda sürtünme katsayısı değerinin 0,12' ye kadar düştüğü görülmüş ve tribolojik uygulamalar için çok yüksek potansiyele sahip olduğu değerlendirilmiştir.

Tez kapsamında yapılan çalışmaların dördüncü ve son bölümünde üretilen kaplamaların biyolojik uygulamalar için daha verimli hale getirilmesi amaçlı olarak SGDP toz bileşimi anti bakteriyel etkisi yaygın olarak bilinen gümüş ile takviye edilmiştir. Kaplama bileşiminde titanyum kütlece %5 azaltılarak yerinde gümüş eklentisi yapılmıştır. SDGP işlemi ile ilgili toz bileşimi başarılı bir şekilde 316L

paslanmaz çelik üzerine kaplanabilmiştir. TO işlemi sonrası yapılan faz analizlerinde gümüş eklentisinin hala metalik formda kaldığı tespit edilmiştir. Mikro yapısal incelemelerde gümüşün kaplamanın belirli bölgelerinde aglomere olduğu görülmüştür. 1N yük altında kuru ortamda ve serum ortamında alümina karşı malzemeye karşı yapılan aşınma deneylerinde kaplamanın 316L paslanmaz çeliğe oranla daha üstün bir başarı sergilediği tespit edilmiştir. Yapay vücut sıvısı içerisinde dört hafta süresince bekletilen kaplama ve 316L paslanmaz çelik yüzeyleri elektron mikroskobu ile incelendiğinde biyo aktivite açısından kaplamaların altlık malzemeye göre daha başarılı olduğu görülmüştür. Staphylococcus aureus (S. aureus) bakterisi kullanılarak yapılan disk difüzyon tipi anti bakteriyellik testlerinde gümüş eklentili kaplamanın anti bakteriyel etki sergilediği kanıtlanmıştır. İyon salınımı testlerinde 28 gün sonunda kaplamalardan yaklaşık 0.2ppm seviyesinde gümüş iyonu salındığı tespit edilmiştir. Bu doğrultuda gümüş eklentili kaplamanın hep vücut içi uygulamalarda (implant, sabitleme çivisi vs.) hem de anti bakteriyel etkinin önemli olduğu yüzey uygulamalarında (kapı kolları, ameliyathane araç gereçleri, tutamaçlar) kullanılabileceği düşünülmektedir.

Sonuçları özetlemek gerekirse; metalik malzemelerin yüzeylerinde SGDP ve TO yöntemlerinin sıralı uygulanması ile titanyum bazlı kaplamalar üretilmektedir. Kapmanın en dış yüzeyinde TiO₂ ağırlıklı oksit tabakası oluşurken, kaplamanın iç kısımlarında intermetalik oluşumu ve titanyumun oksijence zenginleşmesi meydana gelmektedir. Yüzeyde oluşan oksit tabakasının sertliği yaklaşık 1200HV olup, kaplama yüzeyine çok iyi yapışmaktadır. Farklı ortamlarda ve yüklerde yapılan aşınma deneylerinde kaplamalar, Co-Cr ve 316L paslanmaz çelik altlık malzemelere kıyasla çok daha iyi bir tribolojik performans göstermektedir. Biyoaktivite ve anti bakteriyellik testlerinin sonuçları bu kaplamaların biyolojik uygulamalarda da kullanılabileceğini işaret etmektedir.



1. INTRODUCTION

1.1 Surface Modification of Metals by Cold Spray Technique

The cold gas dynamic spray (CS) technique was developed by Prof. Anatolii Payrin and his colleagues in the middle of the 1980s [1], mainly based on spraying coating feedstock through the substrate with the help of pressurised carrier gas. During the spraying process, the feedstock powders' velocities reach the supersonic values (300–1200 m/s) [1–3]. The collision of feedstock with the substrate material leads to coating deposition via plastic deformation of the sprayed powders [1–3]. Since the feedstock must have a high plastic deformation ability for a successive deposition, CS enables coatings, including several types of pure metals, alloys, polymers and composites on different substrate materials. It should be noted that the plastic deformation that occurred during the impact of the soft powders to the surface of substrates generates coatings with high hardness via strain hardening mechanism. Hard materials like ceramics can be deposited when their powders are mixed with ductile powders like aluminium, copper etc. The schematic view of cold spraying equipment/process is given in Figure 1.

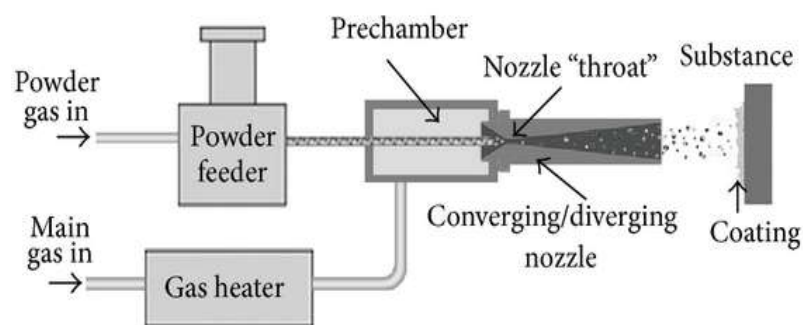


Figure 1.1 : Schematic view of cold spraying equipment [4].

During the CS process, the temperature of the sprayed powders do not reach their melting point and remain in solid-state, unlike the other thermal spray processes [1–3]. Thanks to this feature of the CS process, high-temperature oxidation, vapouring and debonding can be eliminated or minimised

The collision of feedstock powders with the substrate does not always form a coating over the substrate. The collision of particles with the substrate with lower velocities causes sticking or erosion, while higher speeds make a ballistic effect on the substrate [5]. Thus, the particle size and speed must be kept optimum for the cold spraying process. As can be seen from Figure 2, the acceleration of the particles with the size of 10-100 μm to the 300-1200m/s speeds provides cold spray deposition over the substrate.

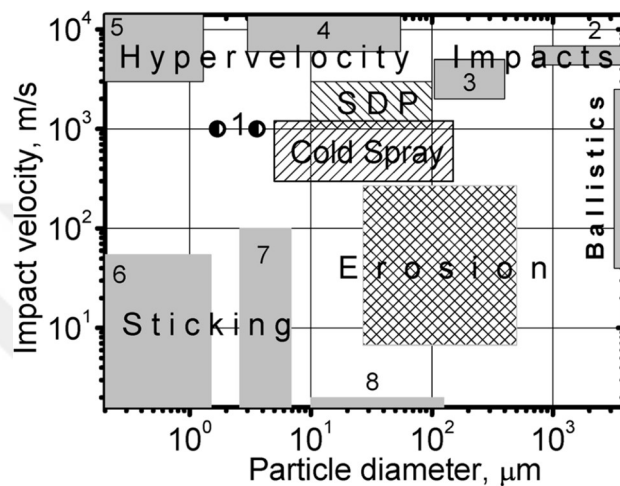


Figure 1.2 : The effect of particle size and velocity on impact mechanism [5].

The type of carrier gas used in the CS process significantly influences the velocity of the powder. The velocities of the powder can be increased by decreasing the molecular weight of carrier gas or increasing its specific heat, as proved by the rule of gas-dynamic [3,6,7]. Furthermore, the inert character of the carrier gases affects the oxidation of feedstock powders. Another parameter for choosing a carrier gas is the cost. Because the amount of the consumed carrier gas is very high, selecting an inert gas for deposition can be costlier. Table 1 compares the features of the carrier gas type that could be used in the CS process.

Table 1.1 : The properties of carrier gasses [2].

Gas	Velocity (m/sn)	Density (kg/m ³)	Noble/Reactive	Cost
Air(80% N ₂ +20%O ₂)	343	1.225	Reactive	Cheap
Nitrogen (N ₂)	349	1.185	Partially Inert	Cheap
Hydrogen (H ₂)	1303	0.085	Reactive	Expensive
Argon (Ar)	319	1.69	Inert	Expensive
Helium (He)	989	0.168	Inert	Very Expensive

Depending on the pressurization of the carrier gas, CS processes can be split into two categories; Low-pressure CS (LPCS) and high-pressure CS (HPCS) systems. In the LPCS process, the gas pressure is limited to a maximum of 8 Bar while HPCS processes gas pressure up to 40 bars [8]. In this respect, LPCS processes provide relatively lower powder velocities than HPCS processes as 300–550 m/s and 900-100 m/s, respectively [8]. Because of the higher velocities reached in HPCS systems, the coatings produced are more uniform (especially at the top of the coatings, as compared to the coatings produced by LPCS processes (Figure 3). On the other hand, portability and low cost are the main advantages of the LPCS systems over the HPCS systems. Additionally, the capability of using compressed air as the carrier gas makes LPCS systems more feasible for field/on-site applications [3,8].

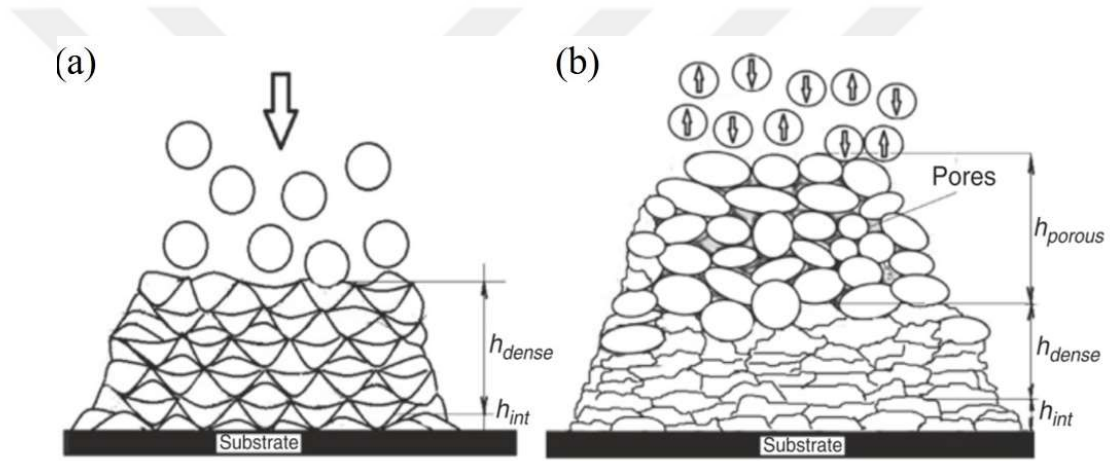


Figure 1.3 : Coating structure in (a) HPCS and (b) LPCS [8].

CS process enables to use of metals, metal alloys and composites as a coating feedstock. It has been reported that removing oxygen from feedstock, decreasing inner stresses of feedstock powders, adjusting the powder size ratios and optimising the spraying parameters leads to the formation of denser coatings due to increment in deposition efficiency [2].

The temperatures reached the CS process ($\sim 300^\circ\text{C}$) are relatively low compared to the other thermal spraying techniques. So, with the CS process, it is possible to use metals with a high oxygen affinity like Ti, Al, and Cu without any oxidation in the coating process [2].

The application of the CS process on metallic materials varies from different applications and sectors. Many studies proved that as-sprayed CS coatings have superior corrosion and wear resistance and bioactivity (especially at Ti-based coatings)

compared to the bare metallic substrate [1–3,6,9,10]. The potential applications of the CS process on metals are summarised in Table 2.

Some examples of the recent articles (published since 2013) dealing with the applicability of CS coatings to wear, corrosion and biomedical related applications are briefly introduced in Table 1.3, 1.4 and 1.5, respectively.

Table 1.2 : The applications of CS Process [3].

Application	Coating Material	Industry/Sector
Wear Resistant Coatings	WC–Co	Oil and gas
Corrosion Resistance	Al and Ni alloys, Ti, Ta	Aerospace Oil and gas Petrochemical Power generation
Bio-inert Devices	Ti	Medical

Table 1.3 : Some recent articles were dealing with the tribological performance of CS coatings.

Studied by.	CS coating	CS System	Testing Methodology	Results.
Stark et al. [11]	Nickel-Encapsulated Hexagonal Boron Nitride coatings on Aluminium 6061 Alloy	HPCS	reciprocating wear test under 24N load Stainless Steel counter face at room conditions	The friction coefficient of Ni-based CS coatings decreased to 0.35 by hexagonal boron nitride reinforcement
Zhang et al. [12]	The MoS ₂ added Cu based coatings on Aluminium 6061 Alloy	HPCS	reciprocating tests under 5N load Al ₂ O ₃ counter face at room conditions	MoS ₂ addition decreased the friction coefficient to 0.15 of CS coating by the self-lubricant effect of MoS ₂ .
Alidokht et al. [13]	Bare Ni and Ni + WC coatings on Mild Steel	HPCS	reciprocating tests under 5N load WC-Co counter face at room conditions	The wear rate of Ni-WC composite coatings is seven times lower than bare Ni coatings.
Paksoy et al. [14]	SiC particle reinforced Al-12Si coatings on 1050 Aluminium Alloy	LPCS	reciprocating tests under 1 to 5N A ₂ O ₃ counter face at the water and dry conditions	The coating showed a lower COF value (0.3) in water conditions due to tribofilm formation on SiC particles.
Chen et al. [15]	SiC added 316Lcoatings on Magnesium Alloy	LPCS	ball-on-disk method under 5N load Si ₃ N ₄ counter face at room conditions.	316L-SiC composite coating performed remarkably better wear performance (2-3 times less wear rate) than the magnesium alloy.

Table 1.4 : Some recent articles dealing with corrosion behaviour of CS coatings.

Studied by.	CS coating	CS System	Testing Methodology	Results.
Singh et al. [16]	Ni-20Cr-TiC and Ni-20Cr-Re coatings on 2.25Cr-1Mo steel	HPCS	Cyclic treatment for 50 cycles each cycle: one hour heating at 900°C in furnace and 20 min cooling at room temperature.	In hot corrosion conditions, CS coatings showed better performance as compared to the T22 steel. (more than %80)
Kumar et al. [17]	Coatings based on nanostructured Ni-20Cr on steel substrate	HPCS	Cyclic treatment in boiler environment for 15 cycles (1500h)	The coating successful to reduce the erosion-corrosion rate of SA 516 steel by 55%
Silva et al. [18]	Al ₂ O ₃ added Al-coatings on steels	HPCS	Open circuit potential measurements Salt Fog tests up to 3000h	the Al-Al ₂ O ₃ /Al composite coating showed higher corrosion resistance as compared to the bare Al.
Chen et al. [15]	SiC added 316Lcoatings on magnesium alloy	LPCS	Dynamic potential polarization tests Salt spray tests	316L-SiC composite coatings evidently reduce the corrosion current density of magnesium alloys
Omar et al. [19]	Deposition of 6061Al alloy on Al7075 alloy	HPCS	Salt spray for 48h	Significant improvements reported in corrosion protection of 7075 sponson spar

Table 1.5 : Some recent articles were dealing with the biological features of CS coatings.

Studied By.	Application	System	Testing Methodology	Results.
Noorakma et al. [20]	HAP coatings on AZ51 Magnesium alloy	LPCS	Simulated bod fluid immersion tests for 14 days	CS'ed HA coating is more bioactive when compared to the untreated substrate AZ51 alloy.
Tang et al. [21]	Fabrication of Tantalum/Hap coatings on Ti6Al4V alloy	HPCS	Simulated body fluid immersion tests for 3 days	TA/HA coatings are an alternative for biomedical applications with the bioactive characteristics of tantalum and HAP
Zhao et al. [22]	Graphene/silver doped aluminium based CS coatings on steel substrates.	HPCS	Antibacterial tests against Escherichia coli bacteria	Coatings have excellent antibacterial efficiency against E-coli bacteria.
Tang et al. [23]	Deposition of HAP/TA coatings on Ti6Al4V	HPCS	Simulated bod fluid immersion tests up to 4 weeks	TA/HAP coatings could be used for improving the bioactivity of metallic biomaterials.
Silva et al. [24]	Copper-based coatings on steel	HPCS	Cell viability tests Antibacterial tests against Staphylococcus aureus Escherichia coli and Candida albicans bacteria	The superior cell interaction and antibacterial efficiency of Cu based CS coatings

1.2 Post Treatments for Cold Sprayed Coatings

In order to overcome the weaknesses arising from micro-pores, particle-particle interaction, adherence at the coating/substrate interface, residual stresses (imposed by combination of thermal effects), etc., CS coatings (especially the LPCS coatings) can be subjected to post-treatment [25]. Different kinds of post-treatments applied to CS coatings with the aim of improving the adhesion strength, minimising the porosities/increasing the density, increasing wear resistance and biocompatibility are explained below.

1.2.1 Heat treatment

Application of heat treatment on CS'ed coatings is one of the favourite techniques for lowering the porosity in the as-sprayed structure. Although the heat treatment temperature differs from the coating composition, diffusion is the primary mechanism for removing or minimising porosities that negatively affect the mechanical properties of CS'ed coating [26–28].

Moreover, the formation of new phases such as intermetallics or metal-carbides within the CS coating during heat treatment, as the result of metallurgical reactions, has the potential to provide better mechanical properties, including hardness and wear resistance [29,30].

1.2.2 Friction-stirring

Friction-stirring enables the formation of ultra-fine grains on the CS coating by applying a rotating tool on the surface of that coatings. As the result of plastic deformation occurred by solid-state interaction between rotating head and CS coating, the microstructure is refined [25,31]. While the thickness of the CS coating diminished, the coating became denser and stronger (because of plastic deformation) than the as-sprayed state. Moreover, the breaking of second phase particles (if exist in the coating structure) can provide homogeneity of dispersion of these second-phase particles and improve the mechanical quality of CS coating [31–33]. It has also been reported that the heat that occurred during the friction-stir process can lead to forming intermetallic phases that significantly contribute to hardness and wear resistance [30,34].

1.2.3 Laser Re-melting

Post-treatment laser re-melting of CS coating provides better surface properties like a denser structure and fine grain structure at the top of the coating compared to the as-sprayed state. With the energy provided by the laser beam, the surface of the coating can be partially melted. After that, with rapid cooling, solidification takes place on the surface, which helps to seal open pores and obtain grain refinement [35,36]. Furthermore, due to non-equilibrium melting and rapid solidification, metallurgical changes on the CS coating could occur like phase transformation and compositional changes. The positive contribution of that changes on the mechanical and electrochemical properties of the coating, i.e. improvement in hardness, wear resistance and corrosion resistance, is reported in the literature [37].

1.2.4 Electrochemical methods

The surface modification of valve metals (Ti, Al, Mg, Zr) CS coatings can be done by utilising electrochemical methods like micro-arc oxidation or anodic oxidation on the coatings. The micro-arc oxidation enables the formation of metal-oxide layers on the surface of the valve metals by applying a specific voltage in an electrolyte solution. Thus, the application of micro-arc oxidation provides the formation of hard, wear and corrosion resistant, and bioactive (titanium-based coatings) metal-oxide top layers on CS coatings. In the literature, it has been reported that, as the result of the metal-oxide formation micro-arc oxidation process, the wear and corrosion performance of CS coatings are remarkably improved [38–40].

Similar to the micro-arc oxidation technique, anodic oxidation also provides metal oxide formation on the base metals. In contrast, the layer thickness of metal-oxide fabricated by anodic oxidation is lower than the micro-arc oxidised ones. For that reason, anodic oxidation aims to change surface morphology and topography and increase surface area rather than improve the mechanical characteristics of the base materials. It has been reported that the application of anodic oxidation on Ti-based CS coatings provides nano-rough surfaces, which have an outstanding contribution to the biological performance [41].

1.2.5 Hot isostatic pressing

Hot isostatic pressing favours the usage of temperature and pressure simultaneously for the densification of powder-based materials. The application of hot isostatic pressing on CS coatings improves the mechanical properties via decreasing the number of defects and adjusting the more homogenous microstructure. The effect of hot isostatic pressing on CS'ed coatings is mentioned in the literature. It has been reported that, via hot isostatic pressing, it is possible to decrease the porosities in the coatings, which directly affects mechanical properties of the coatings, such as tensile strength and hardness [42,43].

1.3 Research Objectives of the Thesis.

The novelty of the thesis bases on the application of thermal oxidation (TO) to titanium-based CS coatings as a post-treatment. Since TO is employed to metals having a high oxidation tendency at elevated temperatures for a certain duration in an oxidative media, it can be assumed as a sub-group of the post heat-treatment process. But different from the purposes mentioned in section 1.2. in this thesis, TO has been applied with the aim of fabricating a protective titanium oxide layer over the titanium-based CS coatings. The motivation was TO studies conducted on bulk titanium and its alloys in which the possibility of obtaining significant enhancements in wear and corrosion resistances as well as biological performance has been documented upon covering of their outermost surfaces by titanium oxide layer [44–50].

Titanium is a metallic material with a high oxygen affinity. Therefore, a passive oxide layer with a thickness of 10 nm readily forms on the surfaces of titanium and its alloys at room temperature. Since this layer is thin and weak against mechanical effects (such as wear), its removal makes titanium and its alloys vulnerable to corrosion and lowers the bioactivity [51]. To make the natural oxide layer on the titanium and its alloys chemically and mechanically more stable, TO could be a good technological solution. [49,52,53]. TO applied above 200°C increases the thickness of the oxide layer[51]. Although, as the result of changing thermal oxidation parameters, this oxide layer can be in different stoichiometries like Ti_3O , Ti_3O_2 , Ti_2O and TiO_2 . the most stable form is TiO_2 [51]. The optimum parameters for thermal oxidation of titanium and its alloys are reported as 600°C and 60 h by Guleryuz and Cimenoglu [49], where the uniform, hard-adherent and wear and corrosion resistance oxide layer can be formed.

Furthermore, thermal oxidation temperature generates an oxygen diffusion zone beneath the oxide layer. The oxygen diffusion zone forms via oxygen dissolution in the titanium matrix. The amount of oxygen dissolved in titanium (it can be up to at. %30 [54]) determines the hardness of the oxygen diffusion zone. Thus, the hardness of the oxygen diffusion zone decreases towards the core and acts as a transition zone between the hard oxide layer and soft substrate [44,51].

In this thesis, TO was applied to the titanium-based coatings deposited on Co-Cr alloy and 316L stainless steel substrates from the feedstock containing 92wt.% titanium and 8wt.% aluminium. The limitations of the CS system (low-pressure cold spray equipment with a pressure of 6 Bar) used in the thesis made it mandatory to use a ductile phase for the successful deposition of the titanium coating. For this reason, aluminium is preferred as the ductile agent. After the CS process, TO applied with the parameters adopted from Ref [49]. Thermal oxidation enabled the formation of an oxide layer on the outermost surface of the coating. The oxide layer was mainly consisting of the rutile phase of TiO_2 and a minor amount of Al_2O_3 . As the result of the microstructural examinations, it was seen that the oxide layer was uniform and well adherent to the titanium-based coating. The hardness of the oxide layer was measured as $\sim 1200\text{HV}$. The adhesion of the oxide layer was examined by scratch and Rockwell C tests. The oxide layer performed excellent performance under shear and compressive type loading. There was no delamination detected/observed at the interface between the oxide layer and CS coating. The wear tests conducted under different loads and conditions proved that the coatings fabricated by sequential application of cold spray and thermal oxidation processes are performing better than the Co-Cr substrate used as the substrate material. The bioactivity of the coatings was examined by the simulated body fluid tests. Compared to the untreated Co-Cr alloy, thermally oxidised coatings showed more bioactive characteristics, which has a crucial role in the biomedical industry. As the result of microstructural, mechanical and biological tests conducted on the thermally oxidised Ti-based coating, the idea of the modification of the coating with 3rd part agents is studied in the scope of the thesis.

First of all, zinc is preferred as the 3rd part agent for improving the wear performance of the thermally oxidised coating. Therefore, different amounts of zinc were added to CS feedstock to reveal the effect of the zinc content on the wear performance of the thermally oxidised coating. After CS deposition, coatings thermally oxidised with the

same parameters used in previous studies. Wear tests conducted on thermally oxidised samples under dry sliding conditions showed that zinc reinforcement has a diminishing effect on the friction coefficient of the coating. The optimum zinc amount reported as 5 wt.% where performed steady-state friction coefficient value of 0.12.

Lastly, as an antibacterial metal, silver was added to the coating composition with the amount of 5 wt.%. After the thermal oxidation process, microstructural examinations, bioactivity studies, antibacterial and wear tests were conducted on the samples. The silver reinforced thermally oxidised coatings showed better bioactivity and wear performance than the 316L substrate material. In addition, the antibacterial tests proved that the antibacterial efficiency of thermally oxidised samples could be improved by silver reinforcement.

2. A NOVEL FABRICATION METHOD FOR TiO₂ LAYER OVER CoCr ALLOY ¹

2.1 Introduction

Among the metallic biomaterials, CoCr based alloys have been widely used in manufacturing of load bearing implants owing to their high static and dynamic strengths, good corrosion resistance and relatively low production cost [55–57]. Although the native oxide (Cr₂O₃) film, which tends to form easily over these alloys in any oxidizing environment, is responsible for their resistance against corrosion attack, it is not sufficient for preventing the release of metal ions (i.e Cr and Co) in-vivo and good integration at implant/bone interfaces [58,59]. These drawbacks have great impact on the long term success of CoCr based implants in the human body [60,61]. In order to overcome these drawbacks, many surface modification techniques, such as bioactive glass coating, TiN coating, tantalum coating, biomimic calcium phosphate coating, hydroxyapatite-titania nanotube composite coating have been applied to CoCr alloys [62–66].

Benefiting from the good biological characteristics of titanium, titanium based coatings can be the most attractive solution in enhancing the osseointegration of CoCr implants. In this context, Plecko et al [67], who compared the osseointegration and biocompatibility of different metallic implants (in the form of screw) by in-vivo test, confirmed improvement in the osseointegration of CoCr implants being similar to that of pure titanium upon application of titanium based coating.

In contrast to their superior biological properties, poor wear performance limits the utilization of titanium and its alloys in manufacturing of knee and hip joint implants [68–71].

¹ This chapter is based on the paper “Cetiner, D., Paksoy, A.H., Tazegul, O., Baydogan, M., Guleryuz, H., Cimenoglu, H., et al. (2019) A novel fabrication method for a TiO₂ layer over CoCr alloy. Surface Engineering. 35, (3), 234–24”

In addition to the rapid progress of wear, generation of heavy wear debris has potential to cause local inflammation in-vivo that accelerates bone loss around the titanium based implants. This process can trigger early implant loosening, which results in the need for replacing the implant by a new one (revision surgery).

Therefore, surfaces of the titanium based implants must be tailored with the aim of reducing wear loss in-vivo. Although, there are several proposed surface modification techniques for titanium and its alloys in the literature [69,72,73], among them thermal oxidation (TO) process is one of the most efficient techniques with low cost and simplicity.

TO is a thermochemical surface hardening process generating chemically and mechanically stable, hard, thick and compact outermost TiO₂ layer with an supporting relatively hard oxygen diffusion zone beneath it as a result of diffusion of oxygen into the substrate [44,49,68,74,75]. Temperature and time are the main parameters of TO process in fabrication of successful TiO₂ layer having a good combination of wear and corrosion resistances. While higher temperatures (above 700 °C) and longer durations cause oxide de-bonding, lower temperatures (below 400°C) and shorter durations generate oxide layers having insufficient thickness for wear and corrosion[51,76]. In this respect, superior combination of corrosion and corrosion-wear resistances have been obtained from Ti6Al4V alloy after TO at 600°C for 60 hours in normal atmospheric conditions[49]. These TO parameters also yielded superior corrosion-wear performance for Ti6Al7Nb alloy [50].

On the basis of above explanations, this study aims to combine cold spray (CS) and TO processes to fabricate a novel coating for CoCr implants. While CS process will be applied for deposition of titanium layer over the CoCr substrate, TO process will be applied as a post treatment to fabricate a hard, thick and compact TiO₂ layer on titanium deposit.

2.2 Materials and Methods

ASTM F75 CoCr alloy was received as a 12 mm diameter rod. Cylindrical samples were cut from the rod and grinded to #400 SiC abrasive paper. The feedstock was prepared by the mixture of 92wt.% titanium powder (Alfa Aesar, <44µm, 99,5 % purity) and 8 wt.% aluminium powder (Alfa Aesar, <44µm, 99,5% purity) for CS

process. For the fabrication of the coatings, RUSONIC Model K-201 low pressure CS equipment with converging-diverging type tubular nozzle having an expansion ratio of 2.3 was utilized. 6 bar (600 kPa) inlet pressure of air were used as a process gas and traverse speed was fixed at 1 mm/s for every deposition. During the spraying, stand-off distance, beam distance and powder feeding rate were set as 10 mm, 2 mm and 2 respectively. Before the TO process, the surfaces of the sprayed coatings were mechanically ground on 240-2500 mesh SiC abrasive papers and polished with 3 μ m diamond slurry and colloidal silica solution. The sprayed coatings were isothermally oxidised in air according to the TO studies reported by Guleryuz and Cimenoglu [49]. TO process was carried out in a laboratory type air circulated furnace (Nabertherm). Samples were heated at a rate of 5 $^{\circ}$ C/min and left in furnace for cooling (cooling rate of 1 $^{\circ}$ C/min) after holding at 600 $^{\circ}$ C for 60 h. The coatings before and after TO were subjected to microstructural survey, surface roughness and hardness measurements. The microstructural characterization and elemental composition of the coatings were performed on the cross-section of the samples and analysed by field emission scanning electron microscope (Philips SFEG XL30, SEM) equipped with energy dispersive X-ray (EDX) spectrometer. Phase composition of the coatings were determined by XRD (GBC MMA diffractometer) measurements by using Cu $K\alpha$ radiation in between the diffraction angle of 10 $^{\circ}$ and 90 $^{\circ}$ at a step size of 0.02 and a count time of 0.6 s. Surface roughness measurements of the coatings in terms of average surface roughness (Ra) were done using a Dektak 6M surface profilometer. Hardness measurements were performed on the surface and the cross-section of the coatings by using a Vickers pyramid indenter. Surface harnesses of the untreated CoCr alloy and the as-sprayed coating were measured by Wilson harness tester under a load of 50 g, while hardness of the oxidized coating was determined by a CSM depth sensing micro-nano hardness tester under an indentation load of 10 g. The cross-sectional hardness measurements of the as-sprayed and the oxidized coatings were performed by using a Wilson micro-hardness tester under the indentation load of 25 g. For evaluating bioactivity of the untreated CoCr alloy and the oxidized coating, the samples were immersed in 1.5X simulated body fluid (SBF)[77] for four weeks. At the end of four weeks, precipitation formed on the surface of the samples were examined by scanning electron microscope (HITACHI TM1000, SEM). Additionally, sliding wear tests were conducted on the CoCr and oxidised samples by utilising a reciprocating wear tester (Tribotech). Counterface was a 6 mm diameter Al₂O₃ ball and test load was 4 N. The stroke and

the sliding speed of the ball were 5 mm and 10 mm/s, respectively. Wear tests were run for 2500 s under normal atmospheric conditions (20 °C and 50% RH). After the wear tests, the wear tracks developed on the surface of the samples were determined by using a 2D stylus profilometer (Veeco Dektak 6M). The worn surfaces of the wear tracks formed on the examined samples were investigated by the SEM (Philips SFEG XL30).

2.3 Results and Discussion

2.3.1 Results of structural examinations

The XRD patterns of as-sprayed and oxidized coatings are given in Figure 2.1. As can be seen in Figure 2.1a, only α -Ti and aluminium peaks appeared on the XRD pattern of the as-sprayed coating, which is in accordance with constituents of the feedstock. It is worth to mention that no diffraction peak implying oxidation, chemical reaction or phase transformation has been detected on the XRD pattern of the as-sprayed coating. On the XRD pattern of the oxidized coating (Figure 2.1b), diffraction peaks of titanium dioxide (TiO_2) in the form of rutile were clearly identified along with aluminium oxide (Al_2O_3). When peak heights are of concern, it is suggested that the oxide layer formed during TO process is mainly consisted of TiO_2 with minor amounts of Al_2O_3 . Additionally, slightly shifted diffraction peaks of α -titanium appeared on the XRD pattern due to the penetration of X-ray beyond the oxide layer. Since dissolution of oxygen atoms in titanium matrix (beneath the oxide layer) during TO has been well documented [49,78] shifting of α -titanium peaks on the relevant XRD pattern can be attributed to the expansion of titanium lattice as the titanium matrix is enriched with oxygen.

Figure 2.2 presents the cross-sectional SEM micrographs of the as-sprayed and the oxidized samples. In the as-sprayed state (Figure 2.2a), the coating was compact and free from any discontinuity along the coating/substrate interface. In accordance with the XRD analysis, the microstructure of the as-sprayed coating was consisted of bright coloured titanium and dark coloured aluminium, in which aluminium particles were homogeneously distributed in the titanium matrix. EDX analysis revealed the average composition of the coatings comprised 4wt.% aluminium. Figure 2.2b shows the cross-section SEM micrograph of the oxidized coating. It can be seen that the surface of the oxidized coating was completely covered with homogeneous, compact and dense

oxide layer having thickness of about 3 μm . No indication of detachment was observed at the interface of the oxide layer and titanium based coating beneath it during the SEM examination.

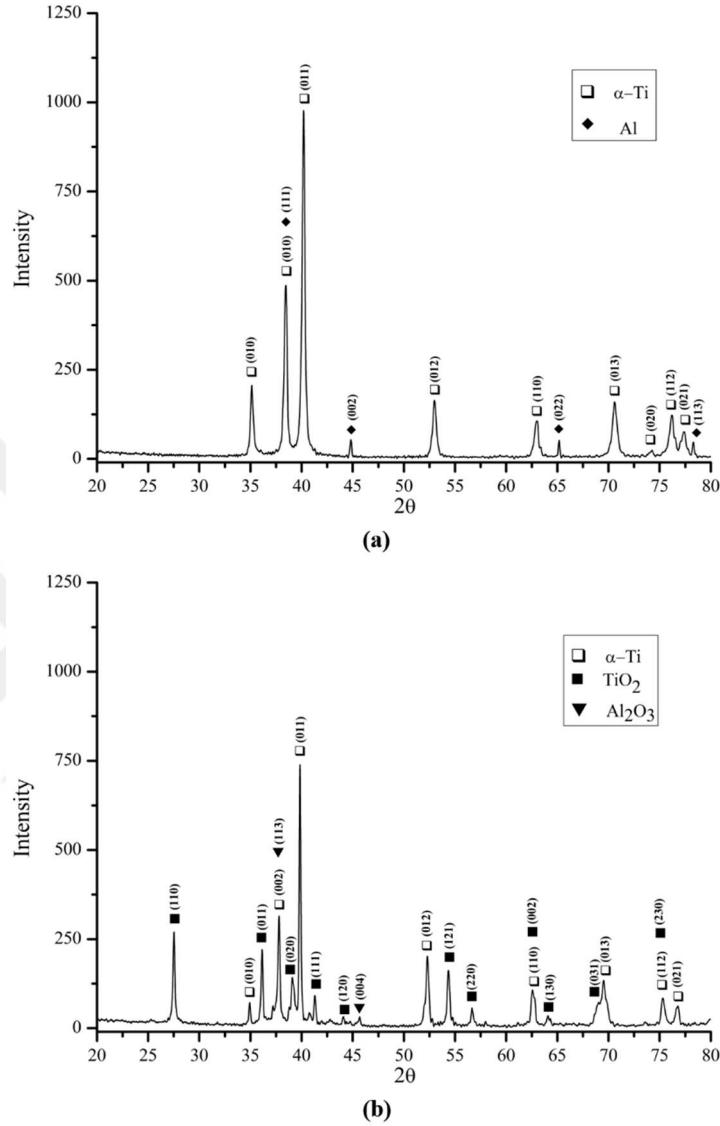


Figure 2.1 : XRD patterns of a) the as-sprayed and b) the oxidized coatings.

The nominal composition of the oxide layer was determined as 24Ti-2Al-74 O (at.%) by EDX analysis confirming the presence of minor amount of Al_2O_3 in along with TiO_2 . Apart from the formation of oxide layer, applied TO process substantially changed the microstructure of the underlying layer by generating bright, grey and dark coloured regions, whose nominal compositions were identified as 76Ti-24O (at.%), 37Ti-54Al-9O (at.%) and 17Ti-63Al-20O (at.%), respectively. In general, EDX analysis revealed enrichment of the titanium matrix (bright coloured) with oxygen in comparison to the as-sprayed coating. Additionally, transition from bright coloured

region to grey and dark coloured regions was accompanied by increase of aluminium and reduction in oxygen concentration. The results of the EDX analyses during SEM examination revealed that during TO, oxygen not only reacts with Ti and Al to form the oxide layer but also diffuses into the titanium matrix owing to availability of easy diffusion paths, for oxygen, such as defects and grain boundaries in the as sprayed coating structure. In addition to this, some of the aluminium in the titanium matrix partially diffused into the titanium particle because of higher aluminium diffusion efficiency at the oxidation temperature of 600°C applied in this study [79,80].

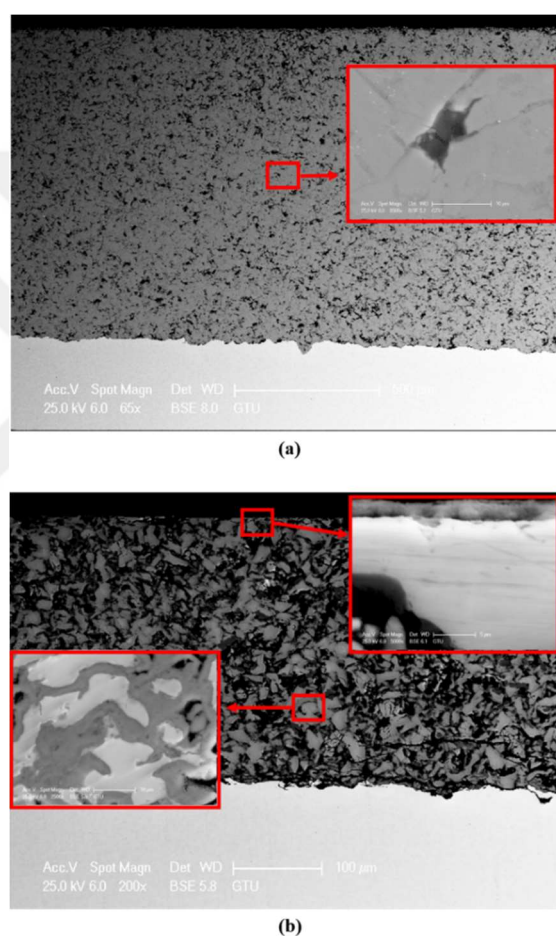


Figure 2.2 : Cross-sectional SEM micrographs of (a) the as-sprayed and (b) the oxidized samples.

Surface roughness measurements showed that the applied TO process caused surface roughening of the titanium coating (average surface roughness, R_a , increased from 0.10 to 0.64 μm). This increase in the surface roughness is ascribed to the growth mechanism of oxide layer, which is consistent with the results of the TO studies in literature, and can be beneficial for osseointegration by providing potential sites for cell attachment in-vivo [81,82].

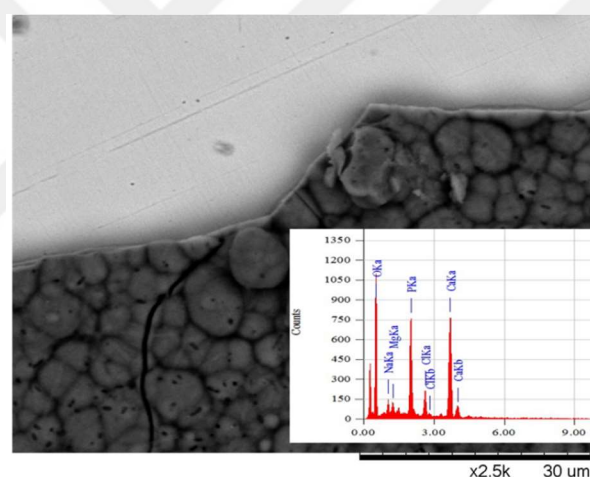
Average surface hardness values of the as-sprayed and the oxidized coatings were measured as $96 \pm 9 \text{ HV}_{0.05}$ and $848 \pm 232 \text{ HV}_{0.01}$, respectively. The surface hardness value of the oxidized coating is at least eight times higher than that of the as-sprayed coating as the result of formation of the TiO_2 layer after TO. The high standard deviation in the surface hardness value of the oxide layer can be attributed to the contribution of relatively high surface roughness ($R_a \sim 0.64 \mu\text{m}$) to the indentation response of the oxidized surface. At the cross-section (i.e in the layer between oxide layer and substrate) average hardness value was determined as $392 \pm 89 \text{ HV}_{0.05}$. As compared to the as-sprayed state, about four times higher hardness has been measured beneath the oxide layer due to the solid solution hardening, as the results of both the penetration of oxygen beyond the oxide layer and diffusion of aluminium into the neighbouring titanium particles during TO process.

2.3.2 Results of simulated body fluid tests

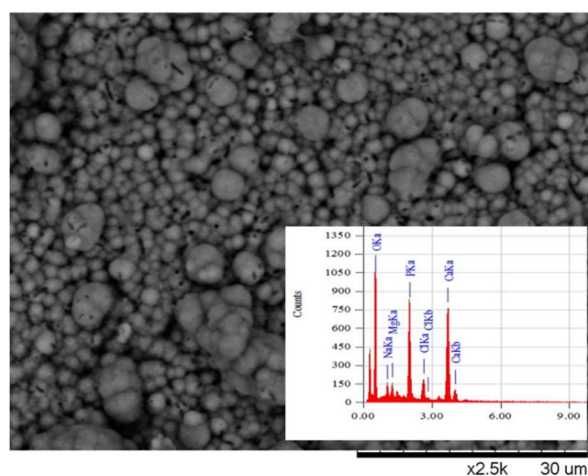
Figure 2.3 shows SEM micrographs and their respective EDX spectrum for the CoCr alloy and the oxidized samples immersed in 1.5X SBF for four weeks. The surfaces of the samples were covered with a numerous micron-sized sphere-like precipitates, which were rich in calcium and phosphorus. The results of EDX analyses and the morphologies of these precipitates implied that they were hydroxyapatite. Apatite layer deposited on the surface of the oxidized sample seems to be more homogeneous and thicker than that formed on the CoCr sample. When the relative intensity of the peaks for Ca and P from the EDX spectrum are considered, the thickness of the apatite layer deposited on the surface of the oxidized sample can be inferred to be higher than that on the surface of the CoCr alloy. Additionally, the deposited apatite layer on the CoCr alloy contained large and severe cracks and spalled locally as shown in Figure 2.3a. This could be attributed to weak interaction (interfacial bonding) between the apatite layer and the surface of CoCr alloy. In the case of the oxidized sample, the apatite layer deposited on the TiO_2 layer was almost crack-free and stable (Figure 2.3b), which indicates enhancement in the bioactivity of CoCr alloy.

Results of the SBF immersion test are in agreement with previous studies [50,83], which reported accelerated deposition of Ca and P rich precipitates on the TiO_2 layer. Since hydroxyapatite has a composition similar to that of bone, deposition of hydroxyapatite during SBF test is generally assumed as a primary indicator of a

bioactive surface, which has high potential to lead a good bonding between the implant and the bone in-vivo [53,84]. It has been documented that deposition of hydroxyapatite on a material surface in aqueous solutions is related to the functional (hydroxyl) groups such as Si–OH, Ti–OH, Zr–OH, Nb–OH, Ta–OH, and surface morphology. The mechanism underlying the hydroxylation of metal oxides has been detailly described in Refs. [85–88]. Surface hydroxyl groups on metal oxides are protonated or deprotonated depending on the pH (proton concentration) of the aqueous solution. Thus, they present electrically charged sites for ion-exchange reactions facilitated by adsorption of cations or anions from aqueous solutions. Adsorption of cations (e.g. calcium ions) and anions (e.g. phosphate ions) eventually leads to nucleation and precipitation of hydroxyapatite which has a strong lattice coherency with rutile form of TiO₂ [52,89]. Additionally, relatively rough surface of TiO₂ provide suitable sites for nucleation of apatite.



(a)



(b)

Figure 2.3 : SEM micrographs along with EDX analyses of the deposited layer formed on a) the CoCr and b) the oxidized samples after four weeks SBF immersion.

2.3.3 Results of sliding wear tests

The characteristic 2D profiles of wear tracks formed on the surfaces of the CoCr and the oxidized samples during dry sliding conditions are depicted in Figure 2.4. As a result of higher material removal by the rubbing action of a Al_2O_3 ball, wider and deeper wear tracks have been formed on the surface of the CoCr sample as compared to the oxidized sample. The depth of the wear tracks was measured as $32.1 \pm 1.15 \mu\text{m}$ for the CoCr sample and $0.80 \pm 0.04 \mu\text{m}$ for the oxidized sample. It should be notified that the depth of the wear track formed on the oxidized sample ($\sim 0.80 \mu\text{m}$) is well below the thickness of the oxide layer ($\sim 3 \mu\text{m}$).

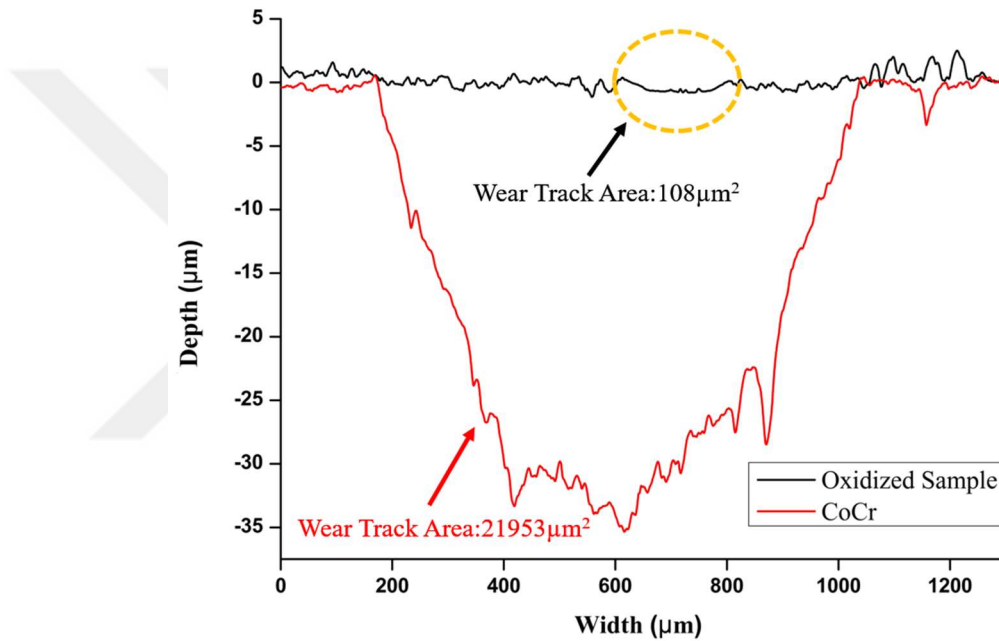


Figure 2.4 : The 2D profiles of the wear tracks formed on the surfaces of the CoCr and the oxidized samples.

Figure 2.5 presents the characteristics SEM micrographs of the worn surfaces. Worn surface of the CoCr samples showed abrasive wear appearance with the presence of number of grooves aligned parallel to the sliding direction. As for the oxidized sample, it is clear that the oxide layer was worn by gradual material removal without any evidence of plastic deformation and severe delamination. However, evidences of micro-cracking and chipping were identified during detailed SEM examinations. These observations suggested contribution of micro-cracking and micro-chipping to progress of wear on the TiO_2 layer under the test load of 4 N.

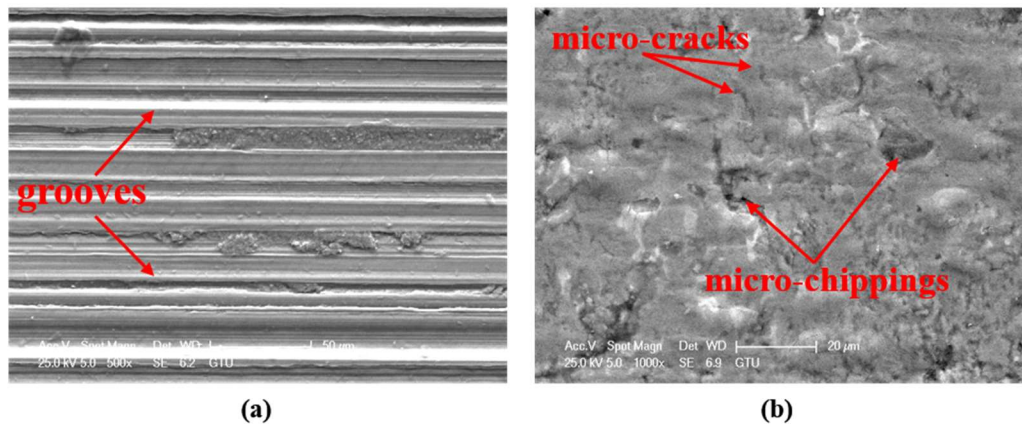


Figure 2.5 : SEM micrographs of the worn surfaces of a) the CoCr and b) the oxidized samples after dry sliding tests with respect to the test load utilized in this study.

Although wear testing conditions (i.e. application 4 N load by a 6 mm diameter Al_2O_3) created a contact pressure (about 1300 MPa) well above than that encountered in the human body (for example about 15 MPa for knee cap according to Ref. [90]), this study showed the promising protection of CoCr implants by the TiO_2 surface layer. In order to further investigate this finding, wear tests with wider load range (lower than 4N) and in different aqueous media (such as SBF and saliva) are planned as the future work.

2.4 Conclusion

As a novel surface modification approach, CoCr samples were subjected the TO process in air at 600°C for 60 hours after deposition of a Ti+4wt.%Al coating by the CS process. Structural features, bioactivity and sliding wear characteristics of the fabricated coating can be summarized as follows:

1. Application of TO altered the structure of the as-sprayed CS coating by generating a outermost TiO_2 layer with a diffusion layer in which aluminium diffused into the neighbouring titanium particles in addition to the inward diffusion of oxygen.
2. The oxide layer, which was mainly comprised of the rutile form of TiO_2 with a minor amount of Al_2O_3 , exhibited a rough morphology ($R_a=0.64 \pm 0.05 \mu\text{m}$) and preserved its stability without any indication of delamination at the oxide layer/diffusion layer interfaces. The hardness of the oxide layer was $848 \pm 232 \text{ HV}_{0.01}$.

3. As the primary indication of enhancement in bioactivity, better hydroxyapatite deposition characteristic has been observed after SBF tests on the oxidised sample as compared to the CoCr alloy.
4. Dry sliding wear tests conducted under a very high contact pressure level (~1300 MPa) for implants confirmed that novel combination of CS and TO processes is promising for CoCr alloys to provide significant enhancement in wear resistance.

2.5 Acknowledgement

This study has been prepared as a part of the project under contract no. 214M246 financially supported by the Scientific and Technological Research Council of Turkey (TUBITAK).



3. THERMAL OXIDATION OF COLD SPRAYED TITANIUM BASED COATING DEPOSITED ON Co-Cr ALLOY ²

3.1 Introduction

In the bio-medical industry, Co-Cr alloys are mostly used in manufacturing of load bearing implants due to their high static and dynamic strengths, and relatively low production cost [91–93]. Their enhanced corrosion resistance is due to the covering of their surfaces by an extremely thin native oxide film (i.e. Cr_2O_3). Despite rapid formation of this oxide film in any oxidizing environment, its thickness is not sufficient for long term protection against chemical and mechanical attacks (ie. corrosion and wear, respectively) in-vivo [94,95]. In this respect, body fluids, which contain water, salt, dissolved oxygen, bacteria, protein and various ions such as chloride and hydroxide [59], have higher potential for chemical break down of this native oxide film. This phenomenon not only accelerates the degradation of implant surfaces by corrosion attack but also causes release of metal ions (i.e. Cr and Co) from the implant, which may lead cytotoxicity in-vivo [96]. As reported by Shirdar et al. [66], who synthesized hydroxyapatite (HA)-titania nanotube composite coatings by dip coating sol-gel method, it is possible to decrease the progress of corrosion and release of metal ions from Co-Cr alloy upon coating. Other hand, mechanical degradation of implant surface not only cause accumulation of wear debris in the tissues surrounding the implant but also accelerates the rate of corrosion as the native oxide film is removed [97–99]. Wear debris are also found to be biologically active and the small size wear debris has tendency to dissolve in body fluids whereas relatively coarse wear debris may act as the abrasive particles for the implant [100,101]. Germain et. al. [102], who examined biological effects of wear debris on cells in vitro, reported cytotoxicity of Co-Cr particles.

² This chapter is based on the paper “Cetiner, D., Paksoy, A.H., Tazegul, O., Baydogan, M., Guleryuz, H., Cimenoglu, H., et al. (2018) Thermal Oxidation of Cold Sprayed Titanium-Based Coating Deposited on Co-Cr Alloy. *Journal of Thermal Spray Technology*. 27, (8), 1414–1427.”

Hard coatings (i.e. TiN coating by physical vapour deposition technique) are stated to be beneficial for Co-Cr alloys for reducing both the wear loss and metal ion release [63].

Apart from the technical solutions for overcoming above mentioned drawbacks, some surface modification techniques have also been applied to Co-Cr alloys with the aim of enhancing their osseointegration capability. In this respect, HA, which has chemical composition similar to that of bone, has been extensively coated by various techniques [103]. As an alternative to HA coating, coatings comprised of bioactive glass [62] and tantalum [64] have also been applied by considering their ability to form HA on their surface in vivo. Basically deposition of HA over the bioactive glass in a simulated body fluid (SBF) has been explained by a silica-rich hydrogel layer formation as the result of ion exchange between SBF (i.e. H^+ / H_3O^+) and bioactive glass (i.e. $K^+ / Na^+ / Ca^{2+}$). In the case tantalum (Ta) coating, HA forming ability in SBF is attributed to the strong hydroxylation feature of tantalum oxide (Ta_2O_5), which naturally forms in any oxidative media.

Recently promising results in terms of enhancement in bioactivity and dry sliding wear resistance have been obtained [104] from titanium based coatings fabricated by the combining cold spray (CS) and thermal oxidation (TO) processes. Successful deposition of titanium over Co-Cr alloy by CS has been maintained by adding 8 wt.% aluminium into the feedstock, while TO at 600°C for 60 hours under normal atmospheric conditions generated a titanium oxide (TiO_2) top layer. Although we have observed that TO process carried out at high temperature has potential to activate the reactions within CS coating (i.e. between aluminium and titanium along with their interactions with diffused oxygen), detailed structural characterization and its effects on the mechanical behaviour was not reported therein.

The current study aims to focus on structural characterization and mechanical performance of coatings fabricated by combining the CS and TO processes. In this respect, a tensile adhesion test determined the integrity and durability of the fabricated coating and scratch and Rockwell C tests evaluated the adhesion between the outer oxide layer and the underlying layer. Wear tests have been run in 0.9 wt.% NaCl, isotonic sodium chloride solution. Since aluminium is still a serious concern due to its potential harmful effects [105,106], such as toxic activity and health problems including peripheral neuropathy, and neurological dysfunction, possibly including

Alzheimer's, the in vitro release of aluminium ions from the substrate-free coatings has been examined and compared with Ti6Al4V alloy in 0.9 wt.% NaCl, isotonic sodium chloride solution.

3.2 Experimental Procedure

In the present study, titanium based coatings were deposited on F75 grade Co-Cr alloy from a feedstock containing 8 wt.% aluminium (Alfa-Aesar, spherical shaped powder < 325 mesh / 44 μm diameter, purity of %99) in titanium powder (Alfa-Aesar, spherical shaped powder < 325 mesh / 44 μm diameter, purity of %99) using the CS process. For the fabrication of the coatings, a CS equipment (Model K-201, Rus Sonic Technology, USA) with a converging-diverging type tubular nozzle having an expansion ratio of 2.3 was used. Cold spray process parameters were kept identical to that of Ref 19. Thus, 6 bar inlet pressure of air was the process gas and the traverse speed was fixed at 1 mm/s for every deposition. Stand-off distance and distance between passes were set as 10 mm and 2 mm, respectively. Before the TO, the surfaces of the CS coatings were mechanically ground on 240-2500 mesh SiC abrasive papers and polished with 3 μm diamond slurry and 0,05 μm colloidal silica solution. Cold sprayed samples having an average surface roughness (R_a) of about 0,1 μm were subjected to the TO process in a laboratory type air circulated furnace (Nabertherm, Germany). Samples were heated at a rate of 5 $^{\circ}\text{C}/\text{min}$ and held at 600 $^{\circ}\text{C}$ for 60 h and then furnace cooled with cooling rate control (cooling rate of 1 $^{\circ}\text{C}/\text{min}$). TO parameters applied in this study were identical to that of Ref [104] and adopted from the experimental results obtained by Guleryuz and Cimenoglu [49] giving an excellent combination of wear and corrosion resistances for Ti6Al4V alloy.

Characteristics of the coatings were investigated by conducting microstructural surveys, measurements of surface roughness and hardness, scratch, Rockwell C, tensile adhesion and wear tests. The microstructural features and elemental composition of the coatings were analysed using a field emission scanning electron microscope (SEM, Philips SFEG XL30, Holland) equipped with an energy dispersive X-ray (EDX) spectrometer. Phase compositions of the coatings were evaluated by X-ray diffraction (XRD) conducted on a diffractometer (MMA, GBC, Australia) equipped with Cu $K\alpha$ radiation. XRD measurements were carried out between diffraction angles of 20 $^{\circ}$ and 80 $^{\circ}$ at a step size of 0.02 and a count time of 0.6 s. Surface

roughness of the coatings was measured by using a 2D stylus profilometer (Dektak 6M, Veeco, USA).

Hardness measurements were performed on the surface and the cross-section of the coatings using a Vickers pyramid indenter. The cross-sectional hardness measurements of the CS and the TO coatings were performed by using a micro-hardness (Wilson, Buehler, USA) tester under the indentation load of 200 g for 15 sec. At least five measurements were made on the cross-section of samples and the reported hardness values are the average of all the measurements on the respective samples. Surface hardness measurements of the oxidized sample were carried out using a depth-sensing micro-nano hardness tester (CSM, Switzerland) at a load of 30 mN. At least five successful hardness measurements were conducted on the surface of the oxidized coatings and the average was the result of the oxide layer hardness. In the present study, to minimize the effect of surface roughness of the oxide layer on the hardness measurement, the average surface roughness (R_a) of the oxidized sample was reduced to 0.1 μm via gentle polishing.

Scratch tests of the oxidized coating were performed by using a micro scratch tester (CSM, Switzerland). Scratching was conducted under a progressively increasing load with a 200 μm radius diamond indenter (Rockwell C). The normal load applied to the indenter was increased linearly from 0.05 to 30 N at a scratch speed of 5 mm/min along a 5 mm distance. Rockwell-C adhesion tests were conducted on a Rockwell hardness tester (Zwick/Roell, Germany) by penetrating the standard diamond indenter under a normal load of 150 kg (1471N). Three indentations were done on the oxidized sample. After the scratch and Rockwell-C adhesion tests, the damage patterns within the scratch trace and the surround of the Rockwell-C imprint were examined using a SEM (TM 1000, Hitachi, Japan).

Tensile adhesion tests were conducted on the oxidized samples having diameter of 12 mm by utilizing a universal tensile testing machine (AG-IC 100kN, Shimadzu, Japan) by following ASTM C633-13 standard proposed for adhesion or cohesion strength of thermal spray coatings [107]. The samples were attached to the upper and lower parts of special apparatus by using Loctite EA9466 epoxy adhesive and were mounted into holding grips of a universal tensile testing machine before being subjected to axial tensile loading. The reported average tensile fracture load was calculated from five tests performed under the same conditions. After the tensile adhesion test, fracture

surfaces were examined using SEM. XRD analysis was carried out to reveal the phase structure of the fracture surfaces after gentle grinding and polishing.

Wear tests were conducted on the Co-Cr and the oxidized samples in 0.9 wt.% NaCl solution by utilizing a reciprocating wear tester (Tribotech Oscillating Tribotester, France) at room temperature. A 6 mm-diameter Al₂O₃ ball was used as the counter face. Wear tests were run for a total sliding distance of 25 m (stroke 5 mm and sliding speed 10 mm/s) under normal loads of 1N, 2N, and 3N. Results of the wear tests were evaluated as volumetric wear loss by calculating the area of the wear tracks developed on the surface of the samples, after measuring their width and depth using a 2D stylus profilometer. Three dimensional surface topographic profiles of the wear tracks were obtained for the samples with respect to the test loads by using a 3D stylus profilometer (Dektak 8-ASP, Veeco, USA). Worn surfaces of the samples were examined by SEM equipped with the EDX spectrometer. At least three tests were repeated in order to ensure repeatability of the results in fresh solution.

In order to evaluate the release of titanium and aluminium ions from the fabricated coatings, samples of substrate-free oxidized coating (having 8 mm diameter) were statically immersed in 0.9 wt.% NaCl solution for 1, 3, 7, 14, 21, and 28 days at 36.5 °C. Immersion tests were made according to the procedure given in Ref [108]. During the immersion test, the container was hermetically closed to prevent contamination and evaporation of the test solution. At the end of the immersion period (1, 3, 7, 14, 21, and 28 days) a sample of the solution was removed from the glass container to determine the concentration of the ion released from the examined samples. The concentrations of released ions were determined by inductively coupled plasma optical emission spectrometry (ICP-OES;7000 DV Optima, PerkinElmer, USA). For evaluation of the results of the ion release tests, samples machined from Ti6Al4V rod having 10 mm diameter have been used as reference. It should be noted that the volume of the solution was kept as 10X of the total surface area of the examined samples.

3.3 Results

3.3.1 Ion release tests

The cumulative concentrations (in ppm) of titanium and aluminium ions released from the oxidized stand-free coating and polished Ti6Al4V alloy into the 0.9 wt.% NaCl

solution with respect to the immersion time are given in Figure 3.1. No detectable amount of titanium ions in the 0.9 wt.% NaCl solution was determined even after 28 days of immersion, while the cumulative concentration of released aluminium ions increased with increasing immersion time and reached to maximum values of about 0.098 ppm and 0.085 ppm for the oxidized stand-free coating and polished Ti6Al4V alloy, respectively, after 28 days of immersion. These results showed that, although the cumulative concentration of aluminium ion released from the oxidized stand-free coating was relatively higher than that from the polished Ti6Al4V alloy after 28 days of immersion, the cumulative concentrations of released aluminium ions for both samples are below the limits of International Agency for Research on Cancer (IARC) [109].

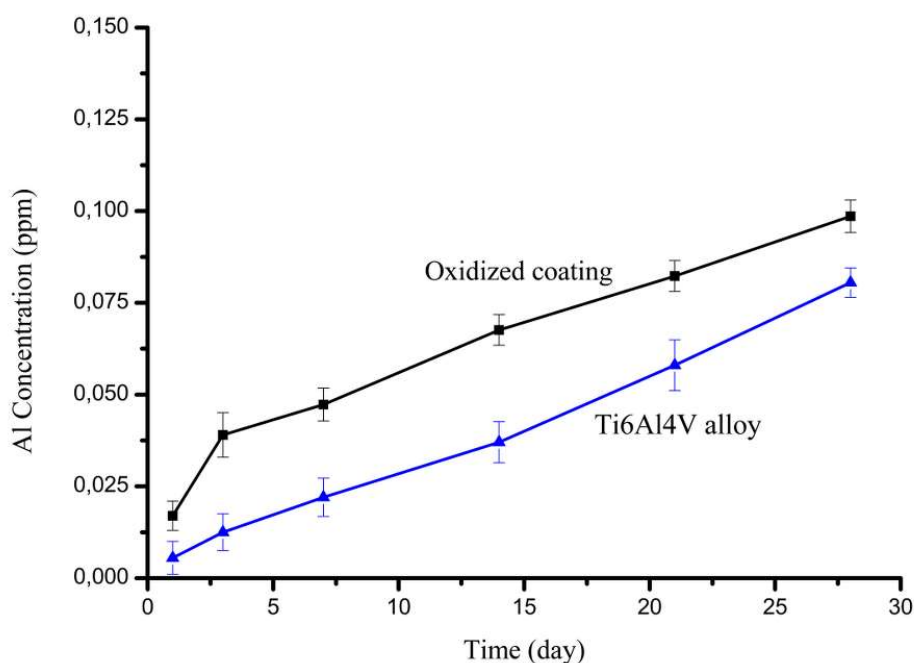


Figure 3.1: The cumulative concentrations (in ppm) of aluminium ions released from the oxidized substrate-free coating and polished Ti6Al4V alloy.

3.3.2 Structural examinations

Figs. 3.2 and 3.3 show the XRD pattern and cross-section SEM micrograph of the CS coating, respectively. Only α -titanium and aluminium peaks appeared on the XRD pattern of the CS coating, resembling the XRD pattern of the feedstock (mixture of 92 wt. % titanium and 8 wt. % aluminium powder). It is worth mentioning that no diffraction peak implying oxidation, chemical reaction or phase transformation during deposition was detected on the XRD pattern of the CS coating. In accordance with the

XRD analysis, the microstructure of the CS coating consisted of bright coloured titanium and dark coloured aluminium, in which aluminium particles were homogenously distributed in the titanium matrix. EDX analysis revealed the average composition of Al in the CS coating as 4wt.%. This indicates that, aluminium content of the CS coating is within the permissible range of commercially available Ti6Al4V alloys (Ref 26) utilized in manufacturing of implants.

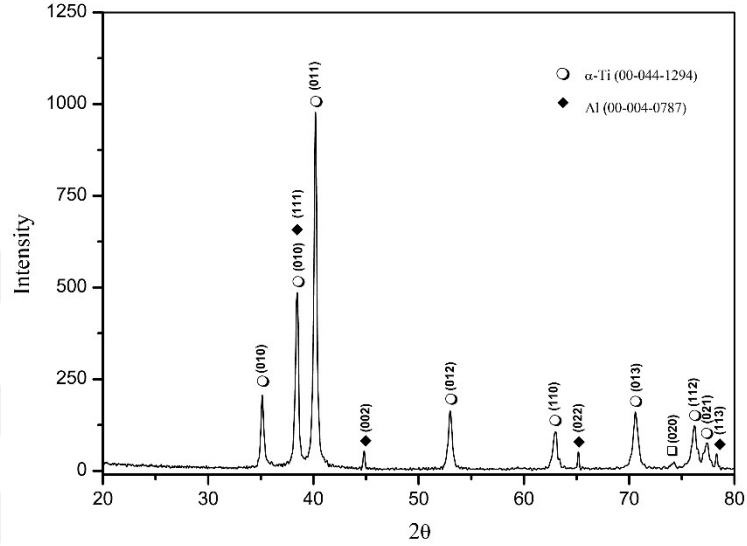


Figure 3.2: The XRD patterns of the CS coating.

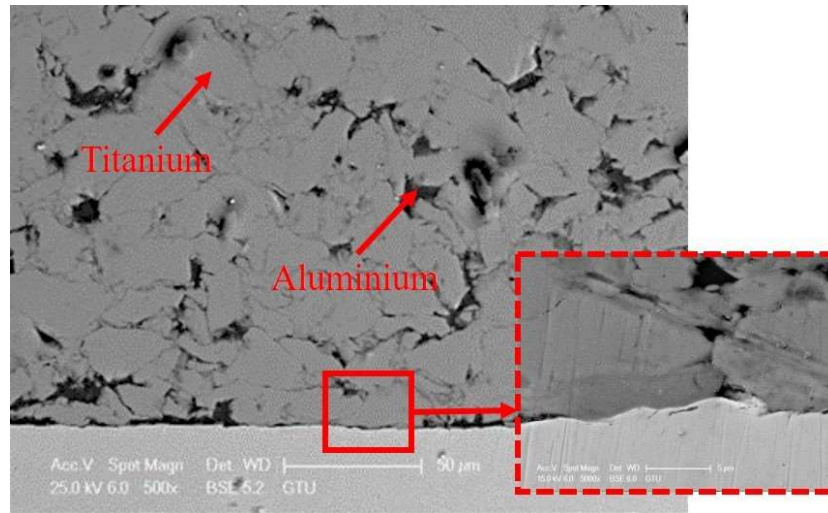


Figure 3.3: Cross-section SEM micrograph of the CS coating.

The interface between the CS coating and the Co-Cr substrate showed good interlocking without any sign of discontinuity. This implies good bonding between the substrate and CS coating, the thickness of which was kept at about 700 μm in this study. The average cross-section hardness of the CS coating was measured as 87 ± 5 $\text{HV}_{0.2}$.

The XRD pattern of the oxidized coating is shown in Fig. 3.4. On the XRD pattern, diffraction peaks of rutile (TiO_2) were identified along with aluminium oxide (Al_2O_3). When peak heights are considered, it is apparent that TiO_2 is much more dominant than Al_2O_3 in the oxide layer. Additionally, diffraction peaks of α -titanium appeared on the XRD pattern due to the penetration of X-rays beyond the oxide layer.

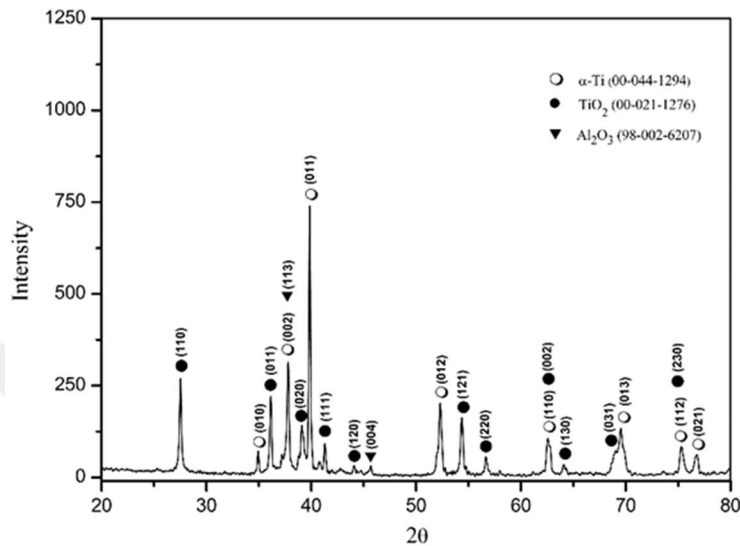


Figure 3.4: The XRD pattern of the oxidized coating.

Fig. 3.5 shows the cross-section SEM micrograph of the oxidized coating. It can be seen that, the surface of the coating was completely covered with a relatively rough ($R_a \cong 0,65 \pm 0,05 \mu\text{m}$) oxide layer having a thickness of about $3 \mu\text{m}$. The nominal composition of the oxide layer was determined as 24Ti-2Al-74O (at.%) by EDX analysis, confirming the presence of a low amount of Al_2O_3 in addition to TiO_2 . No indication of detachment was observed at the interface of the oxide layer and the underlying layer. The average surface hardness of the oxide layer was determined as $1297 \pm 75 \text{ HV}_{0,003}$ at the indentation load of 30 mN which created indentation depths lower than 10% of the oxide layer thickness. The measured hardness value of the oxide layer in this study was in a good agreement with the reported hardness values of TiO_2 [78,110]. Additionally, such a high standard deviation in hardness of the oxide layer, it can be referred as a characteristic scattering caused by low range of penetration depths or small indentation loads for instrumented indentation tests [110].

Apart from the formation of the oxide layer, the applied TO process substantially changed the microstructure of the underlying layer by generating bright, grey and dark coloured regions, whose nominal compositions were identified as 76Ti-24O (at.%),

37Ti-54Al-9O (at.%) and 27Ti-70Al-3O (at.%), respectively. In general, EDX analysis revealed enrichment of the titanium matrix (bright coloured) with oxygen (Ti-O solid solution) in comparison to the as-sprayed CS coating. Additionally, transition from bright coloured regions to grey and dark coloured regions was accompanied by an increase in aluminium and a reduction in oxygen concentration. Depth sensing indentation tests yielded average hardness values of 643 ± 27 HV_{0.01} and 1271 ± 161 HV_{0.01} for bright and grey coloured regions, respectively. Due to the difficulties related to their small size and optical focusing, it was not possible to perform meaningful depth sensing indentations on the dark coloured regions.

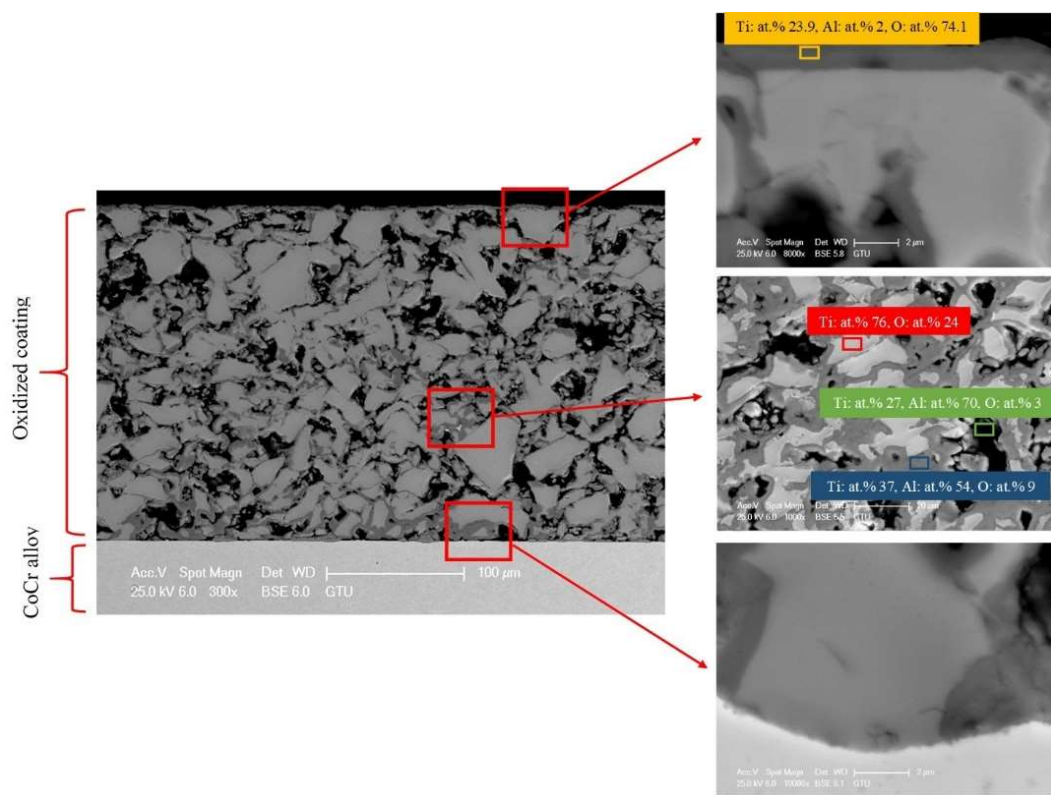
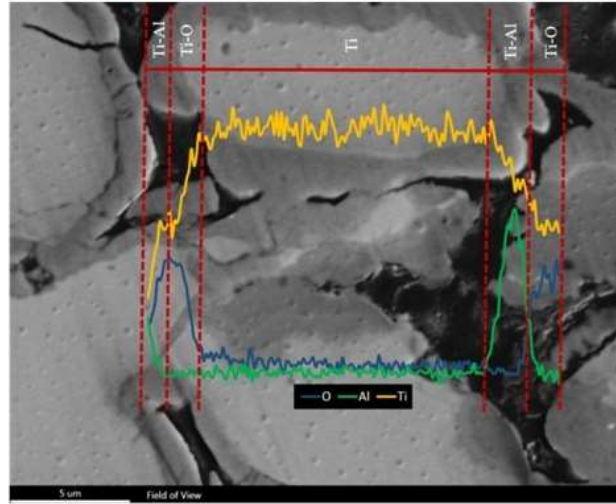


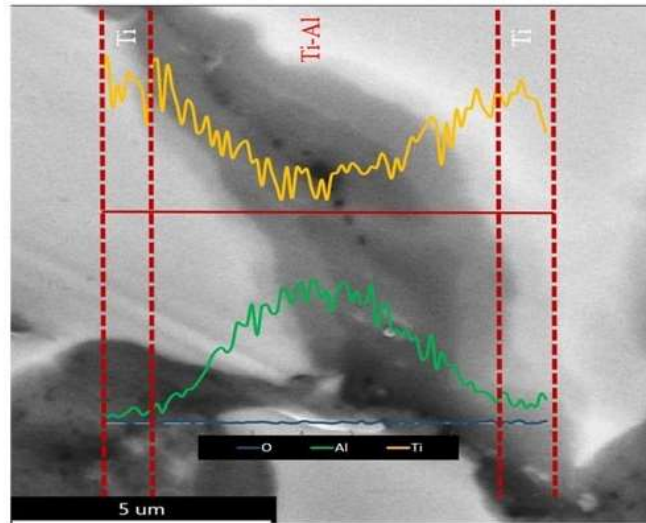
Figure 3.5: Cross-section SEM micrographs of the oxidized coating.

In order to clarify the enrichment of titanium with oxygen and aluminium during the TO process, elemental line scan analysis was conducted beneath the oxide layer during SEM surveys (Fig. 3.6). Line scan elemental analyses confirmed that the titanium particles were surrounded by Ti-Al and Ti-O containing zones. Although oxygen was detected in some of the Ti-Al zones (Fig. 3.6a), oxygen free Ti-Al zones were also identified in other regions (Fig. 3.6b). Furthermore, a gradual decrease in Al concentration was noticed in the Ti-Al zones towards the titanium particles. In short, SEM examination revealed that the TO process did not only cause penetration of

oxygen atoms beneath the oxide layer but also activated diffusion between contacting particles (i.e Al and Ti). For this reason, the layer beneath the oxide layer will be referred as the diffusion layer hereafter. The average overall hardness of the diffusion layer was determined as $387 \pm 33 \text{ HV}_{0.2}$ with a conventional micro-hardness tester.



(a)



(b)

Figure 3.6: a and b. Cross-section SEM micrographs of the oxidized coating showing elemental line scan analysis for oxygen, aluminum and titanium.

3.3.3 Mechanical tests

During the tensile adhesion tests of the oxidized samples, fracture took place in the diffusion layer (Fig. 3.7) at an average tensile load of $1250 \pm 350 \text{ N}$, corresponding to an average tensile fracture strength of $12 \pm 3 \text{ N/mm}^2$. As can be seen in Fig. 3.7, fracture surfaces of the oxidized samples were smooth and free of failure at the oxide layer/diffusion layer and/or diffusion layer/substrate interfaces. In general, fracture

surfaces exhibited trans-particular characteristics without any evidence of plastic deformation. Finally, SEM examinations of the fracture surfaces of the tensile adhesion test samples revealed the brittle nature of the diffusion layer.

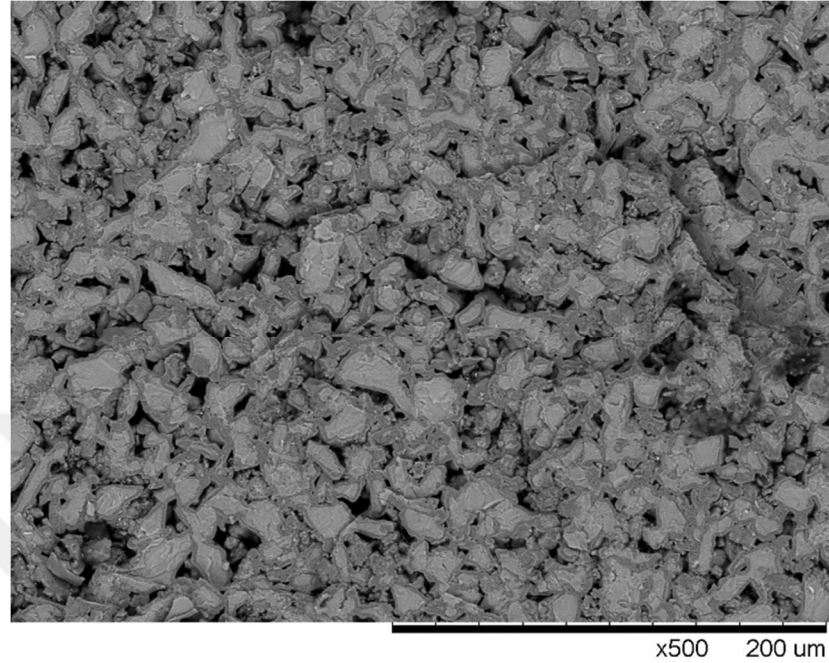


Figure 3.7: SEM micrograph showing the fracture surface of the tensile adhesion test sample.

The XRD pattern of the fracture surface is presented in Fig. 3.8. On the XRD pattern, diffraction peaks of Ti-Al intermetallics (in the forms of TiAl_2 and TiAl_3) and TiO_2 (in the form of rutile) were detected along with α -Ti and a minor peak of Al_2O_3 . Findings of the XRD analysis (Fig. 3.8) are in accordance with the elemental line scan EDX analyses presented in Fig. 3.6 indicating that Ti-Al and Ti-O surrounding titanium could be TiAl_2 and/or TiAl_3 and TiO_2 respectively. The gradual decrease of Al concentration within the Ti-Al zones suggests that TiAl_2 and TiAl_3 type intermetallics are sequentially ordered.

Fig. 3.9 presents the results of scratch tests conducted on the surface of the TO sample. In general, the oxide layer preserved its integrity and durability during scratch testing without any indication of delamination and fragmentation (Figs. 3.9a and b). As can be seen in Fig. 3.9b, crack formation was not clearly identified within the scratch until a normal load of 25 N was applied, above which semi-circular cracks (tensile cracking) became more apparent and dense. Furthermore, local chipping or spalling adjacent to the scratch was not detected until the maximum scratch load of 30 N was reached.

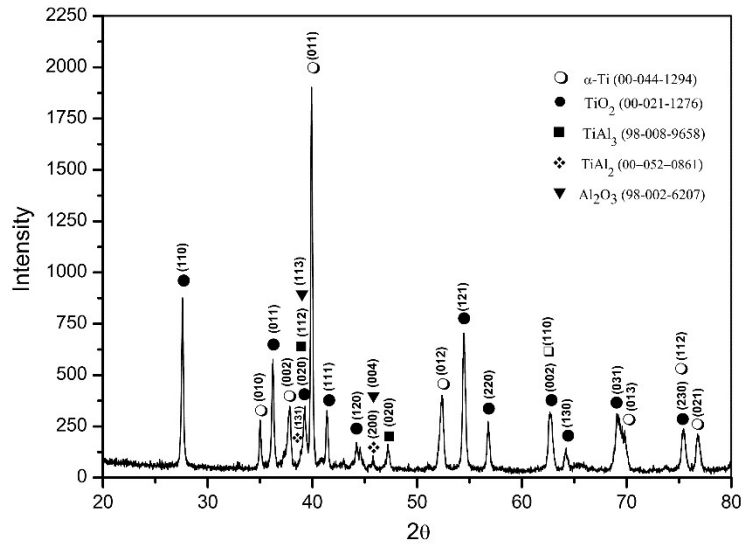


Figure 3.8: The XRD pattern of the diffusion layer of the oxidized coating.

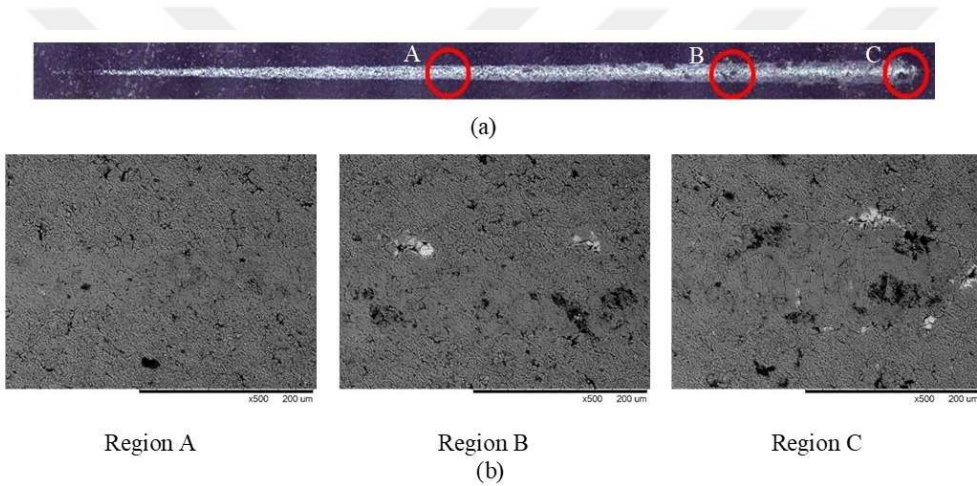


Figure 3.9: a) Light optical microscope micrograph of the scratch trace, b) SEM micrographs showing the damages labelled regions A, B and C, respectively in the scratch trace after the scratch test.

SEM micrographs of the imprint formed on the surface of the oxidized sample after the Rockwell-C adhesion test are presented in Fig. 3.10. Tensile type circular microcracks surrounding the edge of the imprint were observed, without any indication of delamination and lateral flaking and/or chipping. The Rockwell-C test revealed adhesion quality between the oxide layer and diffusion layer in the range of HF1 (HF is representing the German short form of adhesion strength) class according to the adhesion strength quality maps of Daimler–Benz Rockwell-C adhesion test in which HF1-4 define sufficient adhesion [111,112]. The result of the Rockwell-C adhesion test is in good agreement with the result of the tensile adhesion tests, reflecting the significantly good interfacial strength between oxide layer and diffusion layer.

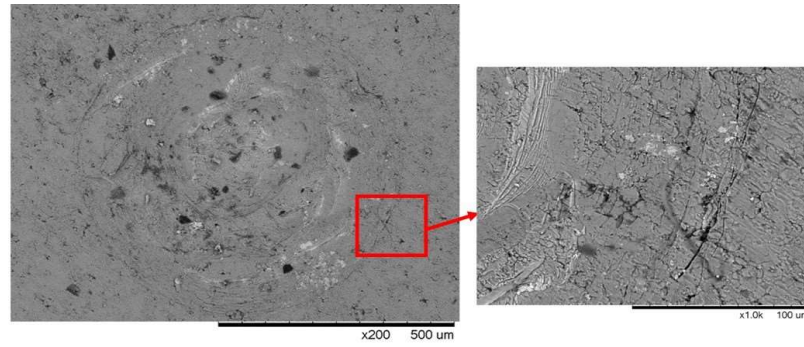


Figure 3.10: SEM micrograph of the damage pattern of the imprint and its surrounding formed on the surface of the oxidized sample after the Rockwell-C adhesion test.

3.3.4 Results of the sliding wear tests

The 3D profiles of wear tracks developed on the surfaces of the as-received Co-Cr and the oxidized samples following sliding wear tests conducted under the loads of 1, 2 and 3 N are presented in Fig. 3.11. As expected, the increase of wear load generated wider and deeper wear tracks on the Co-Cr samples while no measurable wear tracks developed on TO samples under wear loads of 1 and 2 N. However, a wear load of 3 N formed a wear track with a size close to that formed on the Co-Cr sample. It should be noted that the depth of the wear track formed on the oxidized sample under wear test load 3 N ($\sim 0.94 \mu\text{m}$) is well below the thickness of the oxide layer. The quantified average volumetric wear loss values of the Co-Cr alloy and TO samples are listed in Table 3.1.

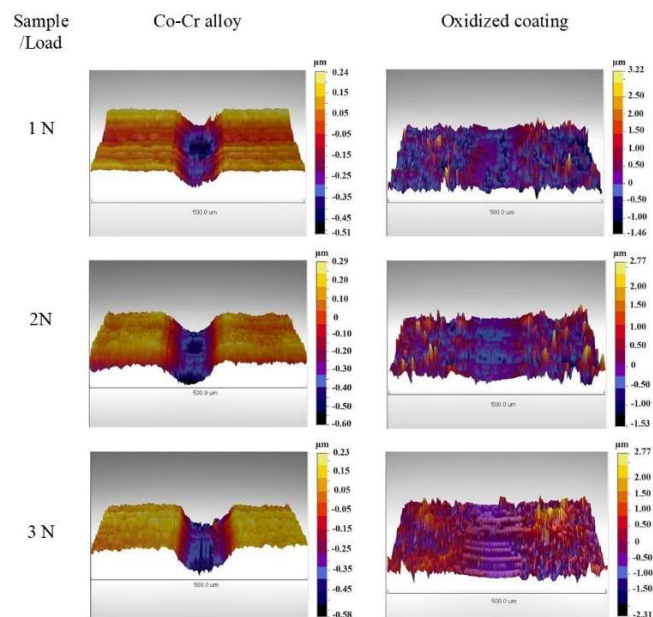


Figure 3.11: The 3D surface topographic profiles of the wear tracks formed on the examined samples after wear testing in 0.9 wt.% NaCl solution.

Table 3.1 : The average volumetric wear loss of the examined samples in 0.9 wt.% NaCl solution.

Test Loads	Volumetric wear loss ($\text{mm}^3 \times 10^{-6}$)	
	Co-Cr alloy	TO coating
1 N	160±10	Not measurable
2 N	185±16	Not measurable
3 N	335±67	355±94

Figure 3.12 show SEM micrographs of the worn surface of the Co-Cr alloys and the oxidized samples. In general, Co-Cr and oxidized samples exhibited different worn surface topographies. For the Co-Cr samples, the worn surfaces can be characterized by a rough surface appearance with numerous grooves aligned in the sliding direction indicating progress of wear by micro-abrasion. The increase of wear load from 1 N to 3 N caused severe deterioration on the worn surface by imposing wider and deeper grooves. In the case of the oxidized sample, SEM examination of the worn surfaces confirmed smoothing of the oxide layer as the asperities were removed by the polishing effect of the counter-face (Al_2O_3 ball).

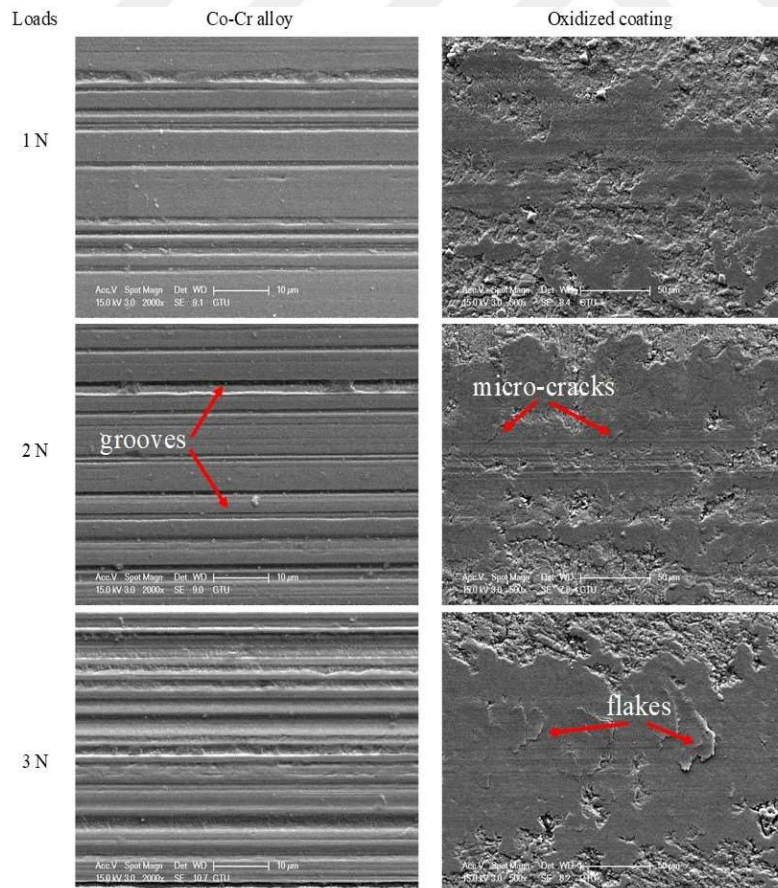


Figure 3.12: SEM micrographs of the worn surfaces of the Co-Cr alloys and the oxidized coatings after wear tests with respect to the test loads utilized in this study.

The increase of the test load to 3 N caused a bigger real contact area between the coating and counter-face (due to the increase in contact pressure) and, therefore, generated more consistent wear track widths. The increase of wear load to 3 N caused micro-cracking and flaking on the worn surface along with the smoothing effect of the counter-face, which can be more clearly seen in Fig. 3.13. These observations suggest that the micro-cracking and flaking-assisted micro-chipping contributed to progress of wear on the surface of the oxidized sample under a wear load of 3 N.

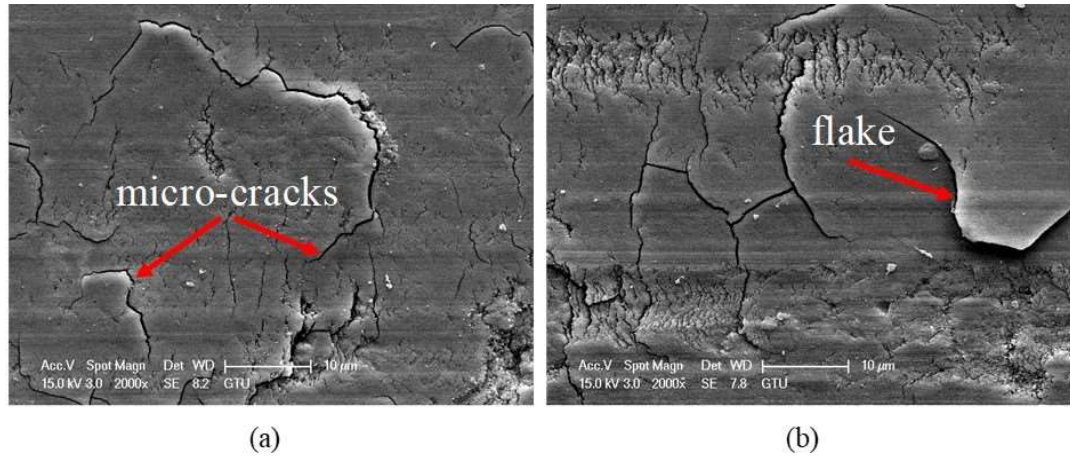


Figure 3.13: SEM micrographs taken from different regions of the worn surface of the oxidized coatings after wear test under the test load of 3N.

3.4 Discussion

Low pressure cold spraying of a Ti92-Al8 (wt.%) powder mixture in air (used as the carrier gas) generated a well-adhered titanium based coating on Co-Cr substrates. The presence of ductile Al powder in the feedstock provided successful deposition of titanium powder having poor plastic deformation ability over the substrate. Although no evidence of a chemical reaction between aluminium and titanium and oxidation has been observed, the Al concentration of the CS coating (~4 wt.%) is quite different than it is in the feedstock. This can be associated to the deposition efficiency of the aluminium during CS process [113–115]. It should be noted that the remaining Al in the coating is within the permissible range of commercially available Ti6Al4V alloy. Subsequent application of TO (at 600°C for 60 hours) substantially increased the surface roughness (from $R_a = 0.1 \pm 0.01 \mu\text{m}$ to $R_a = 0.65 \pm 0.05 \mu\text{m}$) and changed the microstructure of the coating into a dual layer consisting of an outer oxide layer and an inner diffusion layer (as schematically shown in Fig. 3.14). The oxide layer was mainly rutile based TiO_2 (2-3 μm thick) with a minor amount of Al_2O_3 . Ion release

tests conducted in 0.9 wt.% NaCl solution for 28 day confirmed that release aluminium ions from the TO coating is slightly higher than that of Ti6Al4V alloy but well below the permissible limit (27 ppm) of IARC. When the larger real surface area of the oxidized stand-free sample than that of the polished sample arising from its higher surface roughness (i.e $R_a = 0.65 \mu\text{m}$ and $R_a < 0.05 \mu\text{m}$, respectively) is of concern, it can be suggested that there was no significant difference in the cumulative concentration of aluminium ion release between oxidized and Ti6Al4V samples.

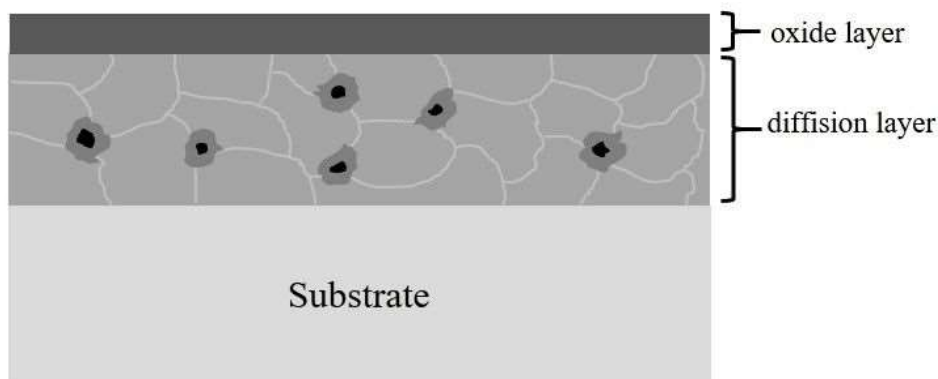


Figure 3.14: Schematic representation of coating structure evolution of the CS coating during TO process.

Beneath the TO layer, diffusion layer developed as the result of penetration of oxygen into the coating and diffusion of aluminium into the neighbouring titanium particles during the TO process. Since the particle boundaries and defects in the as-sprayed CS coating have a high potential to act as preferential diffusion paths, penetration of oxygen atoms is more favourable as compared to bulk titanium. Therefore, particles were enriched with oxygen (solid solution) as the matrix phase throughout the thickness of the coating titanium. In this respect, the hardness of the titanium matrix was increased from $87 \pm 5 \text{ HV}_{0.2}$ to $643 \pm 27 \text{ HV}_{0.01}$ as a consequence of the solid solution hardening mechanism. Since the maximum solubility of oxygen in titanium is 34 at.%, according to Ti-O phase diagram at 600°C [54], excess oxygen around the oxygen diffusion path of the coating led to formation of TiO_2 and Al_2O_3 type oxides within the diffusion layer.

Formation of Al_2O_3 can be associated with reaction of Al particles with the penetrating oxygen atoms. Additionally, aluminium also tended to diffuse towards the neighbouring titanium particles to generate TiAl_2 and TiAl_3 type Ti-Al intermetallics having a hardness of $1271 \pm 161 \text{ HV}_{0.01}$. Since the maximum solubility of aluminium in $\alpha\text{-Ti}$ at the oxidation temperature of 600°C applied in this study is about 12 at.%,

according to the Ti-Al phase diagram [116], surplus aluminium exceeding its solubility limit reacts to form intermetallic phases. Although the Ti-Al phase diagram suggests formation of intermetallics, such as Ti_3Al , TiAl , as well as TiAl_3 and TiAl_2 , in the present study, formation of TiAl_3 and TiAl_2 intermetallics was observed at the TO temperature of 600°C . The free energy of formation of these intermetallics at 600°C was calculated according to data reported by Kattner et al. [117] and given in Table 3.2. At this temperature, formation free energies of TiAl_2 and TiAl_3 are lower than those of Ti_3Al and TiAl , hence, the formation of intermetallic TiAl_2 and TiAl_3 phases was thermodynamically favourable. Although formation of Ti-Al intermetallics is the result of diffusion of Al into Ti during the TO process applied in this study, Al particles were not completely consumed. When the diffusion suppression effect of Al_2O_3 film covering Al particles is considered [79], it is suggested that Ti-Al intermetallics form at the early stages of TO process, where penetration of oxygen beneath the oxide did not yield Al_2O_3 formation.

Table 3.2 : Free energy values (ΔG) calculated for formation of various Ti-Al compounds at 600°C (873 K).

Compound	ΔG (joule/ mol)
TiAl	-22784,1
Ti_3Al	-23777,5
TiAl_3	-31300,7
TiAl_2	-34237,3

Microstructural changes in the diffusion layer (i.e Ti-O solid solution, TiO_2 and Al_2O_3 type oxide and TiAl_2 and TiAl_3 type intermetallic formation) resulted in increased hardening while imposing brittleness leading to fracture during tensile adhesion tests at a stress level lower than the bonding strengths between oxide layer/diffusion layer and diffusion layer/substrate interfaces. On the other hand, scratch and Rockwell C tests confirmed the superior stability and adhesion characteristics of the oxide layer under shear and compressive-type stresses without any evidence of delamination at the oxide layer/diffusion layer interface.

Superior load bearing capacity of the titanium oxide layer fabricated on titanium and its alloys by TO process can be associated with its ceramic nature providing high hardness and good resistance against plastic flow during sliding contact unlike metallic substrate. Furthermore, hardening of the underlying layer (i.e. diffusion layer) during

TO gives extra support to the outer titanium oxide layer by reducing the hardness gradient between the oxide and the underlying layers [51,118,119]. In accordance with these generalized statements the oxide layer fabricated in this study exhibited superior wear resistance under contact pressures of about 1200 MPa, which is much higher than the contact pressure experienced by the human knee joint (maximum 15 MPa) in vivo [90]. Even under such a high sliding contact pressure (i.e 1200 MPa) level, wear progressed on the oxide layer by the polishing effect of the counter-face (Al_2O_3 ball) in a negligible range as compared to the Co-Cr alloy. The bonding between oxide and diffusion layers (analysed by tensile, scratch and Rockwell C adhesion tests in this study) remained stable and did not cause any delamination during sliding wear in 0.9 wt.% NaCl solution.

Since high surface hardness and enhanced wear resistance are among the major requirements for load bearing implants, the findings of this study revealed that formation of a dual layer coating (consisting of an outer TiO_2 layer and the diffusion layer beneath) by combination of CS and TO processes is a promising avenue for manufacturing load bearing orthopaedic implants made of Co-Cr and stainless steel. Apart from the enhanced surface mechanical properties, the proposed surface modification approach can provide bioactive surfaces as compared to the substrate (Co-Cr alloy and stainless steel), benefiting from the enhanced biological properties of the TiO_2 layer. Furthermore, this approach can offer the possibility to adjust the composition of the titanium oxide layer with the aim of enhancing antibacterial characteristics by adding antibacterial agents into the feedstock utilized in CS process. It should be emphasized that results of this study highlight the need to optimize the coating, especially for use under tensile loads, by reducing the brittleness of the diffusion layer. For this purpose, the authors of this study are planning the following future work with the aim of reducing the brittleness of the diffusion layer while preserving the superior surface mechanical properties;

- i) fabricating the CS coating from a lower Al containing feedstock to minimize the reaction between Ti and Al during the TO process
- ii) reducing the TO temperature and time to avoid deep penetration of excess oxygen into the coating

- iii) applying the TO process to a relatively thin CS coating (having thickness much lower than 700 μm) to narrow the diffusion layer.

3.5 Conclusion

Co-Cr samples were subjected the TO process in air at 600°C for 60 hours after deposition of a Ti+Al4 (wt.%) coating by the CS process. Structural and mechanical characteristics of the coatings fabricated with this approach can be summarized as follows:

1. Application of TO altered the structure of the as-sprayed CS coating by generating a dual layer coating structure consisting of oxide and diffusion layers.
2. The oxide layer, which was mainly comprised of the rutile form of TiO_2 with a minor amount of Al_2O_3 , exhibited a rough morphology ($R_a=0.65 \pm 0.05 \mu\text{m}$) and preserved its stability without any indication of delamination at the oxide layer/diffusion layer interface during scratch and Rockwell C tests. The hardness of the oxide layer was $1297 \pm 75 \text{ HV}$.
3. The underlying diffusion layer, which developed not only as the result of the penetration of oxygen beyond the oxide layer during the TO process but also due to diffusion of aluminium into the neighbouring titanium particles, consisted of Ti-O solid solution, Ti-Al intermetallics and oxides. Owing to the formation new phases, the diffusion layer exhibited higher hardness ($387 \pm 33 \text{ HV}_{0.2}$) than that of the as-sprayed CS coating ($87 \pm 5 \text{ HV}_{0.2}$). As a consequence of the new phase structure, the diffusion layer became brittle and exhibited poor resistance against tensile stress during tensile adhesion tests as compared to the oxide layer/diffusion layer and diffusion layer/substrate interfaces.
4. Similar to the results of the scratch and Rockwell C tests imposing shear and compressive type stresses, the oxide layer preserved its mechanical stability against the sliding action of the Al_2O_3 ball during wear tests conducted in 0.9 wt.% NaCl solution. At contact pressures lower than 1200 MPa, the sliding action of the Al_2O_3 ball only caused smoothening of the oxide layer in the contact region with unmeasurable wear loss.

5. Release of aluminium ions from the stand free coating into the 0.9 wt.% NaCl solution is well below the limits of IARC.

3.6 Acknowledgement

This work has been carried out with the financial support provided by The Scientific and Technological Research Council of Turkey (TUBITAK) under contract no. 214M246. The authors would like to thank to Mr. A. Nazim of Gebze Technical University for carrying out SEM investigations and Mr. O.F. Deniz of Gebze Technical University for using 3D surface profilometer. The authors also would like to thank Mr. F. Muhaffel for using depth sensing ultra-micro hardness tester.



4. THERMAL OXIDATION OF COLD SPRAYED Ti-5Al-XZn COATINGS FOR TRIBOLOGICAL APPLICATIONS ³

4.1 Introduction

Cold spray (CS) is an emerging deposition technique, where powder carried by pressurized gas at high velocities deposit on substrates upon impact in solid state [1]. Fabrication of CS-coatings can either be done by using low- or high-pressure systems (i.e LPCS and HPCS, respectively). For deposition of soft/deformable metal powder LPCS is widely preferred to HPCS, owing to its low cost and portability [8]. However, LPCS is not feasible for deposition of hard/brittle powder, unless mixed with soft powder. But the hardness of the coatings formed by the deposition of hard and soft powder mixture may still not be sufficient for wear-related applications. In this context, employing of post-processes, such as electrochemical oxidation [38,39] and laser treatments [120], recently appeared as a promising technical solution to enhance the surface hardness and wear resistance of LPCS-coatings.

Our recent works demonstrated that, as a post-treatment thermal oxidation (TO) has potential to provide superior wear resistance for Ti-based LPCS-coatings as their surfaces were covered with a compact, adherent, hard ($\sim 1300 \text{ HV}_{0,003}$) and thin ($\sim 3 \mu\text{m}$) TiO_2 layer [104,121]. In this study TO has been applied to Zn containing Ti-based LPCS-coatings. The aim was to benefit from the lubricious nature of solid ZnO [122] for further improvement in the tribological performance of the outermost TiO_2 layer via reducing the coefficient of friction (COF) under dry sliding contacts.

³ This chapter is based on the paper “Cetiner, D., Atar, E., Derin, B., and Cimenoglu, H. (2020) Thermal oxidation of cold sprayed Ti-5Al-XZn coatings for tribological applications. Materials Letters. 274, 127959.”

4.2 Experimental

Ti-based CS-coatings were deposited on Co-Cr alloy with a LPCS system with the process parameters given in [104,121]. Four different feedstock, prepared by mixing spherical powders of 85-95wt.%Ti, 5wt.%Al and 0-10wt.%Zn, were sprayed. After grinding and polishing of the coatings to Ra value of $\sim 0.1 \mu\text{m}$, samples were TO'ed at 600°C for 60h in air.

Coatings were examined by light optical (LOM), energy dispersive X-ray (EDX) spectrometer equipped field emission scanning electron (SEM) and atomic force (AFM) microscopes. After TO-process, room temperature dry sliding tribological performances of the coatings were evaluated against 6 mm diameter Al_2O_3 ball by utilizing a reciprocating wear tester. Tests were run for a total sliding distance of 25 m (stroke length 5 mm and sliding speed 10 mm/s) under normal load of 3N. The wear tracks formed on the samples were investigated by the SEM.

4.3 Results and discussion

Along with the cross-section LOM images of the CS-coatings, their surface SEM and AFM images after the TO process are shown in Fig. 4.1. The thickness of the CS-coatings decreased with increasing Zn content of the feedstock, so that at 10wt.%Zn content cavity like defects were formed on the surface. This observation can be attributed to the reduction in deposition efficiency of the feedstock with increasing Zn content arising from its HCP crystal structure [1].

On the surface SEM images of the TO-coatings, bright grey coloured Zn-rich regions ($\text{Zn} > 30\text{at.}\%$) became more evident with increasing Zn content of the coating, while the remaining regions were Zn-poor ($\text{Zn} < 2\text{at.}\%$) and exhibited similar surface appearance with that of Zn-free coating. The increment in Zn content of the coating not only increased the fraction but also the size of the Zn-rich regions, and dominated ridge-like topography as confirmed by AFM studies. According to the results of XRD analysis (figure not shown), the main phases of the Zn-rich and Zn-poor regions were identified as wurtzite type ZnO (ICSD RefCode:98-001-1325) and rutile type TiO_2 (ICSD RefCode:98-004-0452), respectively. Additionally, on the XPS spectra of the Zn containing TO-coatings, Zn ($2p_{1/2}$ and $2p_{3/2}$) and O (1s) peaks were also detected lying within the range of characteristic binding energy values of ZnO [123].

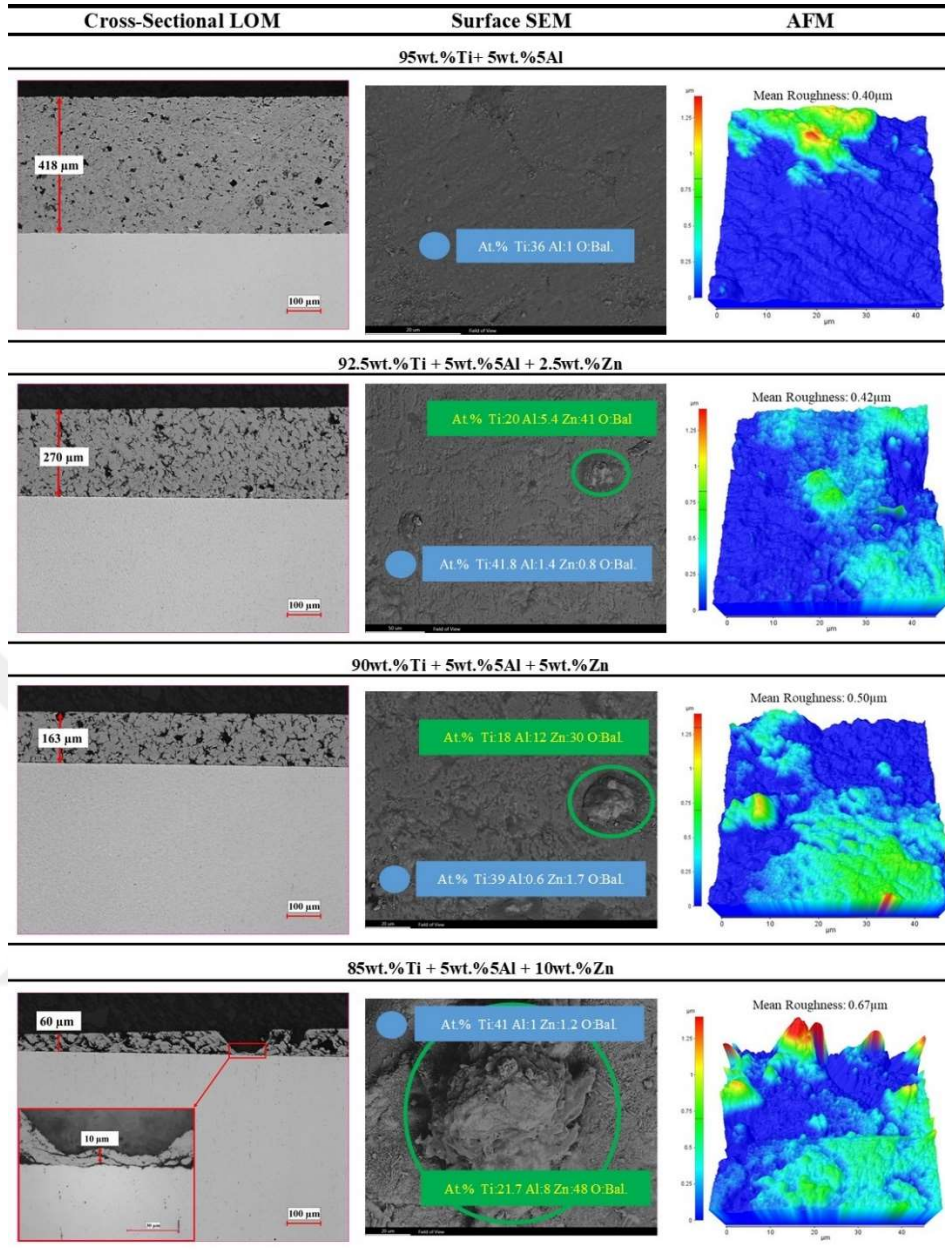
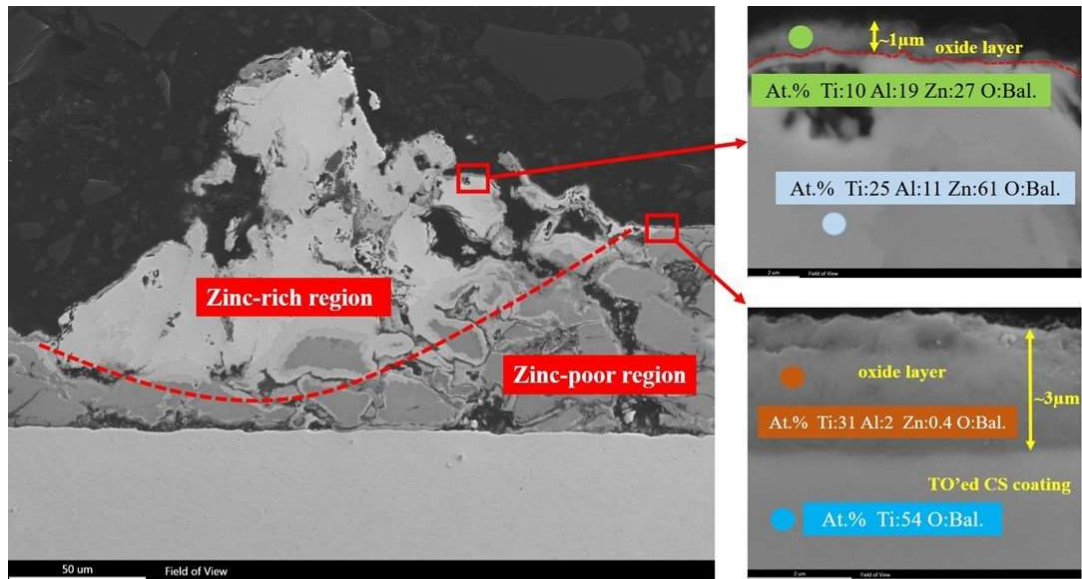


Figure 4.1 : Cross-section LOM images of the CS-coatings, surface SEM and AFM images of these coatings after TO process.

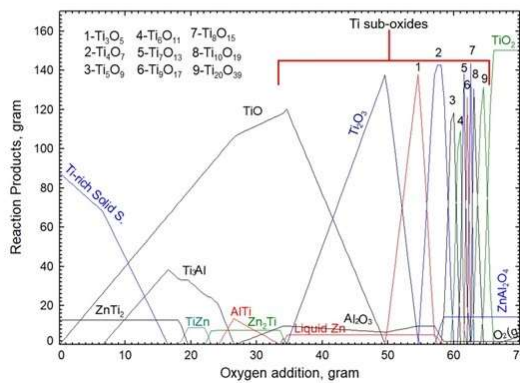
On the SEM image taken from the cross-section of a ridge, Zn-rich and Zn-poor regions appeared in bright and grey colours, respectively (Fig.4.2a). Higher magnification examinations revealed that both of these regions were covered by $\sim 1\mu\text{m}$ and $\sim 3\mu\text{m}$ thick oxide layers, respectively. In order to follow the formation of these oxide layers during TO from the thermochemical point of view [124], FactSage.7.3 was employed. Fig 4.2b and c depict oxide formation modelling for Zn-poor and Zn-rich regions at 600°C , whose compositions were assumed as “90wt.%Ti+5wt.%Al+5wt.%Zn” and “5wt.%Ti+5wt.%Al+90wt.%Zn”, respectively. According to Fig.4.2b, oxidation of the Zn-poor region starts with Ti-O solid solution

formation. Further oxidation favours TiO as a Ti sub-oxide at the expense of Ti-O solid solution, while reactions Ti with Zn and Al promote various types of Ti-Zn and Ti-Al intermetallics. Further oxidation tends the form Al_2O_3 , Ti_2O_3 and other Ti sub-oxides, sequentially. Finally, at the highest level of oxygen, TiO_2 forms with minor amounts of Al_2O_3 and ZnAl_2O_4 . According to Fig.4.2 c, oxidation of the Zn-rich region dictates the melting of Zn at first. In this regard, the main reason of ridge-like morphology of the Zn-rich regions was suggested to be the outward flow of the Zn-melt during TO process, arising from the local accumulation of Zn powder in the structure of the CS-coating. Oxidation proceeds by the formation of TiZn_3 and TiAl_2 type intermetallics. Further enrichment of the surface by oxygen causes formations of limited amounts of Al_2O_3 and/or Ti sub-oxides, while the decomposition of TiZn_3 favours an increase in the fraction of the Zn-melt. Unlike the Zn-poor region, the oxidation of Zn first supports the formations of complex oxides as ZnAl_2O_4 and Zn_2TiO_4 at certain amounts and it continues until all excess liquid Zn turns into solid ZnO.

Friction curves and worn surface images of the TO-coatings are presented in Fig.4.3. The testing load of this study, which generated contact pressure as high as ~ 1.2 GPa for $\text{TiO}_2/\text{Al}_2\text{O}_3$ tribo-couple, did not create any measurable wear track. In general, rubbing action of the counter face favoured smoothening of contact surface via deformation of the asperities without any evidence of delamination. Unlike Zn-free coating, worn surfaces of the Zn containing coatings exhibited glaze-like appearance due to the covering of the wear tracks by a Zn- and O-rich film. This observation indicated that Zn-rich ridges were smeared on the contact surface and thereafter counter face slid on the Zn- and O-rich film. Full coverage of the worn surface by this film was accomplished on the coating fabricated from the 5wt.%Zn containing feedstock. This led to smoothening of the friction curve whereas COF value was reduced to ~ 0.12 , which was 0.27 for the Zn-free coating. Previously, COF values in the range of 0.15 and 0.25 have been reported for ZnO thin films at room temperature, while the bulk ZnO yielded COF values in between 0.6 and 0.7 [125,126]. Lower COF value of ZnO films was attributed not only to its wurtzite structure but also its nano-sized and oriented nature [125–127].



(a)



In order to overcome limitations of LPCS for successful deposition of high Zn containing feedstock and fine-tuning of the Zn content for achieving the lowest COF value after TO-process, it is worth to make some trials on Zn containing ($\geq 10\text{wt.}\%$) Ti-based coatings fabricated by using the HPCS system having a much better ability to produce dense and defect-free coatings.

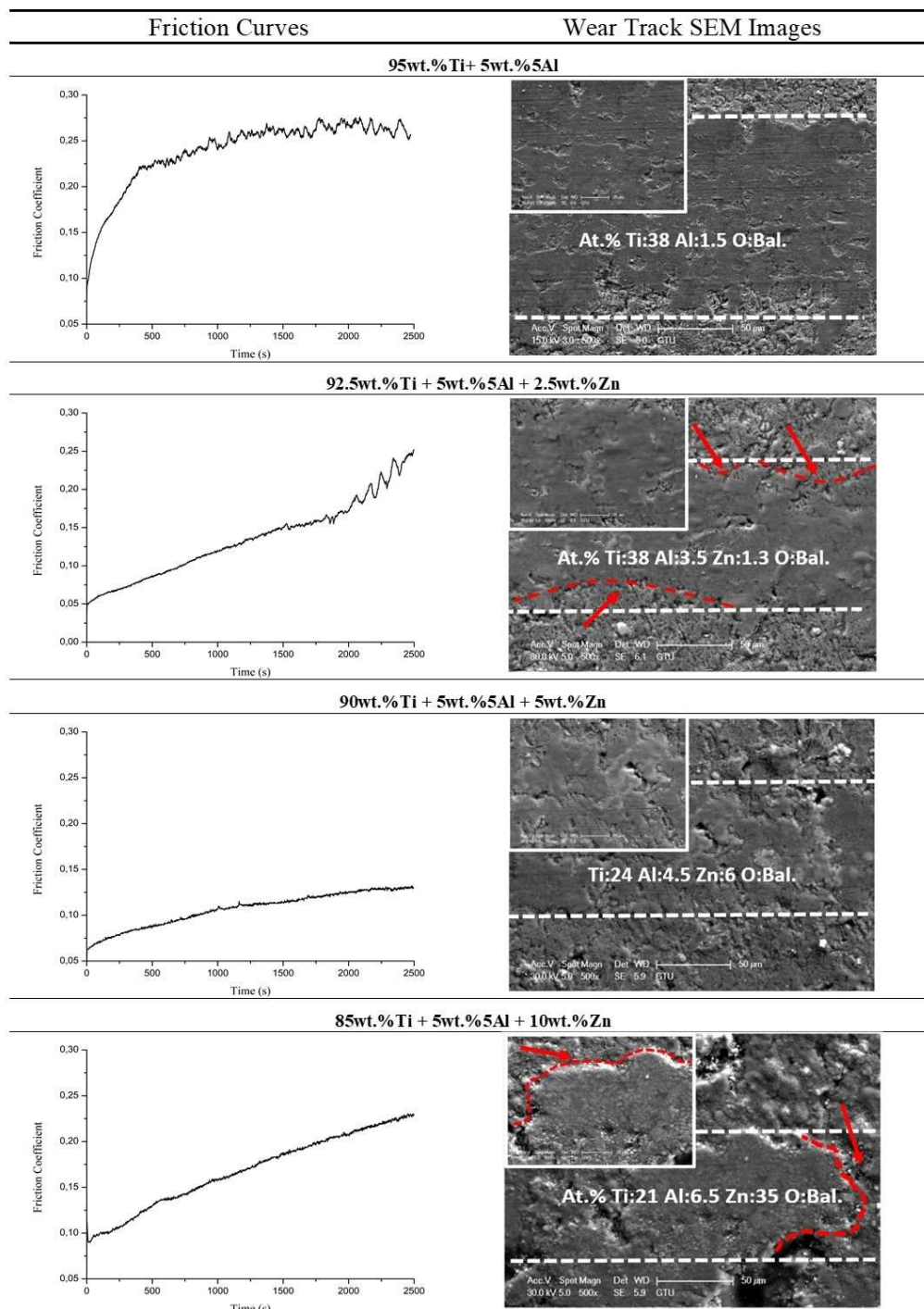


Figure 4.3 : Friction curves and worn surface SEM images of the TO-coatings (smearing free zones in the wear tracks are shown by arrows).

4.4 Conclusion

The results of this study can be summarized as follows:

- i. Up to 5wt.%Zn, feedstock prepared by mixing Ti, 5wt.%Al and Zn powder was successfully deposited on Co-Cr alloy by LPCS system. Increment of Zn content to 10wt.% caused the formation of cavity-like irregularities on the surface of the deposited coating.
- ii. Subsequent application of TO at 600°C for 60h in air favoured the formation of Zn-rich ridges along with TiO₂ layer over the Zn containing coatings, which played a crucial role on their frictional characteristics.
- iii. Among the examined coatings, the coating fabricated from the 5wt.%Zn containing feedstock exhibited superior room temperature tribological performance after the TO process in terms of enhanced wear resistance and reduced COF value against Al₂O₃ ball under dry sliding conditions.



5. CHARACTERISTICS OF SILVER CONTAINING TITANIUM BASED COATING AFTER THERMAL OXIDATION ⁴

5.1 Introduction

There is an intense attraction of long-lasting anti-bacterial coatings in biomedical and health industries not only for medical devices but also for the touch surfaces of health-care-related equipment/instruments such as door handles, touch plates, bed rails, and call buttons the hospitals [128–130]. As one of the most widely used metals in the biomedical and health industries, 316L SS, which exhibits enhanced corrosion resistance due to the naturally formed a protective thin (1-3 nm) Cr_2O_3 layer on its surface [131,132], also suffer the poor antimicrobial or anti-bacterial characteristics. Since bacterial contamination on the surfaces of devices used in medical and health-care related applications has got high potential for serious adverse health issues [133,134], various surface modification techniques such as electrodeposition, sol-gel, pulsed laser deposition, and magnetron sputtering have been applied to 316L SS to fabricate anti-bacterial ceramic/polymeric coatings [135–137] or anti-bacterial agent (such as Zn, Ag or Cu) incorporated coatings [138–140].

This study has been initiated to extend the novel coating that we have previously fabricated on Co-Cr alloys [104,141] to 316L SS substrate in the presence of Ag as the modifier of the coating. This novel coating has been developed by combining the CS and TO processes. At the first step, the mixture of Ti and Al metallic powder is deposited over the substrate by using low-pressure CS equipment. In general CS process bases on forwarding the relative soft metallic powders towards the substrate with supersonic velocities reached by the help of laval nozzle and pressurised carrier gas [1,2,142].

⁴ This chapter is based on the paper “Cetiner, D., Karaguler, N.G., Cimenoglu, H., and Atar, E. (2021) Characteristics of silver-containing titanium-based coating after thermal oxidation. Surface Innovations. In Press.”

The collision/impact of the powders with substrate results in severe plastic deformation of the powders and leads to the formation of CS coating over the substrate [1,2,142]. Thanks to relatively low temperatures reached during spraying, the metallic powders can be deposited in metallic form without oxidation[143]. For that reason, CS has a wide range of application areas like repairing, additive manufacturing and coating production [1,2,142,143].

The subsequently applied TO process is a thermo-chemical surface hardening base on oxygen diffusion into the titanium-based substrates above 200 °C in the air [51]. It generates a uniform, well-adherent, hard (~1200 HV), corrosion-resistant, and bioactive exterior TiO₂ layer with an underlying oxygen diffusion zone, which develops upon the dissolution of oxygen in the titanium matrix. The hardness of the oxygen diffusion zone gradually decreases towards the inner sections of the substrate (with the decreasing amount of the oxygen penetrated) and acts as a transition zone between the hard exterior TiO₂ layer and soft substrate. Higher temperatures and longer duration of TO process favour thicker TiO₂ layers, which may lead to a reduction in the stability above a certain thickness [119]. On the other hand, thinner TiO₂ layers may not provide sufficient protection against corrosion and/or mechanical effects. In this respect, optimum TO process parameters (in the air) forming 3 µm thick TiO₂ layer over bulk Ti-6Al-4V alloy have been determined as 600°C and 60 h [119].

In our previous works, the application of TO at 600°C for 60 h in the air to the CS coatings (composed of 92wt.% Ti and 8wt.% Al) favoured a dual-layered coating on Co-Cr substrate. While the exterior layer was TiO₂ (in the form of rutile), the underlying layer was the mixture of oxygen-enriched titanium and Ti-Al intermetallics. Laboratory tests conducted on this dual-layered coating yielded promising results in terms of enhancement in tribo-corrosion resistance and bioactivity as compared to the Co-Cr substrate. Recently, we have shown the possibility of modifying this coating for wear-related industrial application [144]. In this study, superior tribological characteristics (i.e. high wear resistance and low friction coefficient) have been obtained upon introducing zinc (Zn) into the coating.

As the continuation of our works, an attempt has been made to gain anti-bacterial characteristics to our coating. Since Ag has long been known to be an excellent anti-bacterial metallic material [92,145–147] as the first step Ag containing Ti-based

coating was deposited on the over 316L SS substrate by CS process. Subsequently, the TO process has been applied in the air at 600°C for 60h. Considering the requirements for enhanced mechanical stability for longer service life and biological response if applied to implants, wear and in-vitro biocompatibility tests were also employed on the samples following the TO process in addition to microscopic examinations and anti-bacterial tests.

5.2 Materials and Method

In the present study, the substrate was a medical grade 316L SS cut from a rod having 8 mm diameter. Ag containing coatings were deposited on the 316L SS from the feedstock, which was prepared by mixing spherical powder of 87 wt.% Ti powder (Alfa-Aesar, <325 mesh, purity of %99), 8 wt.% Al powder (Alfa-Aesar, <325 mesh, purity of %99) and 5 wt.% Ag powder (Alfa Aesar, 0,5-1µm, purity of %99,9) by using a low-pressure CS equipment (Model K-201, Rus Sonic Technology, USA) having a converging–diverging-type tubular and an expansion ratio of 2.3. In the CS process, carrier gas was air, the pressure was 6 Bar, transverse speed was 1 mm/s, bean distance was 1,5 mm and stand-off distance was 10 mm.

After grinding (on 240–2500 mesh SiC abrasive papers) and polishing (with 3 µm diamond slurry and colloidal silica solution), CS coatings were isothermally oxidised at 600 °C for 60 h. in an air circulated furnace (Nabertherm, Germany). The heating and cooling rates of the coatings in the furnace were kept as low as possible (i.e. < 5°C/min and <1°C/min, respectively) to minimise the potential thermal stresses generated by thermal expansion coefficient differences between 316L SS substrate and the as-sprayed coating.

Characterisation of the fabricated coatings were performed by X-ray diffraction (XRD) analysis and scanning electron microscope (SEM) surveys. Phase compositions of the coatings were evaluated by X-ray diffraction (XRD) conducted on a diffractometer (MMA, GBC, Australia) equipped with Cu K α radiation. XRD measurements were carried out between diffraction angles of 20° and 80° at a step size of 0.02 and a count time of 0.6 s. SEM examinations were conducted on the surface and cross-section of the coatings by using field emission SEM (Philips SFEG XL30, SEM) equipped with an energy dispersive X-ray (EDX) spectrometer. Moreover, micro-Raman spectroscopy (LabRam 800, Horiba Scientific, Jobin Yvon, France) analysis has been

made on the TO coatings by using an excitation wavelength of 632.8 nm (He-Ne laser) operated at 3 mW at 50x objective magnification to focus the beam having a diameter of about 1 μm .

Anti-bacterial activities of the TO coating were evaluated against *Staphylococcus aureus* (*S. aureus*) ATCC®6538P strain by using "agar disc diffusion" assay as triplicate based on the growth inhibition zone formation. In this method, a stock culture was used to obtain a single colony which was inoculated onto Luria-Bertani (LB) agar plate (1% NaCl, 1% tryptone, 0.5% yeast extract and 1.5% agar) and incubated 16 h at 37 °C. A single colony was transferred into 10 ml LB broth (1% NaCl, 1% tryptone, 0.5% yeast extract) and incubated overnight at 37 °C. The optical density of culture was measured at OD₆₀₀ by using a spectrophotometer and adjusted to standard (1 OD= 10^9 cells). Incubated bacteria were diluted with 1/500 LB and test inoculation value adjusted as 2×10^6 cells. Diluted bacteria samples were inoculated on LB agar plates by spread method, then test samples were put on the agar plate. After that, test samples were incubated overnight at 37 °C. The next day, it was examined whether an area without bacterial growth had formed around the test sample.

In order to reveal the amount of the Ag release from TO coatings, immersion tests were carried out in 0.9% NaCl solution for 28 days. At 1, 3, 7, 14, 21, and 28 days of the testing period, solutions were analysed by inductively coupled plasma optical emission spectrometry (ICP-OES;7000 DV Optima, PerkinElmer, USA) to determine the concentration of the released Ag ions.

Bioactivities of the 316L SS sample and TO coating were evaluated by simulated body fluid (SBF) immersion tests. The samples were immersed in a SBF, which was prepared by the recipe in Ref [77]. During the test, the solution temperature was kept at 36.5 °C and renewed for every two days. At the end of the 1st and 4th weeks, the samples were taken from the solution to examine their surfaces on SEM.

Sliding wear tests were carried out on 316L SS substrate and the TO coating against Al₂O₃ ball (6 mm diameter) to evaluate and compare their tribological performances. Sliding wear tests were conducted in dry sliding and serum (isotonic sodium chloride solution, 0.9% NaCl) conditions at room temperature by using a reciprocating wear tester (Tribotech, France). The test load was selected as 1N in wear tests (creates contact pressure of ~ 850 MPa on TO coating), which is the minimum limit of the

testing instrument. For wear tests, sliding stroke, total sliding length and sliding velocity were set as 5 mm, 25 m and 10 mm/s, respectively. During the wear tests, coefficient of friction (COF) curves were recorded by computer software. After the wear tests, the wear track that developed on the surface of the samples were determined by using a 2D contact profilometer (Veeco Dektak 6M). Finally, the wear tracks that formed on the samples were examined by the SEM equipped with EDX.

5.3 Results and Discussion

5.3.1 Microstructural examinations

In Figs. 5.1 and 5.2, the results of XRD and SEM examinations conducted on the CS coatings are depicted, respectively. In accordance with the constituents of the feedstock used in the CS process, diffraction peaks of α -Ti (ICSD RefCode:98-007-2268), Al (ICSD RefCode:98-008-8994), and Ag (ICSD RefCode:98-006-2942) appeared on the XRD pattern (Fig 5.1) without any indication of oxidation, chemical reaction or phase transformation that could have taken place during the deposition.

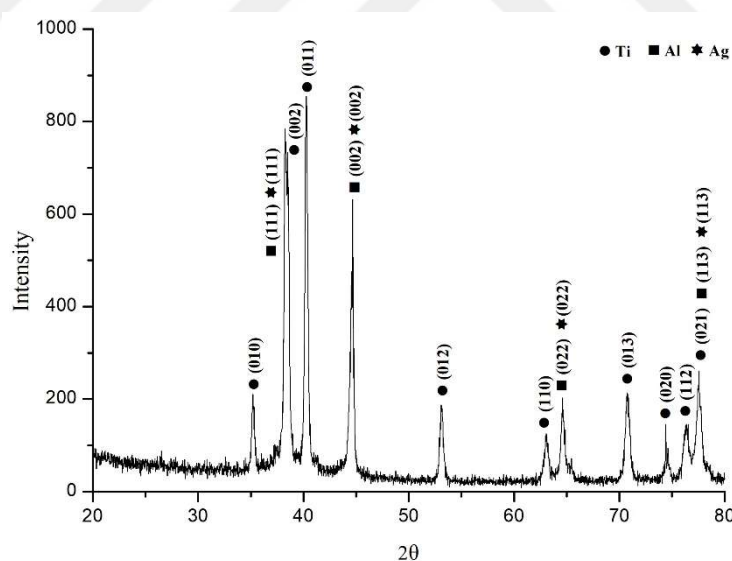


Figure 5.1 : The XRD pattern of the CS coating deposited on the 316L SS.

SEM examinations confirmed the compact nature of the CS coating induced by the impact energy causing exposure of the powder to severe plastic deformation during deposition [1,114]. The EDX analysis taken from the surface of the CS coating (Fig. 5.2a) yielded a nominal composition of 92 wt.% Ti, 4 wt.% Al and 4 wt.% Ag. According to the elemental EDX maps given in Fig. 5.2b, Al and Ag particles were localised within the Ti matrix rather than homogeneous.

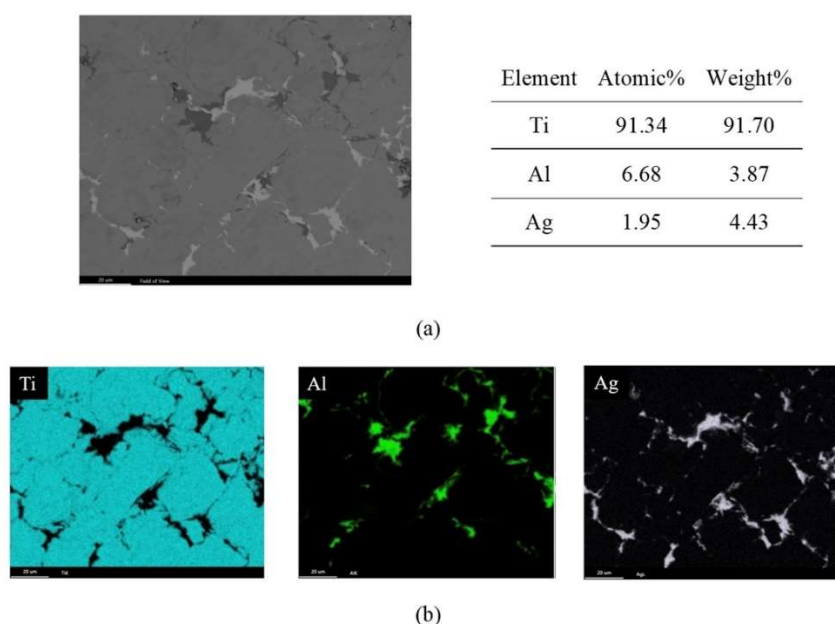


Figure 5.2 : (a) The surface SEM image along with the results of EDX analysis and (b) mapping of Ti, Al and Ag over the CS coating.

The result of XRD examinations conducted on the TO coating is presented in Fig. 5.3. As expected, diffraction peaks of TiO_2 in the form of Rutile (ICSD RefCode:98-004-0452) and Alumina (Al_2O_3 , ICSD RefCode:98-002-6207) belonging to the oxide layer developed over the coating during the TO process appeared on the XRD pattern. Comparison of the peak intensities of TiO_2 and Al_2O_3 suggested the fraction of Al_2O_3 in the oxide layer was minor. The diffraction peaks of α -Ti and Ag, which were appeared on the XRD pattern of the CS coating (Fig. 5.1), were preserved on the XRD pattern of the TO coating. While the appearance of α -Ti peaks can be attributed to the penetration of X-rays beneath the oxide layer, no shreds of evidence of any reactions that might take place between Ag and diffused oxygen and/or Ti and/or Al were identified on the XRD pattern of the TO coating.

Surface SEM micrographs of the TO coating are presented in Fig. 5.4. TO process caused enrichment of the surface with oxygen and yielded a nominal composition of 51 wt.% Ti- 33 wt.% O- 5 wt.% Al and 11 wt.% Ag. (Fig. 5.4a). It should be noted that the amount of Ag on the surface increased remarkably (about 75 %) after the TO process (i.e. from about 4 wt.% to about 11 wt.%) as compared to the CS coating (Fig. 5.2a). On the SEM micrograph of the TO coating, Ag appeared as bright micro-sized spherical aggregates. Similar to the EDX elemental mapping of the CS coating (Fig. 5.2b), distribution Al and Ag over the oxidised surface was not homogenous (Fig. 5.4b).

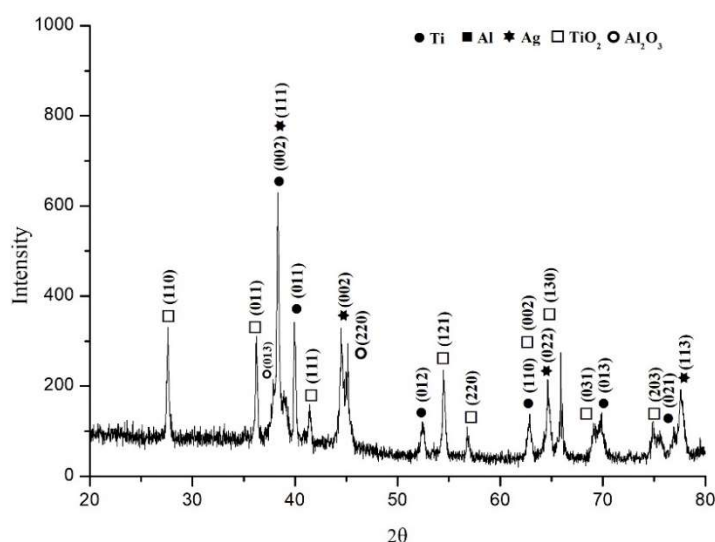
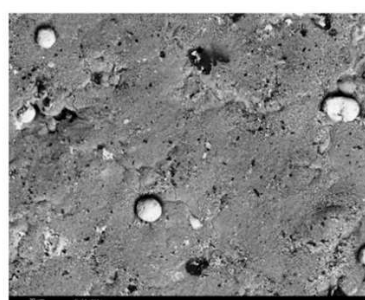


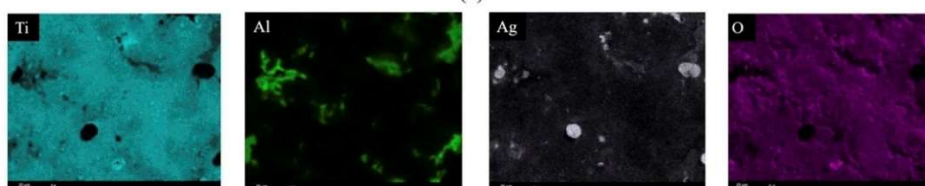
Figure 5.3 : The XRD pattern of the TO coating.

The Raman spectra taken from the bright spherical Ag aggregates and Ag aggregate-free regions of the TO coating are shown in Fig. 5.5. On the Raman spectrum taken from the Ag aggregates-free region, peaks of rutile form of TiO_2 appeared at 234 cm^{-1} , 441 cm^{-1} and 611 cm^{-1} [148–150]. On the other hand, the Raman spectrum of bright Ag aggregates was smooth without any evidence of Ag-O or O-Ag-O binding, whose peaks were more likely locate in between 300 cm^{-1} and 550 cm^{-1} [151,152]. The only peak that appeared on the Raman spectrum of the Ag aggregate at about 230 cm^{-1} corresponded to the rutile form of TiO_2 surrounding the Ag aggregate. Finally, Raman examinations clearly confirmed that the outermost oxide layer of the TO coating consisted of TiO_2 (in the form of rutile) and metallic Ag.



Element	Atomic %	Weight %
O	59.63	32.61
Ti	31.23	51.01
Al	6.07	5.18
Ag	3.07	11.20

(a)



(b)

Figure 5.4 : (a) The surface SEM image along with the results of EDX analysis and (b) mapping of Ti, Al, Ag and O over the TO coating.

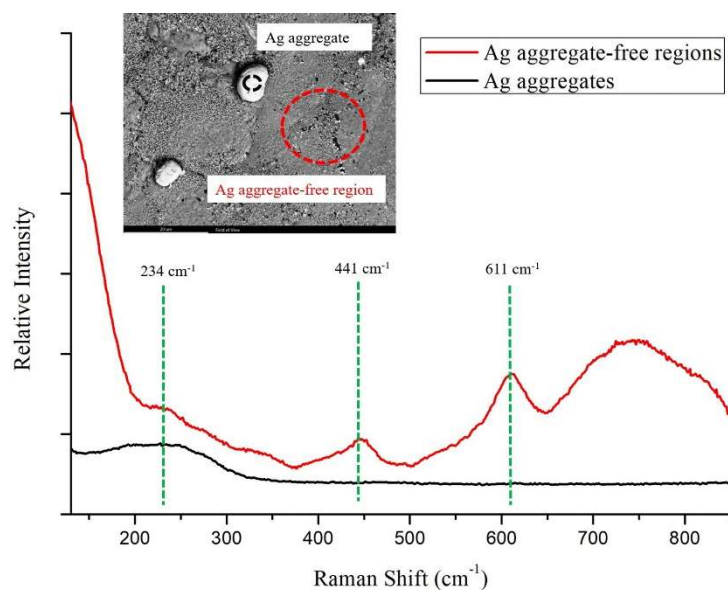


Figure 5.5 : The Raman spectra taken from the TO coating.

The cross-sectional SEM micrograph of the TO coating is given in Fig. 5.6 along with the EDX line scan profiles of Ti, O, Al and Ag, which shows enrichment of the TO coating with O and Ag. In this respect, bright coloured fine Ag particles were clearly observed within the TO coating. Moreover, cross-section SEM surveys revealed good binding of the TO coating having $\sim 3 \mu\text{m}$ thickness with the underlying layer.

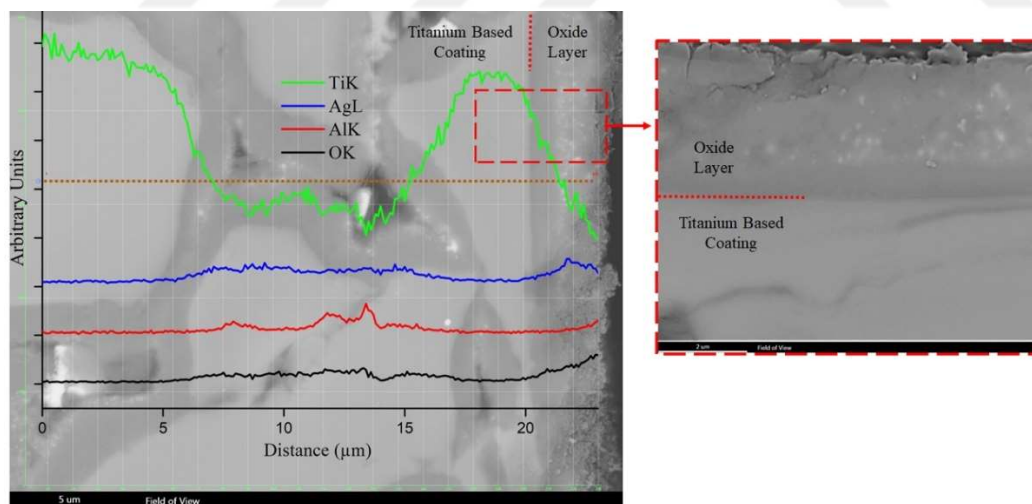


Figure 5.6 : The cross-sectional SEM micrograph of the TO coating along with the EDX elemental profiles of Ti, O, Al and Ag.

According to the thermodynamic approach, oxidation of metallic Ag in the air may be favourable up to 426 K and above this temperature, oxides decompose in association with the change of formation free energy from negative to positive [153,154]. For this reason, metallic Ag in the CS coating maintained its metallic state during the TO at 600 °C, while the surface was enriching by Ag. From this perspective, it is suggested

that fine metallic Ag particles migrated through the Ti matrix and formed agglomerates via diffusion to the adjacent of the Ag particles. This resulted in aggregation in Ag particle with increasing its size. As the consequence of higher surface free energy than that of TiO₂, these Ag aggregates could offer less contact surface with the oxide layer as reported before [155–157]. It has been stated that this type of aggregation of Ag as metallic micro-sized particles in dielectric materials under heat treatment could occur due to the fact that Ag-Ag binding is much stronger than Ag-O binding and the Ag atom has higher surface free energy than the TiO₂.

5.3.2 Anti-bacterial and Ag release tests

Disk diffusion result of a stand free TO coating is given in Fig. 5.7 as an example. The width of the inhibition zone, which forms upon release of Ag ions, was not homogeneous around the examined TO coating. It has been well documented that the size of Ag particles plays a crucial role in the release of Ag ions [158,159]. As compared to fine Ag particles, coarse Ag particles having lower surface area relative to volume yield lower Ag release rate and, therefore, limited anti-bacterial activity. In this respect, the lack of homogeneous inhibition zone thickness around the examined TO coating can be associated with uneven distribution and aggregation of the Ag particles in its structure. Thus, while the Ag enriched regions of the coating provided a wider inhibition zone, Ag poor regions yielded a narrower inhibition zone.

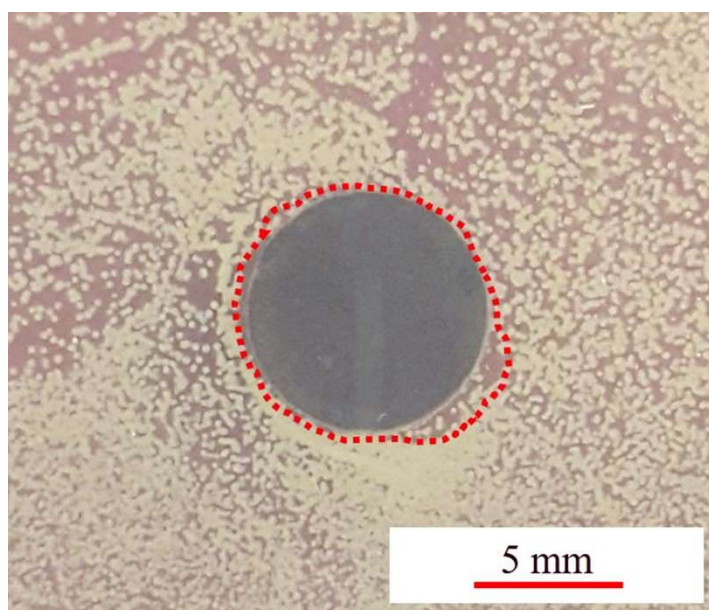


Figure 5.7 : The disc diffusion type tests against *S. aureus* for the TO substrate-free coating after the 24th hour of incubation to the agar plate.

Nevertheless, there is a need for adjusting the distribution of Ag particles within the structure of the coating (i.e. without agglomeration) for obtaining homogeneous inhibition zone thickness during disc diffusion tests, an attempt has been made to confirm the release of Ag ions. As shown in Fig. 5.8, the release of Ag ions from the TO coating into the serum solution increased with increasing duration so that by the end of 28 days, Ag ions in the serum was measured as 0.2 ppm. It has been reported that the concentration of Ag ion in between 0.1 ppb and 10 ppm provides an efficient anti-bacterial effect while the concentration higher from 10 ppm shows toxicity effect [160–162]. In this respect, the cumulative Ag ion release (0.2 ppm) after 28 days is well below the toxicity limit of 10 ppm for humans and close to the lower values of the anti-bacterial effect limits required for anti-bacterial efficiency. On the other hand, when hygiene of touch surfaces is of concern, Ag aggregates with the TO coating are expected to yield good anti-bacterial efficiency under direct contact with bacteria. It should be expressed that optimising the Ag content in TO coating to adjust the anti-bacterial efficiency will be our future work.

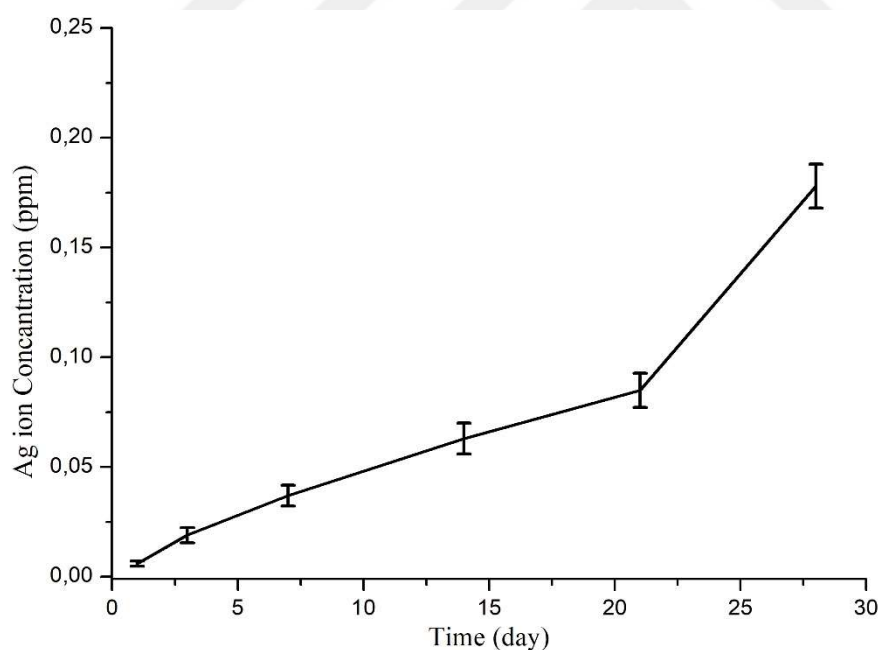


Figure 5.8 : The cumulative concentration of Ag ion released from the TO substrate-free coating.

5.3.3 Bioactivity tests in SBF

Surface SEM images and their respective EDX spectrum taken from the surfaces of the uncoated and TO samples held in the SBF for one week and four weeks are given in Fig. 5.9. After holding one week in the SBF solution, island-like deposits, which

were rich in calcium and phosphorus, tended to form over the oxide layer of the TO sample. However, such a type of deposit formation was hardly realised over the surface of the 316L SS. After the four weeks of duration in the SBF, the surfaces of both samples were totally covered by calcium and phosphorous layers. The chemical compositions and the morphological appearance implied that both of the samples were covered with apatite layers having similar chemistry with bone [163,164]. Moreover, the apatite layer formed on the uncoated 316L SS was severely cracked, suggesting its weak bonding with the underlying steel surface, unlike the TO sample. As the primary indication of the bioactivity, the TO coating not only accelerated the nucleation and growth of apatite but also provided good interaction with the apatite layer. Even though anti-bacterial agents tend to diminish the bioactivity [165], the examined TO coating contained metallic Ag aggregates in its structure exhibited better bioactivity than the 316L SS.

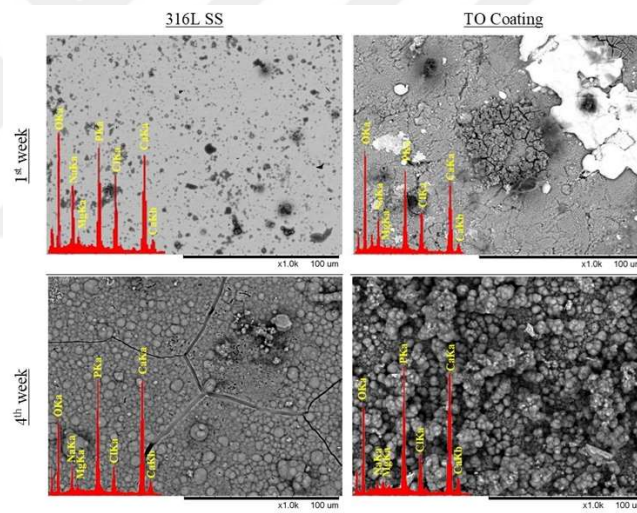


Figure 5.9 : SEM images along with respective EDX analyses conducted on the surface of the examined samples.

5.3.4 Wear tests

The COF curves of the 316L SS and the TO coating against Al_2O_3 ball performed in dry sliding and serum conditions are shown in Fig. 5.10a and b, respectively. The examined samples exhibited similar frictional behaviours during the wear tests in both conditions. The friction curves of the 316L SS were almost stable throughout the testing period in both conditions, but fluctuations on the friction curve obtained in the dry sliding condition were more distinctive than that in the serum condition. Furthermore, a decrease in the mean COF value (from 0.41 to 0.29) in the serum

condition was determined. In TO coating for both testing conditions, the friction curves tended to increase throughout the testing period without any significant fluctuations. However, a slight increment in the mean COF value (0.18) of the TO coating in the serum condition was determined as compared to the mean COF value (0.14) obtained in the dry sliding condition.

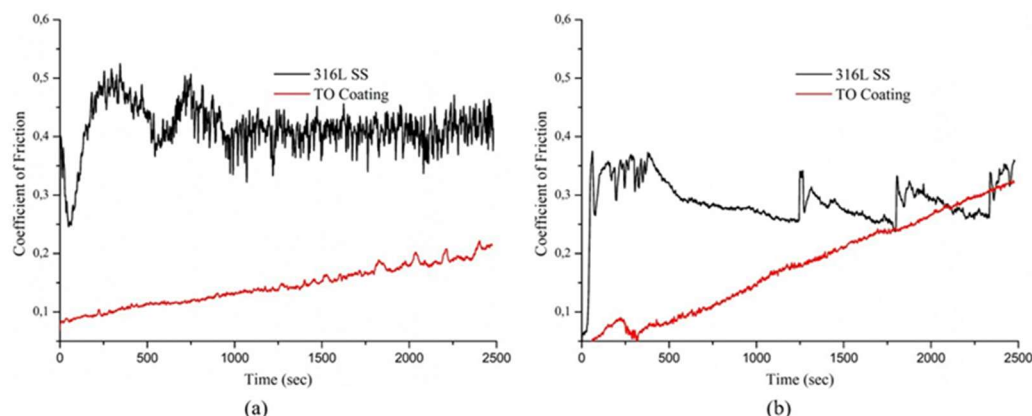


Figure 5.10 : The COF curves of the 316L SS and the TO coating in (a) dry sliding and (b) serum conditions.

The 2D-profiles of wear tracks formed on surfaces of the examined samples during wear tests in dry sliding and serum conditions are presented in Fig. 5.11a and b, respectively. As compared to the dry sliding condition (having width of 400 μm and depth of 10 μm), the applied test load of 1N caused a considerable smaller wear track on the surface of the 316L SS in the serum condition (having a width of 150 μm and depth of 1 μm). As for the TO coatings, the applied test load of 1N, which generated contact pressure as high as ~ 850 MPa for $\text{TiO}_2/\text{Al}_2\text{O}_3$ tribo-pair, did not create any measurable wear tracks on their surfaces in both conditions.

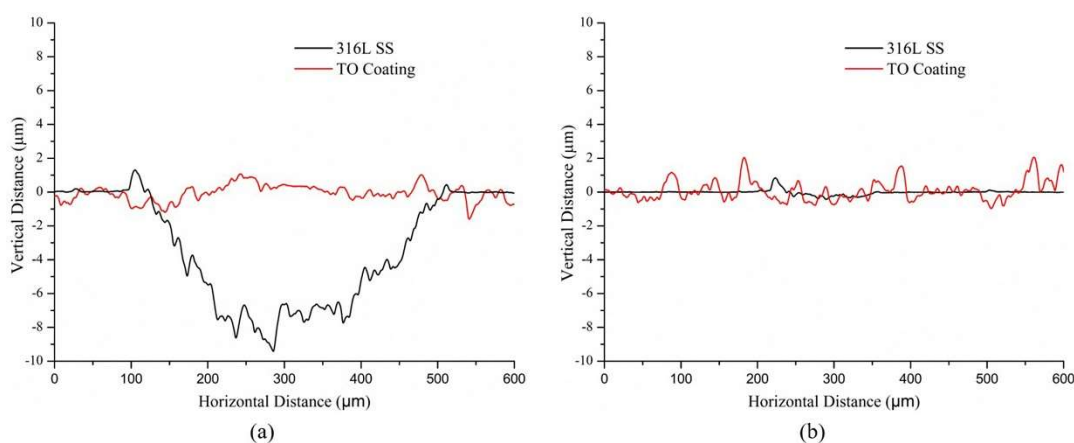


Figure 5.11 : The 2D-profiles of wear tracks formed on surfaces of the examined samples during wear tests in (a) dry sliding and (b) serum conditions.

The worn surface SEM micrographs of the examined samples for both in dry sliding and in serum conditions are given in Fig. 5.12. For the 316L SS samples, the worn surface of the sample tested in dry sliding condition exhibited different topography in contrast to the serum condition (Fig. 5.12). In dry sliding condition, the sliding of Al_2O_3 ball under the test load of 1N caused heavy plastic deformation associated with local delamination on the worn surface of the wear track formed on the 316L SS by imposing wider and deeper wear track (Fig. 5.11) as the result of direct contact of the tribo-pair, which can be characterised as adhesive type wear. The worn surface SEM micrograph of the sample worn in the serum condition showed that the wear mechanism changed from adhesive to abrasive with the evidence of the presence of several micro-grooves and scratches aligned parallel to the sliding direction generated by the ploughing action of the Al_2O_3 ball, which causes relatively smaller wear track on the sample (Fig. 5.11). In the case of the TO coating, the worn surfaces for both in dry sliding and serum conditions exhibited similar topographies. The SEM micrographs of the worn surfaces, as shown in Fig. 5.12, indicated that the wear of the TO coatings progressed smoothening of the oxide layer without any evidence of cracking and spallation as the result of removing the surface asperities by the rubbing effect of the Al_2O_3 ball. Moreover, metallic Ag aggregates did not detach from the contact surface and smeared within the wear track.

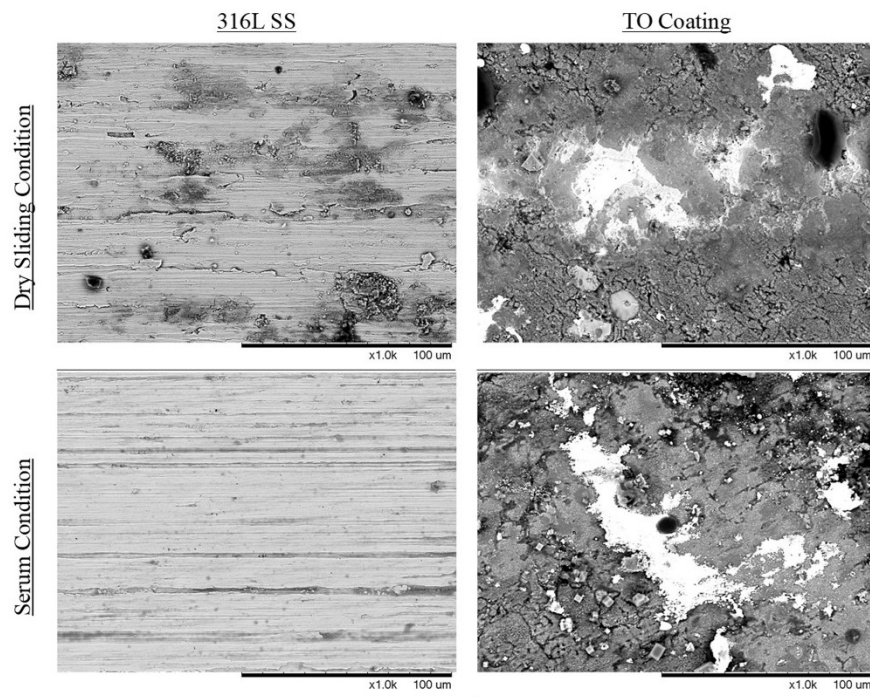


Figure 5.12 : Worn surface SEM images of the examined samples.

The results of sliding wear tests revealed that the exterior oxide layer (mainly in the form of rutile) exhibited superior wear resistance both in the dry sliding and serum conditions under contact pressure of about 850 MPa, much higher than the contact pressure experienced by the human knee joint (max.15 MPa) in vivo [90]. This superior wear resistance of the exterior TiO₂ layer under high contact pressures can be attributed not only to its ceramic nature providing high hardness and good resistance against plastic flow during sliding contact, but also the formation of underlying supporting layer [51] during the TO process upon deeper penetration of oxygen.

5.4 Conclusions

In this study, the features of the Ag incorporated exterior TiO₂ layer developed by sequential application of CS and TO processes has been examined. CS coating was fabricated on 316L SS substrate by deposition of a mixture of 87wt.% Ti, 8wt.% Al, and 5wt.% Ag powder. Then TO process was applied at 600°C for 60 h in air. The findings of this study can be summarised as follows:

1. Application of the TO process changed the structure of the CS coating by forming a ~ 3 µm thick exterior TiO₂ layer with an underlying diffusion layer. In the structure of the exterior TiO₂ layer, a minor amount of Al₂O₃ and metallic Ag aggregates were present.
2. The TO coating showed sufficient anti-bacterial activity against *S. aureus* and release of Ag ions. Aggregation of Ag particles in the coating imposed local differences in Ag ion release rate and therefore formed an inhibition zone with inhomogeneous thickness around the coating during the disc diffusion test.
3. The presence of metallic Ag aggregates in the structure of the TiO₂ based exterior oxide layer did not disturb the nucleation and growth of apatite during the SBF tests and yielded better bioactivity than the 316L SS.
4. TO coating fabricated over the 316L SS exhibited superior sliding wear performance against the Al₂O₃ ball under contact pressure as high as 850 MPa but in dry and wet (0.9% NaCl solution) contact conditions. The sliding action of the Al₂O₃ ball only caused smoothening of the exterior oxide layer without forming a measurable wear track. In the case of the 316 SS, wear progressed via groove and scratch formation on the contact surfaces.

5.5 Acknowledgement

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6. CONCLUSIONS AND RECOMMENDATIONS

The main deliverables of the sequential application of LPCS and TO (at 600°C for 60 in the air) on titanium-based coatings are summarised in this section:

Microstructural Characterisation:

- For successful deposition of titanium on metallic substrates (Co-Cr alloy and 316L stainless steels) by LPCS equipment, the soft metallic powder must be added to the feedstock. The addition of 8wt.% aluminium to the feedstock enables the production of thick and uniform titanium-based coatings. Furthermore, titanium-based coatings reinforced with 3rd part metals like zinc and silver can also be produced by the LPCS system.
- Application of TO altered the structure of the CS coating by generating a dual-layer coating structure consisting of metal-oxide and diffusion layers. As evidenced by cross-section examinations, the oxide layer is uniform along the surface and well-adherent to the CS'ed coating. The thickness of the oxide layer is approximately 3 µm and mainly in the form of the rutile phase of TiO₂. A minor amount of Al₂O₃ was also detected on the oxide composition. With the zinc reinforcement, the ZnO phase also appeared on the composition after the TO process. In contrast, silver reinforcements still standing in metal form after the TO process.
- Some metallurgical changes also occurred beneath the oxide layer during the TO process. The layer beneath the oxide layer was enriched by oxygen and called the oxygen diffusion zone. Within the oxygen diffusion zone, the reaction between neighbouring titanium and aluminium particles led to the formation of Ti-Al intermetallics. For the zinc added coating, TO additionally caused the formation of Ti-Zn type intermetallic.

Mechanical Performance:

- Thermal oxidation applied on CS coatings caused roughening of the surfaces. The surface roughness of the coatings increased almost six times (~0.1 mm to

~0.6 mm) compared to the polished as-sprayed structure. During thermal oxidation, as the result of zinc and silver aggregation on the surface, the roughness of these samples is slightly higher than reinforcement-free coatings.

- The hardness of the rutile based TiO_2 layer is measured as ~1200 HV via the indentation method. Thermal oxidation also favoured increment in the cross-sectional hardness of the diffusion layer. As the result of the formation of new phases like Ti-Al intermetallics, the hardness of the diffusion layer is measured as 380HV, which was 90HV in as-sprayed state.
- The adhesion performance of the oxide layer was evaluated by scratch and Rockwell-C tests. The oxide layer maintained its stability without any indication of delamination at the oxide layer/diffusion layer interface during scratch and Rockwell C tests.
- The tribological performance of the thermally oxidised coatings is evaluated with reciprocating wear tests conducted under different loads and in different testing conditions.
 - Wear tests conducted under 4N load (~1300 MPa contact pressure) in dry sliding conditions confirmed that sequential application of CS and thermal oxidation processes is promising for CoCr alloys to provide superior enhancement in wear resistance.
 - During the wear test applied in 0.9 wt.% NaCl solution under 1, 2 and 3N load, the oxide layer preserved its mechanical stability against the sliding action of the Al_2O_3 ball. For 3N load (~1200 MPa contact pressure), the volumetric wear loss value of the thermally oxidised sample is as low as CoCr alloy. Under the loads applied below 3N, the sliding action of the Al_2O_3 ball only caused smoothening of the oxide layer in the contact region with unmeasurable wear loss.
 - The coating fabricated from the 5wt.%Zn reinforced feedstock exhibited excellent room temperature tribological performance after the thermal oxidation process with a very low COF value (0.12) against Al_2O_3 ball under 3N load in dry sliding conditions.
 - The oxide layer fabricated by thermal oxidation of the coating manufactured from the feedstock containing 5wt.%Ag shows superior

wear performance under 1N loading (~840 MPa contact pressure) in both dry and serum conditions. However, it was determined after the sliding wear tests that the silver reinforcement did not make any positive contribution to the wear performance of the coating.

Biological Performance:

- The potential concerns about the aluminium content of the coatings for in-vivo applications were clarified with ion release tests. Since aluminium has adverse effects on the human body, the aluminium release from the thermally oxidised coatings for 28 days was analysed. The amount of the aluminium release is found as 0.098 ppm, which is well below the limits of the International Agency for Research on Cancer (IARC)
- The bioactivities of thermally oxidised coatings were tested by simulated body fluid test. Ceramic materials like TiO₂ can form functional groups (Si-OH, Ti-OH, Zr-OH, Nb-OH, Ta-OH) on their surfaces in aqueous solutions. So these functional groups make apatite deposition to the surface faster and easier, which is a primary indicator of the bioactive surface. Thus, the surface modification of CoCr and 316L to improve bioactivity can be done by TiO₂ based oxide layer fabricated by sequential application of CS and thermal oxidation process.
- Thermally oxidised silver reinforced coatings showed an antibacterial efficiency, making them an option for surface modification of not only implants but also for the touch surfaces of health-care-related equipment/instruments such as door handles, touch plates, bed rails, and call buttons in the hospitals.

As a recommendation, it will be possible to deposit pure titanium coatings via a HPCS system. Thus, aluminium is no longer needed for coating production, which can remove the possibility of aluminium related healthcare infections. Furthermore, CS is highly flexible for using different kind of reinforcement agents. It is possible to reinforce titanium-based coatings with the different kinds of metal and ceramic agents for several applications. The CS feedstock can be modified with self-lubricant agents like hexagonal boron nitride or molybdenum di-sulphate for wear-related applications.

Also, it is possible to add bioactive agents like zirconium oxide and tantalum or antibacterial agents like copper to the feedstock for biological applications.



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CURRICULUM VITAE

Name Surname : Doğukan ÇETİNER

EDUCATION:

- **B.Sc.** : 2012, Gebze Technical University, Faculty of Materials Science and Engineering, Department of Materials Science and Engineering
- **M.Sc.** : 2015, Istanbul Technical University, Institute of Science and Technology, Materials Science and Engineering Programme

PROFESSIONAL EXPERIENCE AND REWARDS:

- 2013 – Ongoing: Research Assistant
Istanbul Technical University, Chemical and Metallurgical Engineering Faculty,
Metallurgical and Materials Engineering Department

PUBLICATIONS, PRESENTATIONS AND PATENTS ON THE THESIS:

Presentations

- **Cetiner, D.**, Paksoy, A.H., Tazegul, O., Atar E., et al. (2016) Structural Characterization of Thermally Oxidized Titanium Based Coating. 16th International Conference of Materials (IMSP'2016), Denizli, Turkey, October 12-14
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Patents

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