ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

PRODUCTION AND CHARACTERIZATION OF PURE RHENIUM AND W-Re COATINGS FOR TRIBOLOGICAL APPLICATIONS

Master Thesis by

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TRİBOLOJİK AMAÇLI SAF RENYUM VE W-Re KAPLAMALARIN ÜRETİMİ VE GELİŞTİRİLMESİ

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PREFACE

Firstly, let me begin with thanking to my advisor Prof.Dr. Mustafa Ürgen for participating me in this brilliant project and for inspiring me with his perception of dealing with problems in a cause and effect relation. Then I also would like to thank Assoc.Prof. Kürşat Kazmanlı for always knowing some things about everything when I am confused and sharing his profound knowledge and useful tips, never getting bored.

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I also would like to thank to my family for trying to offer me the best all along my life, and my sister for being the source of my joy and cheer, and also my grandmother for implanting some of her unique optimism into my genes.

There are two persons in my life that is needless to thank them, but better feel happy for their being. Gamze Tanrıvermiş is one of them who is a perfect soul-mate and with whom we will be together if not always physically but that's for sure, spiritually. Ali Değer Özbakır who appeared in my life miraculously and now covered two-thirds of it and he is who I dedicated my life regardless of the official or common definitions bonding us together.

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September, 2007 Nazem Göçkan

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ABBRAVIATONS

HSS **:** High Speed Steel

PVD **:** Physical Vapor Deposition

EDS **:** Energy Dispersive Spectroscopy

XRD **:** X-Ray Diffraction

hBN **:** Hexagonal Boron Nitride

MSIP-PVD **:** Magnetron Sputtering Ion Plating Physical Vapor Deposition

TABLE LIST

FIGURE LIST

PRODUCTION AND CHARACTERIZATION OF PURE RHENIUM AND W-Re COATINGS FOR TRIBOLOGICAL APPLICATIONS

SUMMARY

This thesis was conducted within the framework of the research project named "Development of High Performance Rhenium Based Hard Nano-Composite Coatings for Tribological Applications" (Project No. 105M146) and supported by TÜBİTAK. The aim of this study is to obtain surfaces which can equally perform well tribologically both at room and high temperatures. The basic theoretical concept used for achieving this aim is the 'crystal chemistry approach'; in which the lubricity of the third bodies formed at the contact is interrelated with their electronegativity. According to this approach one of the most favorable metals for producing highly lubricious oxides is rhenium (Re). Hence, this study is mainly structured on the production and tribological characterization of Re and W-Re alloys. The main approach governed throughout the work was to find out coating procedures to produce hard surfaces giving low friction coefficients and also staying away from wearing off the counter-faces that they are working with. There are very limited studies in the literature about the production of pure Re and W-Re coatings physical vapor deposition (PVD) techniques.

In the beginning of the coating studies, the adhesion problems encountered was solved by surface engineering approach in which a thin bonding layer of Ti (~0.60 μm) was introduced to the system. With the success of this approach, the following coating procedures were conducted with deposition of this interlayer.

Because there are no other studies that can be used as reference, on the production of Re coatings with magnetron sputtering, the parameters such as magnetron power and argon pressure, affecting the deposition process were determined. Structural effects produced by the variation of these parameters were investigated. The effect of magnetron power was observed as a linear increase in thickness with increasing power. W-Re films were slightly thinner then pure Re films produced with the same parameters. The effect of argon pressure of the system was observed by applying

three different chamber pressures of 0.5, 1.0 and 1.5 Pa. The thickest of the films was obtained from the coating with 1.0 Pa chamber pressure. This result was attributed to the optimum ionization efficiencies and collisional scattering inside the chamber. The hardness of the films was between 17 – 23 GPa. The hardest of the films of the three different magnetron powers was the one coated at 300 W. The XRD patterns of the two coatings produced by applying a power of 200 and 400 W totally corresponded to the diffraction pattern of pure rhenium. While coatings produced by using 300 W power have slightly shifted peaks relative to the positions of pure Re. The coatings exhibiting shifted peaks in their XRD patterns possessed higher internal stress hence higher hardness. But the effect of chamber pressure was not reflected to the hardness values since the hardness of the films of different pressures were found to be nearly the same around 22 GPa.

With the knowledge of crystal chemical approach, the highly lubricious oxides of rhenium were predicted to positively influence its tribological properties, as they could act as solid lubricants. Therefore ball-on-disc and fretting type wear tests were conducted over pure Re and W-Re coated samples both at room temperature and at high temperatures (50°C, 100°C, and 150°C). Alumina and 440C type steel balls were used as the counterface materials. The friction coefficients of pure Re coatings were 0.13 for room temperature ball-on-disc tests ran against alumina counterbody. The depth of wear tracks is at most % 4 of the total thickness of the films. But the tests against steel counterbody gave higher coefficients of friction. The average values were found to be 0.5. However this time the wear tracks on the samples were less apparent while the wear on the steel balls were catastrophic. The tribological behavior of W-Re alloy coatings showed the same trends as for pure Re coatings, however the friction coefficients achieved in this case were higher. In the case of tests ran against alumina ball, the average coefficient of friction was 0.35 and the wear depths were less than 0.8 μm. The friction coefficient was 0.65 in the case of tests ran against 440C steel balls. Again the steel balls were highly worn while there was no considerable wear on the coated disc samples. The fretting tests at room temperature also gave similar coefficients of friction showing that the tests have reproducibility.

The fretting tests conducted at high temperatures in addition to room temperature tests, resulted showing opposite behaviors for pure Re and W-Re. For pure Re

coatings the coefficient of friction values increased with increasing temperature while contrarily they were decreasing for W-Re coatings. The highest coefficient of friction was reached at 50°C with 0.63 on W-Re and then with increasing temperature, the coefficient of friction values were decreased down to 0.2. The high temperature tests showed that the combination of volatile oxides of rhenium with hard tungsten gave the most successful results in characterization of rhenium's tribological behavior.

In conclusion, the project aiming to research and introduce the tribological behavior of pure Re and W-Re coatings produced by Magnetron Sputtering PVD technique, resulted in a successful outcome of obtaining W-Re and rhenium's tribological behaviors both separately and also comparatively. According to its volatile oxides rhenium showed very low wear and friction with a solid lubricant characteristic at room temperature. On the other hand, W-Re coatings showed a superior tribological behavior at high temperatures with a combination of highly lubricious rhenium and a hard tungsten matrix.

TRİBOLOJİK AMAÇLI SAF RENYUM VE W-Re KAPLAMALARIN ÜRETİMİ VE GELİŞTİRİLMESİ

ÖZET

Bu tez çalışması TÜBİTAK destekli, "Tribolojik Amaçlı, Üstün Özellikli Renyum Esaslı Sert ve Nano-Kompozit Yapılı Kaplamaların Geliştirilmesi" (Proje No. 105M146) adlı araştırma projesi kapsamında gerçekleştirilmiştir. Bu çalışmanın amacı hem oda sıcaklığında hem de yüksek sıcaklıklarda üsün tribolojik özelliklere sahip yüzeyler elde etmektir. Bu çalışmada ele alınan esas teori "kristal kimyası yaklaşımı"dır. Bu yaklaşımda, temas bölgesinde oluşan üçüncü bileşenler elektronegativiteye bağlı olarak yağlayıcı özellik gösterirler. Bu yaklaşım göz önünde bulundurulduğunda en yüksek ölçüde yağlayıcı oksitlere sahip olan metal renyumdur (Re). Bu sebeple bu çalışma Re ve W-Re alaşımlarının üretimi ve tribolojik olarak karakterizasyonu üzerinde yapılandırılmıştır. Bu çalışmada güdülen ana yaklaşım, düşük sürtünme katsayıları veren ve aynı zamanda birlikte çalıştığı karşı yüzeyi aşındırmayan sert yüzeyler üretimine yönelik kaplama yöntemleri geliştirilmesidir. Literatürde saf Re ve W-Re kaplamaların fiziksel buhar biriktirme (PVD) yöntemi ile üretimine yönelik sınırlı sayıda çalışma bulunmaktadır.

İlk olarak kaplamaların üretimi esnasında karşılaşılan, saf Re kaplamaların yapışma probleminin üstesinden gelebilmek amacıyla, yeni bir yüzey mühendisliği yaklaşımı üzerinde çalışılmıştır. Dolayısıyla çok daha ince bir Ti bağlayıcı ara tabaka (~0.60 μm) sisteme dahil edilmiştir. Bu yaklaşımın başarıya uğraması sonucunda, ileriki tüm kaplama işlemleri bu bağlayıcı ara tabakanın mevcudiyetinde gerçekleştirlmiştir.

Re kaplamaların manyetik alanda sıçratma yöntemi ile üretimi konusunda referans alınabilecek bi çalışma bulunmadığından, sıçratma gücü ve argon basıncı gibi kaplama prosesini etkileyen parametrelerin ortaya çıkarılması amacıyla, farklı parametrelerin uygulandığı kaplama işlemleri gerçekleştirilmiş; bu parametrelerin kaplamaların yapısal özellikleri üzerindeki etkileri gözlemlenmiştir. Sıçratma gücünün artışıyla kaplama kalınlığında doğrusal bir artış olduğu görülmüştür. W-Re

kaplamaların kalınlığı aynı parametrelerde üretilen saf Re kaplamalardan hafifçe daha düşüktür. Sistemin argon basıncının etkisi üç farklı (0,5 – 1,0 – 1,5 Pa) kaplama basıncı uygulanarak gözlenmiştir. En kalın film tabakası 1 Pa basınç uygulandığı kaplama işlemi sunucunda elde edilmiştir. Bu sonuç kaplama ortamındaki optimum ölçüdeki iyonizasyon ve şıçratma verimi ile ilişkilendirilmiştir. Kaplamaların sertlikleri 17 – 23 GPa arasında değişmektedir. Üç farklı sıçratma gücü ile kaplanan filmlerin en serti 300 W uygulanarak gerçekleştirilen kaplamadır. 200 W ve 400 W ile yapılan kaplamaların XRD paternleri bütünüyle saf renyumunkilerle uyuşmaktadır. 300 W güçte yapılan kaplamanınki ise saf renyum piklerinden hafifçe kayma göstermiştir. XRD paterninde, piklerde kayma gösteren kaplamalar yüksek iç gerilmeye dolayısıyla yüksek sertliğe sahiptir. Bunun yanında farklı basınçlarda kaplamnan filmlerin sertlikleri yaklaşık olarak 22 GPa civarındadır; dolayısıyla kaplama basıncının sertlik üzerindeki etkisinin kayda değer olmadığı söylenebilir.

Kristal kimyası yaklaşımına dayanarak renyumun yüksek uçuculuktaki oksitlerinin katı yağlayıcı özelliği göstererek renyumun tribolojik davranışını olumlu yönde etkileyeceği öngörüsünde bulunulmuştur. Dolayısıyla saf Re ve W-Re kaplamalar üzerine oda sıcaklığında ve yüksek sıcaklıklarda (50°C, 100°C ve 150°C) çeşitli aşınma testleri uygulanmıştır. Karşı-malzeme olarak alümina ve 400C çelik toplar kullanılmıştır. Saf Re kaplamaların oda sıcaklığında, alümina karşı malzemeyle yapılan testlerinde sürtünme katsayıları 0,13 bulunmuştur. Aşınmış bölelerin derinlikleri toplam film kalınlığının % 4'ü kadardır. Fakat çelik malzemeye karşı yapılan testlerde sürtünme katsayıları daha yüksek bulunmuştur. Ortalama değerler 0,5 civarındadır. Bu sefer numuneler üzerindeki aşınma izleri daha az olmakla beraber çelik toplardaki aşınma çok daha şiddetlidir. W-Re alaşımı kaplamaların da tribolojik davranışı saf Re kaplamalara benzerlik göstermiştir; farklı olarak bu kaplamalarda elde edilen sürtünme katsayıları biraz daha yüksektir. Alümina topa karşı yapılan testlerde ortalama sürtünme katsayısı 0,35 civarındadır; aşınma derinlikleri ise 0,8 μm'den düşüktür. 440C çelik topa karşı yapılan testte sürtünme katsayısı 0,65 bulunmuştur. Aynı şekilde kaplanmış numuneler üzerinde kayda değer bir aşınma gözlenemezken çelik toplardaki aşınma çok daha ileri seviyededir. Oda sıcaklığındaki fretting testleri de benzer sonuçları vermiş ve böylece deneylerin tekrarlanabilirliği kanıtlanmıştır.

Yüksek oda sıcaklığı testlerine ek olarak yapılan yüksek sıcaklık fretting testleri, saf Re ve W-Re kaplamalarda farklı sonuçlar doğurmuştur. Saf Re kaplamalarda sürtünme katsayısı sıcaklıkla artarken W-Re alaşımı kaplamalarda bunun tersi olarak sıcaklıkla düşüş göstermiştir. W-Re kaplamalar için en yüksek sürtünme katsayısı 0,63 değerine 50°C'de ulaşmış, sıcaklık yükseldiğinde sürtünme katsayısı 0,2'ye kadar düşmüştür.

Elde edilen sonuçlar gayet umut vericidir. Saf Re kaplamaların oda sıcaklığındaki sürtünme katsayıları 0.13 değerlerindedir. Yüksek sıcaklık testlerinde de W-Re kaplamaların sevindirici tribolojik davranış göstermiş olması, saf Re kaplamalar yerine daha ekonomik olan bir renyum alaşımı kaplamanın kullanımına fırsat yaratmıştır. Yüksek sıcaklık testleri sonucunda, renyumun tribolojik davranışının araştırılmasında renyumun uçucu oksitlerinin yüksek sertlikteki tungsten ile birleşiminin en başarılı sonuçları ortaya koyduğu görülmüştür.

Sonuç olarak, manyetik alanda sıçratma yöntemi ile üretilen saf Re ve W-Re kaplamaların tribolojik davranışının araştırılması ve ortaya konulması hedeflenen bu proje Re ve W-Re'nin tribolojik karakteri hakkında hem ayrı ayrı hem de karşılaştırmalı olarak başarılı sonuçlar ortaya koymuştur. Renyum uçucu oksitlerine bağlı olarak oda sıcaklığında yüksek katı yağlayıcı özelliği dolayısıyla düşük aşınma ve sürtünme göstermiştir. Diğer yandan, W-Re kaplamalar yüksek sıcaklıkta, renyumun yüksek ölçüde yağlayıcı oksitleri ile sert tungsten martisi birleşimi sayesinde üstün tibolojik özellikler sergilemiştir.

1. INTRODUCTION

Production of hard and abrasion resistant coatings, for tribological and for the development of cutting performance, with Physical Vapor Deposition (PVD) techniques is a scientific and technological research area where new developments are often achieved. The scientific and technological importance of this subject is well appreciated and R&D efforts in this area are supported. Also taking into consideration the energy conservation and environmental aspects of the subject, the projects are strongly supported related to development of wear resistant materials that possess solid lubricant properties. Moreover the limiting of the use of oil and liquid lubricants is becoming a critical environmental issue. The future aim is not to use or very limitedly use of oil, and petroleum based liquid lubricants. One of the most promising approaches for achieving this aim is to modify the surfaces of the materials instead of bulk material modifications. One of the recent research areas related to the production of hard and wear resistant coatings is the production of thin film structures utilizing various PVD techniques.

Within the scope of this study, it is aimed to produce and characterize a new, rhenium based, coatings with PVD techniques. The coatings are produced whose oxides are expected to give good solid lubricant properties according to the crystal chemistry approach. During friction and wear the heat generated at the contact area stimulates the oxidation at these areas; hence the properties of the oxides formed starts to control the tribological behavior of the materials. According to the crystal chemistry approach rhenium oxides are the most lubricious ones. Moreover Re is one of the rare metals that combines high stiffness (elasticity modulus 450 GPa), high temperature strength, thermal shock resistance with high wear resistance. It doesn't have any known toxicity. However, Re is an expensive metal and it is possible to shape it with machining and casting. Today chemical vapor deposition and electron beam PVD techniques are used for near net shaping of Re parts. Instead of bulk material, the usage of the coatings of Re metal or commercially available W-Re alloys would sure be more economical.

The experimental studies concerning the subject covered the production of coatings with PVD techniques – optimization and characterization. Magnetron sputtering was used as the PVD technique. The relationships between the coating parameters (magnetron power, argon pressure) and properties were established. The coating parameters were optimized. The coatings were characterized with respect to their structural (composition, stochimetry), mechanical (hardness, adhesion, surface roughness) and tribological (room and high temperature wear behavior, character of the wear debris) properties.

2. SOLID LUBRICATION AND SELF-LUBRICATING MATERIALS

Solid lubricants are materials which naturally have low shear strengths and thus able to lower friction in sliding applications (Donnet and Erdemir, 2006). The working range of solid lubrication has been greatly extended during last twenty years; remarkable progress has been made in the design, development, and uses of solid lubricant films. When the economics of manufacture are to be considered, application of solid lubricants as a thin film provide an economical and effective means of minimizing wear problems. Because of the environmental concerns, modern tribology inclined to limit or reduce the use of liquid lubricants as much as possible, but increase the use of solid materials and coatings with self-lubricating properties (Donnet and Erdemir, 2004).

In general, no single coating can provide both low and consistent friction coefficients and high wear resistances. This is mainly because friction is very sensitive to test conditions, temperatures, and environments. The type of counterface materials and test configurations can also make a big difference in the frictional property of the solid lubricant (Donnet and Erdemir, 2004).

2.1. General Characteristics of Solid Lubricants

Solid lubricant coatings have many attractive features compared to oil lubricants and are primarily used to control friction and wear under severe application conditions (such as high vacuum, aerospace, high-speeds, high loads, and very low or high temperatures) or also in the presence of strong radioactivity, where conventional materials and lubricants cannot provide the desired levels of performance or durability (Donnet and Erdemir, 2004). One of their obvious advantages compared to oil lubricants are their superior cleanliness when environmental concerns are taken into account (Stachowiak and Batchelor, 2001). Some of the key advantages of solid lubricants in tribological applications over liquid and grease lubricants are their better lubrication performance in vacuum, their ability to endure extreme pressures, their insensitivity to temperature differences. Additionally some provide excellent

electrical conductivity and insensitive to nuclear radiation; most of them are able to be stored very long times and have better industrial hygiene due to little or no hazardous emissions; since they are in solid state, there is no danger of spillage that can contaminate environment while liquid and gas lubricants may evaporate, drain, creep, or migrate during storage and may release hazardous emissions; liquid lubricants may spill or drip and contaminate environment (Donnet and Erdemir, 2001).

Solid lubricant coatings still have problems such as limited lifetime, difficulty in replenishment, and oxidation and aging-related degradation beside their attractive properties. Some of the shortcomings of solid lubricants are:

1. Most solid lubricants except soft metals, are poor in thermal conduction, thus are not able to carry away heat from sliding interfaces.

2. Their friction coefficients may be high or fluctuate significantly depending on test environment and contact conditions.

3. Their renewal is more difficult than that of liquid lubricants.

4. Oxidation and aging-related degradation may occur over time and present some problems with transition-metal dichalcogenides.

5., They may experience irreversible structural/chemical changes upon exposure to high temperatures or oxidative environments that may cause loss of lubricity and the generation of some abrasive, non-lubricious by-products (Donnet and Erdemir, 2001).

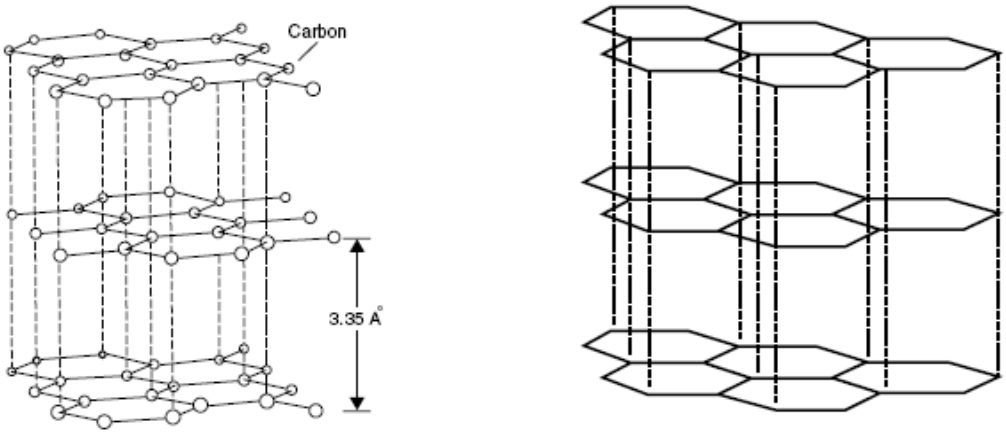


Figure 2.1: Schematic illustration of layered crystal structures of graphite and hexagonal boron nitride, respectively (Donnet and Erdemir, 2001).

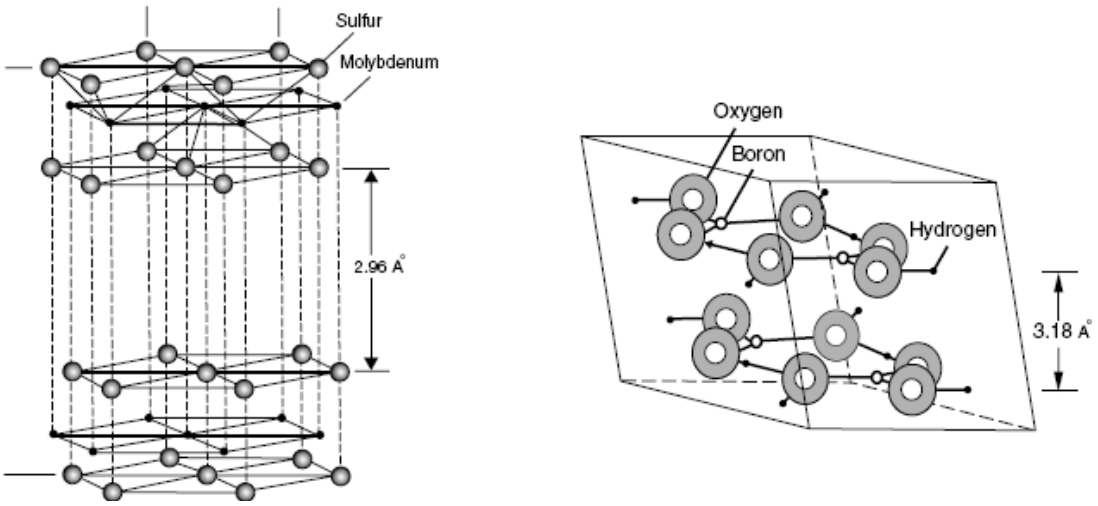


Figure 2.2: Schematic illustration of layered crystal structures of molybdenum disulfide and boric acid, respectively (Donnet and Erdemir, 2001).

2.2. Classification of Solid Lubricants

These materials are classified into different systems, according to their chemical bond and crystallographic structure (Lugscheider et. al., 2001). Unique lubricating properties of some of the solid lubricants (i.e. molybdenum disulfide, graphite, hexagonal boron nitride, boric acid) are mainly associated with their layered or lamellar crystal structures as given in Figure 2.1 and Figure 2.2; while others (such as diamond and diamond-like carbon) provide lubrication mainly because of their extreme chemical inertness. Oxide-based materials are generally hard to shear at room temperature, but some of them become highly shearable and hence can provide fairly low friction coefficients at elevated temperatures. These oxides are often referred to as "lubricious oxides". A classification made by Donnet and Erdemir (2001), based on the chemistry, crystal structure, and lubricity of the most widely used and recently developed solid lubricants is given in Table 2.1.

Table 2.1: A classification of solid lubricants based on the chemistry, crystal structure, and lubricity (Donnet and Erdemir, 2001).

Classification	Examples
Lamellar solids	Mo_2S
	W_2S
	hBN
	Graphite
	Graphite fluoride
	H_3BO_3
	GaSe, GaS, SnSe
Soft metals	Ag

	Pb
	Au
	In
	Sn
Mixed oxides	$CuO-Re_2O_7$
	$CuO-MoO_3$
	$PbO-B_2O_3$
	$CoO-MoO_3$
	Cs_2O-MoO_3
	$NiO-MoO_3$
	Cs_2O-SiO_2
Single oxides	B_2O_3
	Re_2O_7
	MoO_3
	TiO_2 (sub-stoichiometric)
	ZnO
Halides and sulfates of alkaline earth metals	CaF_2, BaF_2, SrF_2
	$CaSO_4$, $BaSO_4$, $SrSO_4$
Carbon-based solids	Diamond
	Diamond-like carbon
	Glassy carbon
	Hollow carbon nanotubes
	Fullerenes
	Carbon-carbon and carbon-graphite-based composites
Organic materials/polymers	Zinc stearite
	Waxes
	Soaps
	PTFE
Bulk or thick-film (>50 μm) composites	Metal-, polymer-, and ceramic-matrix composites consisting of graphite, WS_2, MoS_2, Ag, CaF_2, BaF_2, etc.
Thin-film (<50 μm) composites	Electroplated Ni and Cr films consisting of PTFE, graphite, diamond, B_4C, etc., particles as lubricants
	Nanocomposite or multilayer coatings consisting of MoS_2, Ti, DLC, etc.

Additionally the same authors made a classification for solid lubricants according to their hardness. In this classification they divided them in two broad categories: soft (hardness less than 10 GPa) and hard (hardness more than 10 GPa) solid lubricants. If they are to be compared according to their hardness, the hard solid lubricants exhibit higher wear resistance in addition to lower friction when compared with soft lubricants, which can provide low friction but not always high wear resistance. These hard solid lubricant coatings include some of the carbon-based coatings (such as diamond and DLC) and certain oxides. Soft solid lubricant coatings include polymers, soft metals, halides and sulfates of alkaline earth metals, and the well-

known lamellar solids, including transition-metal dichalcogenides, graphite, and boric acid (Donnet and Erdemir, 2004).

2.2.1. Lamellar Solid Lubricants

This is the most studied type of solid lubricants by scientists and most widely used by industry. The best-known examples are transition-metal dichalcogenides, graphite, hBN, and H_3BO_3. MoS_2, graphite, and boric acid are natural minerals, but other lamellar solids, such as WS_2, fluorinated graphite, and transition-metal diselenides and ditellurides, are synthetic and are much less used than the naturally occuring ones (Donnet and Erdemir, 2001).

Without lubrication by liquids or gases, most of the solid contacts end up considerable adhesion between the sliding surfaces. This phenomenon causes a large coefficient of friction. However, for materials exhibiting anisotropy of mechanical properties, low shear stresses cause failures to result in low coefficient of frictions. Anisotropy of mechanical properties, or in other words, planes of weakness, is characteristic of lamellar solids. The lamellar solid lubricants owe their self-lubricicity to these weak lamellae being able to slide over one another at relatively low shear stresses (Stachowiak and Batchelor, 2001). This mechanism is schematically illustrated in Figure 2.3.

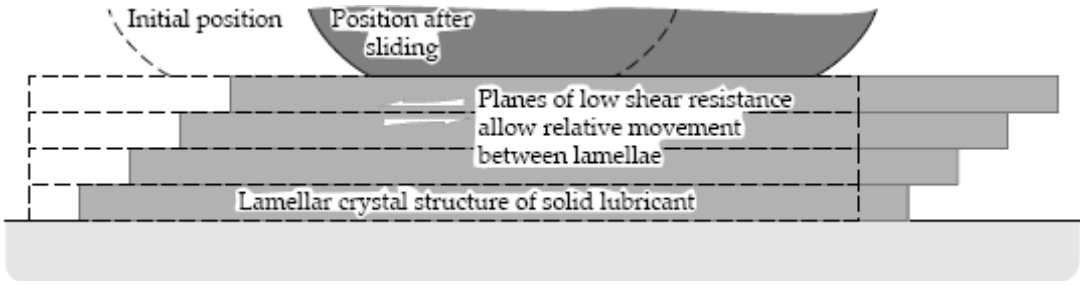


Figure 2.3: Mechanism of lubrication by lamellar solids (Stachowiak and Batchelor, 2001).

The bonding between lamellas has to be weak in the case of good solid lubrication. Although adhesion between lamellae is highly undesirable, adhesion of lamellae to the worn surface is essential. In other words, materials which do not show adhesion to a worn surface are quickly removed by sliding. This is schematically illustrated in Figure 2.4.

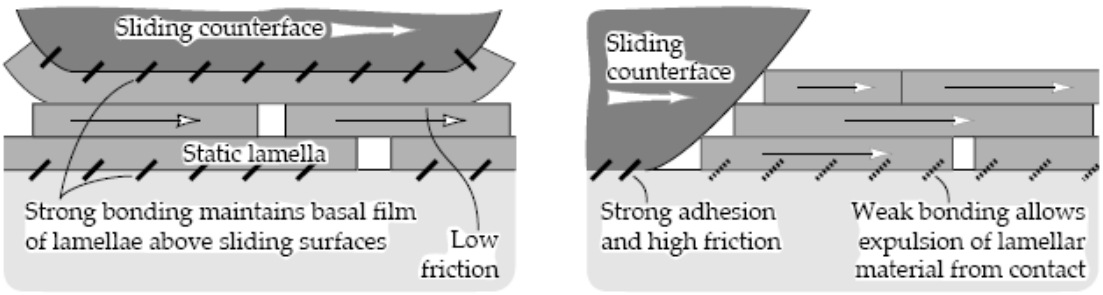


Figure 2.4: Effect of adhesion strength of the solid lubricant lamellae to the worn surface on friction (Stachowiak and Batchelor, 2001).

Unfortunately all lamellar solids are not able to exhibit interlamellar sliding at low shear stresses. Even materials having many chemical and crystallographical similarities, they can exhibit a large difference in the level of adhesion between lamellae. In some materials continuous sliding between layers is prevented by strong adhesion forces, while in some others very low values of both friction and adhesion can be obtained. For some materials the source of the strong force between lamella is the strong electrostatic attraction between corresponding negative and positive ions. Materials which are easily shearable usually have a much weaker van der Waals bonding between lamellae (Stachowiak and Batchelor, 2001). The difference between these mechanisms is illustrated schematically in Figure 2.4.

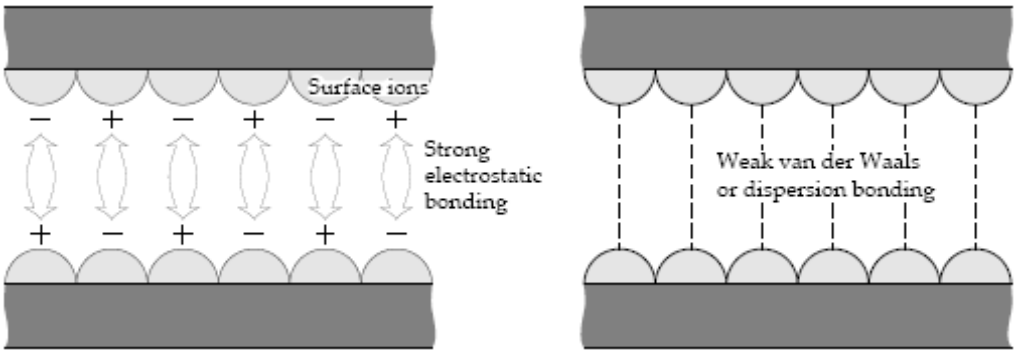


Figure 2.5: Mechanism of electrostatic strong bonding and weak dispersion bonding between lamellae (Stachowiak and Batchelor, 2001).

2.2.2. Lubricious Oxides

In tribological applications, during friction high temperatures at contact areas cause oxidative conditions to develop and make coatings be exposed to these conditions. The coatings exposed to these environments oxidize and the properties of the oxidized surface start to govern the friction and wear properties. Hence, the properties and service life of the coated material depends both on mechanical and on oxidation properties of the coating (Solak et. al.,2003).

Especially some certain oxides (e.g., Re_2O_7, MoO_3, PbO, B_2O_3, NiO, etc.) become soft and highly shearable at elevated temperatures and hence can be used as lubricants. When applied as thin or thick coatings (by means of PVD, plasma spraying, fusion bonding, etc.), these solids can provide acceptable levels of friction coefficients and long wear life. They can also be mixed with other solid lubricants to obtain lubrication over much wider temperature ranges. Major drawbacks of oxide based lubricants are that they are inherently brittle and thus may fracture easily and wear out quickly. Furthermore, most oxide-based lubricants do not provide lubrication down to room temperature. Potential applications for lubricious oxides include high-temperature seals, bearings, and gears, valves and valve seats, variable stator vanes, and foil bearings (Donnet and Erdemir, 2001).

The oxides of Re, Ti, Ni, W, Mo, Zn, V, B, etc., become highly lubricious and can provide fairly low friction at elevated temperatures. Mixed oxides (e.g., $CuO\text{-}Re_2O_7$, $CuO\text{-}MoO_3$, $PbO\text{-}B_2O_3$, $PbO\text{-}MoO_3$, $CoO\text{-}MoO_3$, $Cs_2O\text{-}MoO_3$, $NiO\text{-}MoO_3$) can also provide wider operational ranges and can be prepared as alloys or composite structures to provide longer durability. The lubricious layers that form by oxidation of alloy surfaces are very desirable and exceptionally advantageous when compared with the solid lubricant coatings with finite lifetimes. At high temperatures, as the oxide layer is depleted from the surface by wear, the alloying ingredients diffuse toward the surface where the oxygen potential is higher; they oxidize again to replenish the consumed lubricious layers that have low shear strength and/or surface energy to decrease friction (Donnet and Erdemir, 2001).

A number of researches are being conducted in recent years. For instance, Ezirmik et. al. (2007) investigated the effect of copper addition on the temperature dependent reciprocating wear behaviour of CrN coatings. The aim of their study was to observe the temperature dependent wear behavior of CrN and CrN–Cu coatings depending on the structural and compositional changes of third body formed at the tribocontact. They found that the debris character changed with the temperature and observed that at 50°C wear rates increase but with further increase in temperature to 100°C and 150°C no wear was observed on the coatings (Ezirmik et. al., 2007)

Solak et. al. (2003) worked on the oxidation behavior of molybdenum nitride coatings. They investigate the oxidation behavior of Mo–N coatings and to determine the mechanism of oxidation through gravimetric tests and compare to metallic

molybdenum. They found that the resistance of Mo–N coatings to oxidation was poor because of their non-protective nature and the volatility of the oxides at moderately high temperatures. When they compared these results, they showed the similarity of the oxidation behavior of Mo–N with the oxidation of metallic molybdenum system. Reaction temperatures, oxidation reaction products and oxide scale morphologies were found to be similar in both systems (Solak et. al., 2003).

Stachowiak and Batchelor (2001) sustained their theory about lubricious oxides in this way: At high temperatures, metal oxides might become relatively ductile and begin to act as solid lubricants. Although, in general, metal oxides exhibit a lubricating effect at high temperatures, not all of them showed a reduction in the coefficient of friction in the range of temperatures which are useful for practical applications. Yellow lead oxide, PbO, was probably the most useful of the metal oxides and can provide good lubrication at high temperatures. The steel sliding tests conducted at temperatures of approximately 600°C revealed that among the many oxides tested, only lead oxide (PbO) and molybdenum trioxide (MoO_3) offered a substantial reduction in the coefficient of friction compared to the unlubricated case (Stachowiak and Batchelor, 2001).

In a series of fundamental studies, Gardos (2000a, 2000b) demonstrated that at a very narrow range of anion vacancies and at high temperatures, crystalline TiO_2 (rutile) and rutile-forming surfaces can provide very low friction coefficients to sliding tribological interfaces. Further work demonstrated the formation of Magnéli phases on sliding surfaces containing titanium-based alloys and compounds. His findings suggested that Magnéli phases are principally the result of tribooxidation and that once formed, they can dominate the tribological behavior of sliding ceramic interfaces, mainly because of their unique shear properties. However, TiO_x-based solid lubricants have not yet found wide use, mainly because of the difficulty in achieving and maintaining the very narrow range of oxide stoichiometry needed for good lubricity (Donnet and Erdemir, 2001).

Intensive studies are being carried on the wear properties of lubricious oxides and their mechanisms, and also about the introduction of new lubricious oxides and improving their performances. Lugscheider et al. (2000), deposited tungsten and vanadium oxides by magnetron sputtering ion plating PVD process (MSIP) in a reactive d.c. mode and studied especially about the influence of the oxygen content

in the sputtering atmosphere as well as the deposition temperature on the phase generation, then investigated the high temperature stability of these oxides. Their investigations demonstrated that it was possible to deposit vanadium- and tungsten-oxides by a d.c. reactive magnetron sputtering ion plating process on high speed steel and carbide with good tribological properties. Furthermore, the high temperature phase stability up to 600°C for the vanadium oxide and 800°C for the tungsten oxide was shown (Lugscheider et al. 2000).

Gulbinski et. al. (2003), reported a research focused on molybdates of silver and silver and copper containing vanadium oxide bronzes $Me_xV_2O_5$. The aim of their reported research was to elaborate thin film deposition methods of selected oxides (MoO_3, V_2O_5) and their derivative phases, to characterise the phase composition of deposits and to study their tribological behaviour at elevated temperatures during friction in air. They analysed transformation processes of coatings during high temperature tests and related friction behaviour to phase changes, which take place in them. For both materials, they proved that the friction coefficient decreases from high values (0.7–0.8) to about 0.4 with increasing temperature and than, to about 0.3 while sublimation or melting begins. Additionally they obtained the most interesting results for phases belonging to the Ag_2O-MoO_3 and Ag–V_2O_5 systems as high temperature friction coefficients reached 0.2 at 450 and 600°C, and also these phases were stable and didn't decompose during melting (Gulbinski et. al. 2003).

Gassner et. al. (2004), worked on the characterization of VN coatings prepared by reactive unbalanced magnetron sputtering, and verifying the concept of solid/liquid oxide lubrication for VN coatings. They concluded with the hopeful result that the friction coefficient against alumina as well as austenitic stainless steel balls showed a remarkable drop to a relatively low value at 700°C compared to room temperature, related to the formation of numerous low-melting, easy-shearable Magnéli phases (Gassner et. al., 2004). Also a different research again on the lubricious characteristic of Magnéli phases of vanadium was done by Kutschej et. al. (2004), but this time V was incorporated into the $Ti_{1-x}Al_xN$ coatings. Thus Ti-Al-V-N coatings were prepared with different contents of V to verify the concept of lubricious oxide formation while maintaining or even improving the excellent mechanical properties of $Ti_{1-x}Al_xN$ depending on the possibility of forming lubricious phases based on easily shearable oxides of vanadium (V_nO_{3n-1}) often also referred to as Magnéli

phases. The friction coefficient they measured against alumina was about 0.8 at room temperature and decreased to 0.27 at 700°C for a V content of 25 at.% in the target. This decrease was attributed to the formation of V_2O_5 providing lubrication at elevated temperatures. But they obtained a prerequisite for formation of these lubricious phases that is the necessary flash temperature in the contact zone needed for oxidation of V and melting of the formed V oxides, thus determining the running-in distance during ball-on-disk testing. On the other hand, the conversion of V_2O_5 to lower oxidized V oxides with higher melting points limited the availability of the low-friction effect (Kutschej et. al., 2004).

Some recent works were also conducted about the formation of TiO and shear deformable Magnéli phase oxides of titanium (Ti_nO_{2n-1}). Sumitomo et. al. (2005), conducted the investigation of the formation of Ti-oxides in Cl-implanted titanium films oxidized in air at low temperature to simulate oxidation conditions similar to local heating during dry machining; and also they studied the Ti-oxide formation in the oxide tribo-film formed on the surface of cutting tools of Cl-implanted TiCN coated tools. It was suggested that in the presence of volatile Ti-Cl compounds, the oxidation of titanium occurred more readily, but reduction in the available oxygen vacancies caused by Ti-Cl bonding caused the reaction to terminate at an intermediate stage. This resulted in the formation of the Magnéli phases. Also significant intermediate Ti-oxides were observed in the oxide tribo-film formed on the cutting surface of Cl-implanted TiCN coated cutting tools. Finally they concluded that the Magnéli phase oxides acted as an in-situ formed lubricant which led to the improvement in tribological properties (Sumitomo et. al., 2005). At the same time Aizawa et. al. (2005), conducted a research on the self-lubrication mechanism via the in situ formed lubricious titanium oxide tribofilms. Similarly, they suggested that the formation of lubricous intermediate titanium oxides with TiO and Ti_nO_{2n-1} was sustained to preserve low frictional and wearing state at the presence of chlorine atoms in the inside of TiN or TiC films (Aizawa et. al., 2005).

2.2.3. Soft Metals

Certain metals (e.g., In, Sn, Pb, Ag, Au, Pt, Sn, etc.) can provide low friction on sliding surfaces because of their low shear strengths and rapid recovery as well as recrystallization. The reasons of their usage as solid lubricants are the attractive

properties which are not available in other solid lubricants. For example, in addition to its soft nature, silver has excellent electrical and thermal conductivity, oxidation resistance, good transfer-film forming tendency, and a relatively high melting point; thus, it has been commercially used to lubricate the high-speed ball bearings of rotating anode X-ray tubes for many years. The Mohs hardness values of soft metals are generally between 1 and 3. Reported friction coefficients of soft metals range from 0.1 to 0.4, depending on the metal and test conditions. Pb, In, and Sn provide better lubricity at room temperature than Ag, Au, and Pt. At elevated temperatures, Pb, Sn, and In melt and undergo oxidation. Ag, Au, and Pt have fairly high melting points, do not oxidize appreciably, and hence are preferred for high-temperature lubrication purposes. Au remains in metallic form regardless of the temperature, while Ag_2O decomposes as the temperature increases and Pt oxidizes only slightly. Bronze and babbitts prepared by alloying some of these soft metals with Al, Zn, Cu, have been used as bushings, bearings, and other tribological applications for a number of years. (Donnet and Erdemir, 2001).

Soft metals are generally produced as thin films on surfaces to be lubricated. Simple electroplating and vacuum evaporation can be used to deposit most of these metals as self-lubricating films, but dense and highly adherent films are produced by ion plating, sputtering, or ion-beam-assisted deposition techniques. Film-to-substrate adhesion is extremely critical for achieving long wear life or durability, especially on the surfaces of ceramic tribomaterials. The thickness of the soft metallic films also plays a major role in both friction and wear. Too thin a film tends to wear out quickly. Also, the friction coefficients of most soft metals tend to decrease as the ambient temperature increases, mainly because of additional softening and rapid recovery from strain hardening. Thick films result in large contact areas and hence high friction (Donnet and Erdemir, 2001).

The combination of very high thermal conductivity with low shear strength and chemical inertness makes silver and gold coatings ideal for applications involving high frictional or ambient heating, such as sliding ceramic interfaces. However, when a highly thermally conductive film like silver is present at the sliding interface, the wear rate decreases dramatically, mainly because frictional heat is dissipated rapidly from the sliding interface. The low friction coefficient of silver also helps in reduced frictional heating (Donnet and Erdemir, 2001).

Silver is used as a lubricant in X-ray tubes, certain satellite parts, ball bearings, bolts, and other sliding parts in nuclear reactors. When applied as a dense and adherent coating on the surfaces of these components, it can effectively dissipate frictional heat that can otherwise cause thermomechanical and tribochemical wear. Used on ceramic surfaces, it shears easily, thereby reducing the friction and microfracture-induced wear of the sliding ceramic surfaces. Silver and other soft metallic coatings can also protect the sliding surfaces against environmental and/or tribochemical degradation under dry and oil-lubricated sliding contact conditions. One of the major shortcomings of metallic solid lubricants is that most of them react with sulfur and chlorine (if present in the operating environment) and may undergo rapid corrosive wear (Donnet and Erdemir, 2001).

3. CRYSTAL CHEMICAL APPROACH

Achieving and maintaining low friction at high temperatures (i.e., 300-1000°C) have been very difficult in the past and are still the toughest problems encountered in the field of tribology. Several researches were conducted exploring the feasibility of lubricating hot surfaces with vapor, liquid, and solid lubricants. But the application and environmental issues limited the use of most of the developed materials as they often faced unwanted oxidation and/or chemical breakdown and thus rendered these lubricants useless. Solid lubricants are certainly more appealing than the others for use at high temperatures. Certain oxides (e.g., Re_2O_7, MoO_3, PbO, B_2O_3, NiO, etc.), become soft and highly shearable at elevated temperatures and hence can be used as lubricants. Oxide-based self-lubricating materials can be prepared as alloys or by designing appropriate coatings or composite structures. The lubricious layers that form by oxidation of metallic surfaces or alloys would be very desirable and exceptionally advantageous when compared with the solid lubricant coatings with finite lifetimes. At high temperatures, as the oxide layer is depleted from the surface by wear, the most useful alloying ingredients diffuse toward the surface where the oxygen potential is higher, and oxidize again to replenish the consumed lubricious layer which has low shear strength and/or surface energy to decrease friction (Erdemir, 2000).

The crystal chemical approach proposed by Erdemir (2000), provides a way to formulate and use new alloys or oxide-based materials that exhibit low-shear and hence low friction at high temperatures. It classifies lubricious oxides on the basis of lubrication performance and operational limits. This approach was proposed to serve as a guide for determining the types of lubricious oxides needed on a sliding surface at high temperatures. The major benefit of this model is that it may provide a scientific means to better design and formulate future tribological coatings that provide not only superior wear resistance but also sufficient lubricity during dry machining or sliding applications. The crystal chemical approach also helps explain the lubrication mechanisms of these oxides or oxide systems that form on

tribological surfaces as the crystal chemistry of certain oxides relates strongly to their shear rheology and hence their lubricity at high temperatures. Additionally one can estimate the solubility limits, extent of chemical interactions, compound-forming tendencies, surface energy, and melting point of one oxide when a second oxide is present in the system with the help of this approach.

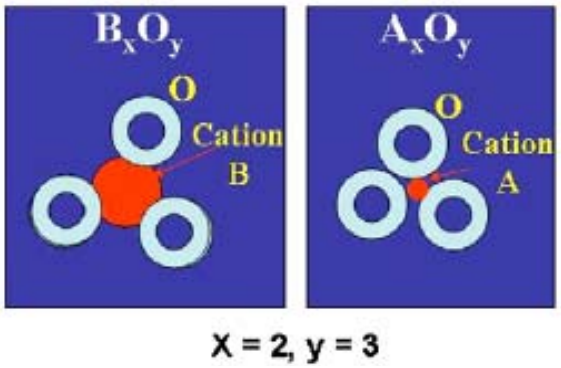
The interaction between the sliding contact interface of two solid bodies have to be taken into account by means of continuous physical, chemical, and topographical changes. The extent of the tribological events that occur at such an interface is further exacerbated if the solid bodies are chemically different or if a third or more bodies are present, the operating environment is oxidizing, and the ambient temperature is high. In tackling the very complexity of numerous thermal, mechanical, and chemical events that occur at such an interface on various time and length scales, it is important to consider the kinetics of oxidation and the rates of cation diffusion, oxide stoichiometry, heat of formation, electrostatic electronegativity, surface energy, and other atomic-scale events that occur at the sliding interfaces of solid bodies. When sliding occurs in open air and at high temperatures or high velocities, most sliding interfaces (including metals and non oxide ceramics) become oxidized. Thin oxide films that formed on the sliding surfaces may, in turn, dominate the friction and wear behavior of these interfaces. If the sliding bodies differ chemically or there is a third or fourth body at the sliding interface, two or more oxides may form on the sliding surface and dominate friction and wear (Erdemir, 2000).

3.1. Principles of Crystal Chemical Approach

It is proposed by Erdemir (2000) for the first time that using the principles of crystal chemistry, one can also establish model relationships between the quantum chemical properties and the lubricity of oxides at high temperatures. Specifically, it is possible to establish a correlation between ionic potential or the cationic field strengths of an oxide and its shear rheology and hence with its lubricity.

The crystal-chemical approach is based essentially on the ionic potential (φ) of an oxide and is defined as $\varphi = Z/r$ (where Z is the cationic charge and r is the radius of the cation). In general, the higher the ionic potential, the greater the extent of screening of a cation in an oxide by surrounding anions as illustrated in Figure 3.1.

Likewise, the field strength of a cation (defined as $\rho = Z/a^2$ where "a" is the distance between the cation and anion of an oxide) can also be used to determine the degree of screening of that cation. Oxides with highly screened cations (such as V_2O_5, WO_3, and Re_2O_7) are generally soft and, hence, shear rather easily to provide low friction at elevated temperatures. Their cations are well separated and completely screened by the oxygen anions. As a result, their ability to enter into extensive chemical interactions with other cations is greatly hindered. Most of their bonding is with surrounding oxygen anions. On the other hand, oxides with lower ionic potentials (such as Al_2O_3, Fe_2O_3, and MgO) are very strong and, hence, very difficult to shear. Their cations are free to interact with each other and form strong covalent or ionic bonds that make them very difficult to shear even at elevated temperatures. Also in Table 3.1 the ionic potentials of certain lubricious and high-friction oxides are compared (Erdemir, 2005).



Oxide case	Cationic charge	Cationic radius (Å)	Ionic potential
B_xO_y	3	0.5	6
A_xO_y	3	0.2	15

Figure 3.1: A schematic illustration of the concept for ionic potentials of two oxides having the same cationic charge but different cation radius (Erdemir, 2005).

Table 3.1: Relationship between friction coefficients and ionic potentials of certain oxides (Erdemir, A., 2000).

Oxide form	Electronic charge (*Z*)	Radius of cation (Å)	Ionic potential (*Z* / *r*)	Melting point (K)
ReO_3	6	Re^{6+} (0.51)	11.7	433
B_2O_7	7	Re^{7+} (0.56)	12.5	569
B_2O_3	3	0.25	12	723
V_2O_5	5	0.64	8.4	945
MoO_3	6	0.67	8.9	1068
WO_3	6	0.68	8.8	1743
TiO_2	4	0.64	5.8	2123
Al_2O_3	3	0.50	6	2313
SnO_2	4	0.71	5.6	-
ZrO_2	4	0.79	5	3073
MgO	2	0.63	3.2	3173
NiO	2	0.69	2.8	

CoO	2	0.72	2.7
ZnO	2	0.74	2.7
FeO	2	0.74	2.7

In most tribological situations, two or more dissimilar solid bodies may be rubbing against each other, and often the sliding surfaces are covered by more than one kind of oxide. The crystal chemical approach introduced above can also be used to predict the lubricity of such complex oxide systems. In these cases, one has to consider the absolute difference in ionic potentials of the oxides in the system. The eutectic temperature and compound-forming tendencies of two oxides are closely related to the cationic field strengths or ionic potentials of the involved elemental species. The ability of an oxide to dissolve in or react with other oxides or to form complex oxides is estimated from the difference in relative ionic potentials of the oxides in the system. In general, the greater the difference in ionic potential, the lower the eutectic temperature and the greater the tendency to form complex oxides and the higher is the lubricity of these oxide systems. This correlation has two possible explanations. First, as the difference in ionic potential increases, the ability of these oxides to form a low-melting-point or readily shearable compound improves; hence, they tend to exhibit much lower hardness than their constituents and can shear readily at elevated temperatures. This property is attributed to the anions being able to better shield or screen the cations, thus making them less likely to interact with neighboring cations. The second reason is that the ability or affinity of ionic species to form highly stable compounds (that exert very little chemical or electrostatic attraction) improves as the difference in ionic potential increases. Lower attraction between sliding surfaces means lesser adhesive forces across the sliding contact interfaces, hence, lower friction. (Erdemir, 2000; Erdemir, 2005)

4. EXPERIMENTAL PROCEDURE

4.1. Coating Process

Re and W-Re films with Ti bonding interlayer were deposited with DC magnetron sputtering and cathodic arc evaporation PVD techniques. Ti as a bonding interlayer was evaporated by cathodic arc physical vapor deposition while Re and W-Re was sputtered with DC magnetron. The W-Re alloy target had a composition of W %75 and Re %25. The distance between the sputtering source and the substrate was set to be 5.5 cm for all the coatings. For sputtering, pure argon gas was used. A coating system (Ti-Gold Model 8) having an arc PVD cathode and an unbalanced magnetron gun combined with a DC power supply were used for deposition. The schematic diagram of this system is shown in Figure 4.1. The effects of magnetron power and the chamber pressure on the structure of Re films were investigated at the end of the coating processes.

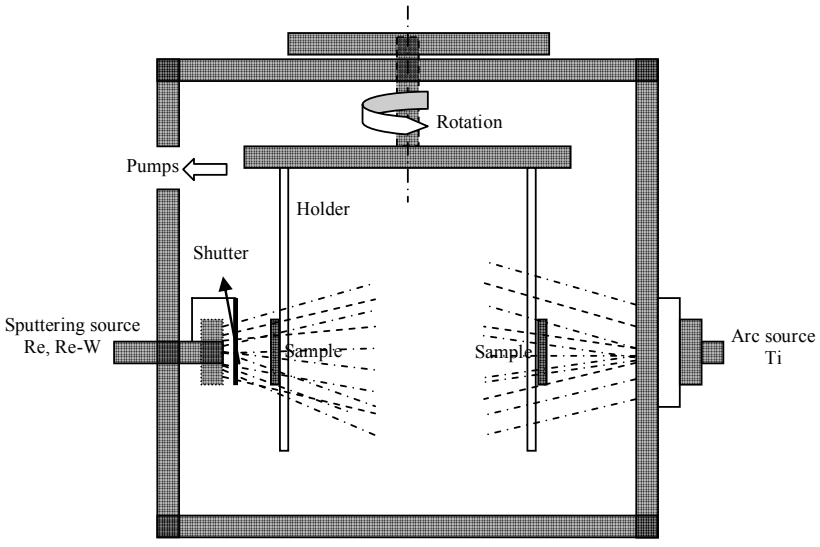


Figure 4.1: Schematics of the CAPVD and UBMS system, (Öztürk et. al., 2007)

4.1.1. Sample Preparation

Si wafer and hardened M-2 type high speed steel (0.95-C, 4.2-Cr, 5.0-Mo, 6.0-W, 2.0-V) were used as substrates. The substrates were first polished with 9 micron and then with 1 micron diamond suspensions. After polishing, the substrates were

ultrasonically cleaned in acetone for 15 minutes, and finally soaked with isopropyl alcohol and dried.

4.1.2. Pure Re Coating

For the first set of three samples, the observed parameter in coating was the magnetron power. Three samples Re200-1.0; Re300-1.0; Re400-1.0 were first metal ion etched/bombarded for both heating and cleaning, with Ti cathode under - 600 V, - 800 V and - 1000 V bias voltages for 1 minute each.

Ohring stated that if the interlayer is thin, a good adhesion is obtained but if the layer is thick poor adhesion occurs (Ohring, 2002). Considering this fact, substrates are coated with Ti for 5 minutes in order to obtain an interlayer film with proper thickness. This coating was done with 70 A current and 150 V bias voltages. Then the Ti coated substrates were finally deposited with Re for 30 minutes at magnetron powers of 200 W, 300 W and 400 W. The chamber pressure was maintained constant at 1.0 Pa with an argon flow rate of 40 sccm and the temperature inside the chamber was adjusted to 60°C.

The second set of coatings was deposited in order to observe the effects of variations in chamber pressure. Therefore, two samples Re300-0.5; Re300-1.5 were deposited at 300 W and at the same conditions as the first set except the chamber pressures which were specified as 0.5 Pa and 1.5 Pa and compared with previously deposited sample, Re300-1.0.

4.1.3. W-Re Coating

Economical constraints imposed on coating metallic Re, directed this research towards assessing the properties on Re alloy coatings. Therefore, the usage of commercially available W-Re alloys will surely be more economical. If W-Re film coating did exhibit the similar unique properties as metallic Re coating, then this study would be more exciting.

In this set of experiments W-Re alloy thin films were produced. The W-Re target was of % 75 W, % 25 Re composition. After the substrate heating and cleaning by high voltage sputtering routine, first Ti bonding layer was deposited by cathodic arc evaporation in the same procedure as the previous metallic Re coatings (with 70 A current and 150 V bias voltages, for 5 minutes). Then W-Re film was deposited for

30 minutes, but this time in order to obtain a thicker coating, based on the previous experiments' results, 400 W magnetron power was used. Argon flow was controlled to have a fixed value of 1.0 Pa chamber pressure. After the coating process, high speed steel and the Si wafer substrates were arranged for the structural characterization and wear tests.

All of the coated samples with their coating parameters were summarized in Table 4.1.

Table 4.1: Coating parameters of the deposited samples

Sample	Magnetron Power (W)	Chamber Pressure (Pa)	Time (min)	Temperature (°C)	Ti Interlayer
Re200-1.0	200	1.0	30	60	Coated for 5 minutes with -150 V bias
Re300-1.0	300	1.0			
Re400-1.0	400	1.0			
Re300-0.5	300	0.5			
Re300-1.5	300	1.5			
W-Re300-1.0	300	1.0			

4.2. Characterization

Due to the investigated properties, the characterization procedures of the deposited films were examined under two main titles. First of them was the structural characterization in which the effects of coating related issues on the structure of the Re and W-Re films were examined. The second one is the wear behavior characterization which was done in order to introduce the tribological nature of Re based thin films.

4.2.1. Structural Characterization

In order to characterize the structure of the Re and W-Re films produced by magnetron sputtering PVD technique and investigate the effects of coating parameters on the structural properties of the films, a set of experiments including

thickness, micro-hardness, surface roughness measurements and XRD, phase and morphology analysis were conducted.

4.2.1.1. Thickness Measurements

The thickness of the coatings was determined by both investigating the cross-section images of the films taken by SEM (Jeol JSM-6400 SEM) and by using the Calotest spherical abrasion technique (Eifeler Nord Coating Caloprep) over the HSS substrates. A steel ball of 10 mm diameter and abrasive paste were used for cratering. In this method the thickness was measured by optical inspection of the spherical cap abraded into the coating. The graphic representation of the method is seen in Figure 4.2.

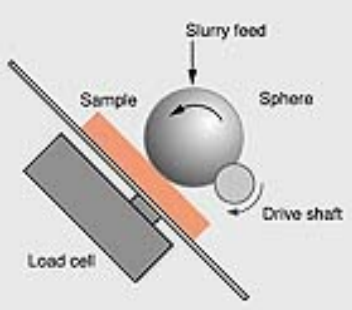


Figure 4.2: Calotest thickness measurement method with spherical abrasion

4.2.1.2. Micro-Hardness Measurements

Hardness measurements were carried out with an ultra micro-hardness tester (Fischer HP 100) with a load sensitivity of 0.2 mN and a depth sensitivity of 0.01 nm. A total load of 50 mN was applied in 120 steps with a time interval of 0.5 s at each step. The Vickers pyramid indenter penetrates to the one tenth of coating thickness, which is approximately 300 nm. Each measurement was repeated 30 times over the whole surface of the samples for obtaining an average hardness value.

4.2.1.3. Microstructural Investigations

The investigation of both the grain growth structure and the thickness of the films were done over the cross-section images of the coatings deposited on Si wafer substrates, with a Jeol JSM-5410 Scanning Electron Microscope (SEM). With this analysis, differences in growth morphologies of pure Re and W-Re films were observed and zone models of coatings were determined.

4.2.1.4. Energy Dispersive Spectrometry Analysis

The composition of W-Re films was determined by using a NORAN 2100 Freedom EDS analyzer equipped on Jeol JSM-5410 model scanning electron microscope.

4.2.1.5. X-Ray Diffraction Analysis

The phase structure of the coatings was analyzed by a glancing angle X-ray diffractometer with a thin film attachment (Philips Model PW3710) using Cu Kα radiation over the 2θ range of 20–140° at a voltage of 40 kV and a current of 40 mA. The 2θ scan method with a fixed incidence angle of 2° was used. In order to determine the formation of rhenium oxides, the samples were heated with an Edmund Bühler GmbH REP 1806 heater equipped on the XRD device.

4.2.2. Tribological Behavior Characterization

Investigation of the wear properties of Re and W-Re coatings were conducted with both ball-on-disc and fretting test methods, against different counterfaces and with different temperatures. Immediately after the wear tests, the wear debris around the wear tracks were characterized with micro Raman spectroscopy and the worn surfaces were examined with optical profilometry. According to the highly volatile and lubricious characteristics offered by the crystal chemical approach, the oxides of rhenium are predicted to play an important role on the tribological properties of Re thin films.

4.2.2.1. Ball-on-Disc Tests

Ball-on-disc tests were conducted with CSM Instruments Tribometer. The counterface materials were alumina and 440C series steel balls of 10 mm diameter. Tests were performed under 2 N normal loads, with sliding speeds of 10 cm/s and 20 cm/s and a constant distance of 500 m. The temperature and humidity ranges during the tests were 18-23°C and 39-56 %RH respectively. Within the scope of these tests, the wear behavior of Re and W-Re films were both separately and comparatively investigated. The results of the tests were compared due to two different sliding speeds (10 cm/s and 20 cm/s) and against two different counterface materials (alumina and 440C steel balls).

4.2.2.2. Fretting Wear Tests

Fretting tests were conducted with a Plint & Partners TE 70 Micro Friction device. The parameters were chosen for the test to demonstrate the most severe conditions. Parameters used in the tests are given in Table 4.2.

Table 4.2: Parameters applied in fretting wear tests

Frequency (Hz)	10±0.02
Stroke Length (µm)	100±10
Load (N)	2
Time (min)	34
Temperature (°C)	Room Temperature, 50°C, 100°C, 150°C
Humidity	39-56 %RH

4.2.2.3. Optical Profilometry

The wear tracks and worn surfaces of the films and the counter materials were investigated over the 3D images and 2D representations obtained by a Veeco Wyco NT1100 optical profilometer. Also the wear volumes of the worn surfaces were calculated and the surface roughness values of the films were determined with the help of optical profilometry.

5. Results and Discussion

5.1. Improving the Adhesion of Films

In the first trials of rhenium coating on HSS and silicon wafer substrates, a good adhesion could not be acquired between the substrate and the film. This situation could had possibly been because of the stress induced by rapid cooling or thermal shock that the film experienced after opening the chamber door without giving the adequate time for substrate to cool down. Thus the coating process was repeated, this time with long enough time for cooling of the substrate, 12 hours after the coating. Again the detachment of the film from the substrate was observed, even a little adhesion of the film was absent for the coating flied away by just blowing on it.

Adhesion is a matter of bonding and electrical and chemical interactions at the substrate-coating interface. Usually when metal films with a high affinity of oxidizing, were coated on oxide substrates or metals forming intermetallic compounds, a compound interface is produced increasing the adhesion of the film to the substrate metal (Ohring, M., 2002). Based on the Hume-Rothery rule, there are several requirements for materials to form a compound interface as a substitutional solid solution. These are as follows:

1. *Atomic size factor:* Solvent and solute atoms must differ in atomic size by less than 15% in order to form this type of solution.
2. *Crystal structure:* Both elements must exist in the same crystalline lattice.
3. *Electronegativity:* Metals with similar electronegativity are prone to form substitutional solution.
4. *Valances:* A metal is more susceptible to dissolve another metal with higher valency than with a lower valency, if other factors are equal. (Callister, W.D., 2007)

A metal which forms a compound interface with rhenium, namely shows good adhesion to rhenium film, could be used as a bonding interlayer so as to achieve the

adhesion of Re film on HSS substrate. Thus it was necessary to take some material's properties into account in understanding the reasons of poor adhesion and for choosing a proper interlayer material. Therefore an investigation on comparing the crystal structure, atomic radius, thermal expansion coefficients and electronegativities of rhenium and some other potential interlayer materials was made. The mentioned properties are compared between Re and Ti, Cu, WC, Fe in Table 5.1.

Table 5.1: Comparison of some material's properties of Re with potential interlayer metals (webelements.com, 2007)

	Re	Ti	Cu	WC	Fe	Si
Melting Point (°C)	3180	1668	1084	2870	1538	1414
Crystal Structure	hexagonal	hexagonal	face-centered cubic	hexagonal	body-centered cubic	face-centered cubic
Atomic Radius (pm)	135	140	135	135	140	110
Thermal Expansion (25°C) ($\mu m \cdot m^{-1} \cdot K^{-1}$)	6,2	8,6	16,5	4,5	11,8	2,6
Electronegativity (Pauling scale)	1,90	1,54	1,90	-	1,83	1,90

Due to the properties compared above, especially the crystal structures, the atomic radii and the thermal expansions, it could clearly be seen that Re has tendency to form solid solution with Ti. With the prediction of formation of an interlayer compound, a new solution approach was figured out for the adhesion problem. Therefore a new coating was done using titanium, copper, tungsten carbide, stainless steel and silicon substrates. The result was consistent with the prediction. Rhenium film showed a perfect adhesion to the Ti substrate. Also the adhesion of the film to the Cu and WC substrates was noticeable, but it was unsatisfactory to apply these substrate materials as a bonding interlayer. The adhesion to the stainless steel and Si wafer substrates was poor in accordance with the discrepancy of the compared properties according to the Hume-Rothery rules. Since Ti has shown a compatibility with rhenium's crystal structure, atomic radius and thermal expansion and shown an excellent adhesion, it was chosen as the interlayer material. Consequently the following coating processes were conducted with a previous coating of a Ti bonding interlayer.

5.2. Effect of Magnetron Power on the Thickness of the Films

The thickness of the Re coatings are compared in Figure 5.1. The thicknesses of Ti interlayer varying between 0.5 – 0.58 µm, are not included to the total thicknesses as the bonding layer has been deposited by cathodic arc evaporation thus it would not reflect the true effect of magnetron power. In general, the deposition rate is proportional to the power consumed. It is verified by the cross-section images of the films on Si wafer substrates that the resultant deposit thickness is clearly dependent on magnetron power at constant chamber pressures.

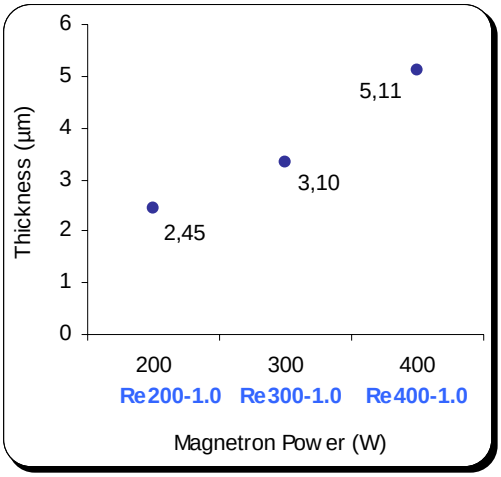


Figure 5.1: Variation of coating thickness with magnetron power

The total thickness (both Re an Ti layers) of the W-Re coating was 3.96 µm. In order to obtain a precise value, the second measurement was done with SEM upon the Si wafer sample. The cross-section image of the sample is shown in Figure 5.2. The thickness of Ti bond layer is 0.70 µm and the W-Re film is 2.62 µm, which is similar to the total value obtained by Calotest measurement. It was found to be lower than the Re metallic film coated at the same conditions. The sputtering yields of Re and W are 0.9 and 0.6 respectively with an argon kinetic energy of 600 eV (angstromsciences.com, 2007). The ratio of W to Re of the target and the lower sputtering yield of tungsten could result in a lower thickness value than Re metallic coating as our present condition.

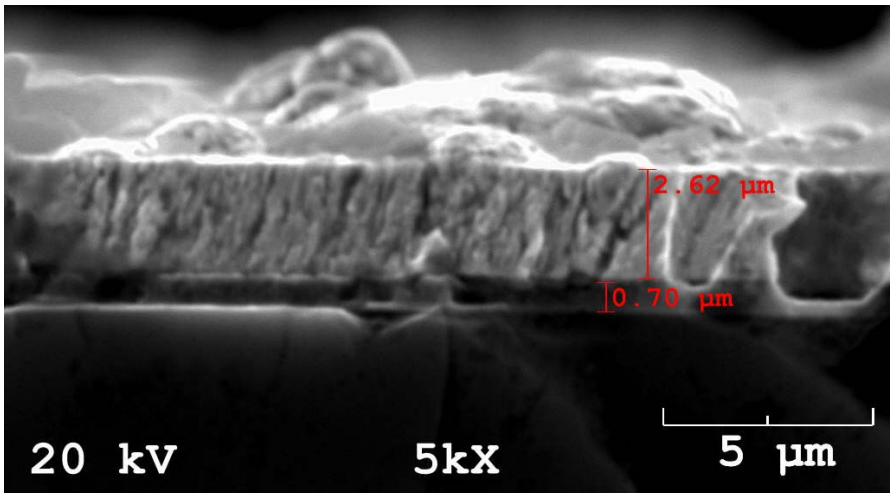


Figure 5.2: Cross-section image of the W-Re film showing its thickness

5.3. Effect of Argon Pressure on the Thickness of Re Films

Argon gas was used for the sputtering of Re and W-Re films. To investigate the effects of pressure on the structure of rhenium films, the argon partial pressure was adjusted in order to have constant chamber pressures, which are 0.5, 1.0 and 1.5 Pa.

The relative film deposition rate depends on the sputtering pressure. At low pressures, the cathode sheath is wide and ions are produced far from the target; their chances of being lost to the walls are high. The mean-free electron path between collisions is large and electrons collected by the anode are not replenished by ion-impact-induced cathode secondary emission. Therefore, ionization efficiencies are low. As the pressure is increased, the electron mean-free path is decreased, more ions are generated, and larger currents flow. But if the pressure is too high, the sputtered atoms undergo increased collisional scattering and are not efficiently deposited (Ohring, 1992).

Investigation of the argon pressure effect on thickness of the rhenium films is shown in Figure 5.3. It can clearly be seen that the results were in accordance with Ohring's statement. Thus, the optimum total chamber pressure is found to be 1.0 Pa, which is necessary for obtaining the thickest rhenium film at 300 W magnetron power.

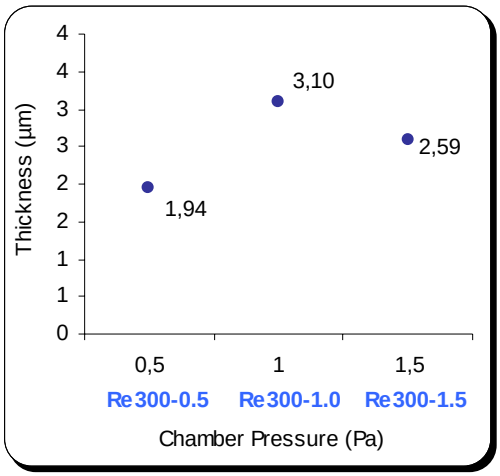


Figure 5.3: Variation of coating thickness with chamber pressure

5.4. Effects of Coating Parameters on the Hardness of the Films

The effects of magnetron power and chamber pressure on the hardness of the Re films are shown in Figure 5.4 and Figure 5.5. The resultant hardness comparison through the different magnetron powers was made; it was found that the coating produced at 300 W had the highest hardness of the three. When the x-ray diffraction analyses of the coatings were investigated, it was seen that the two coatings produced by applying a power of 200 and 400 W totally corresponded to the diffraction pattern of pure rhenium while coatings produced by using 300 W power have slightly shifted peaks relative to the positions of pure Re. The coatings exhibiting shifted peaks in their XRD patterns possessed higher internal stress hence higher hardness explaining the reason of the obtained result. No notable effect of chamber pressure on the hardness could be distinguished. The hardness of the films of different pressures was found to be nearly the same around 22 GPa.

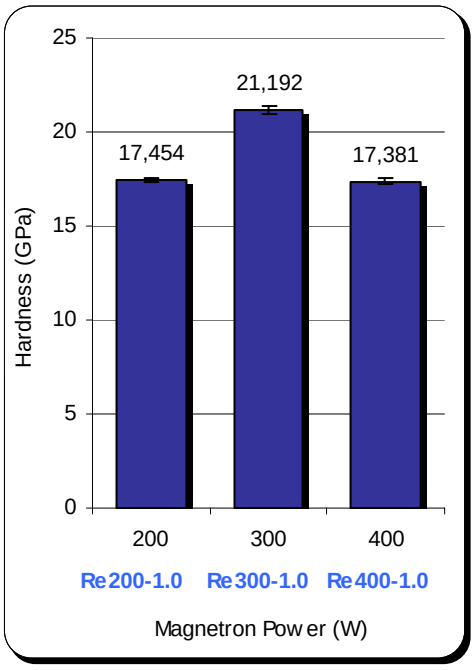


Figure 5.4: Effect of magnetron power on the hardness of the films

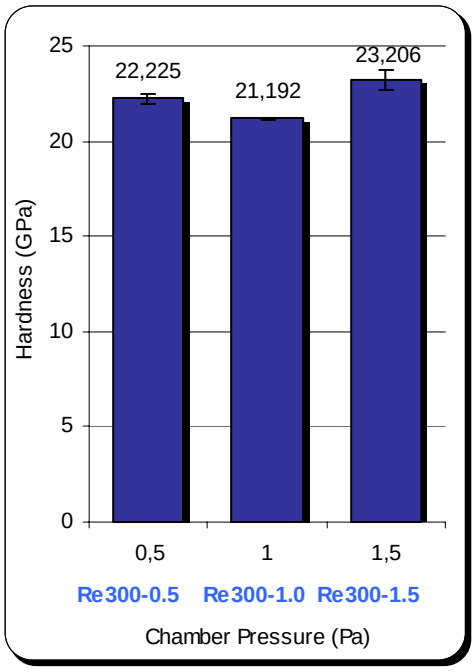


Figure 5.5: Effect of chamber pressure on the hardness of the films

The hardness value of W-Re films was found to be lower than pure rhenium coatings. It had a value of 12021 ± 152 MPa.

5.5. Microstructural Investigation of the Coatings

Cross-section images were used for both measuring the accurate thickness values and for determining the grain growth structure of the films. The relevant images of pure Re coatings coated under different magnetron powers and chamber pressures are shown in Figure 5.6. – 5.10. Consulting to the substrate and melting temperatures of rhenium and the argon pressure of the system, the growth of the film is found to correspond to the Zone 1 of Thornton's model. The morphologies of the coatings obtained in Zone 1 at low substrate temperatures were porous, and consisted of tapered crystals with domed tops leading to a rough surface. This unique tapered morphology is a result of low surface diffusivity of incident atoms at low substrate temperatures. Very few nuclei form and grow to dome shaped crystallites with voids in between (PalDey and Deevi, 2002).

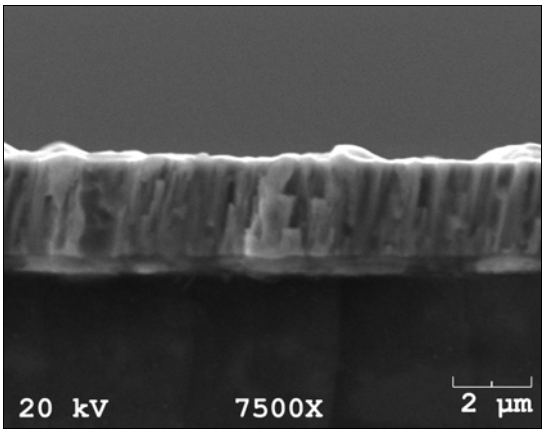


Figure 5.6: Cross-section of Re200-1.0

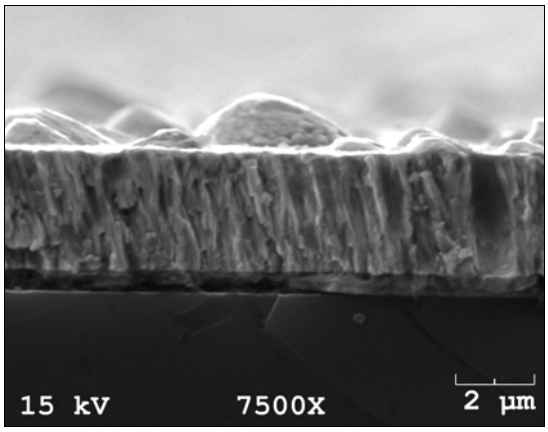


Figure 5.7: Cross-section of Re300-1.0

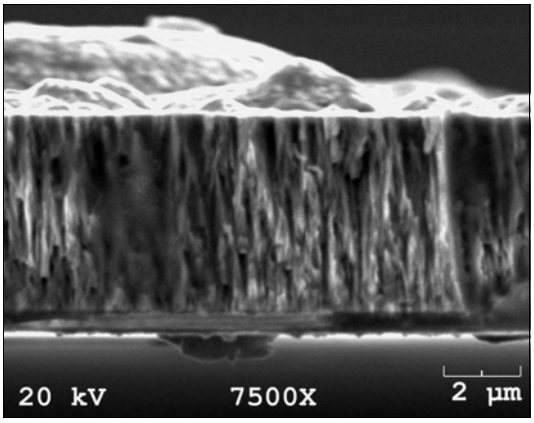


Figure 5.8: Cross-section of Re400-1.0

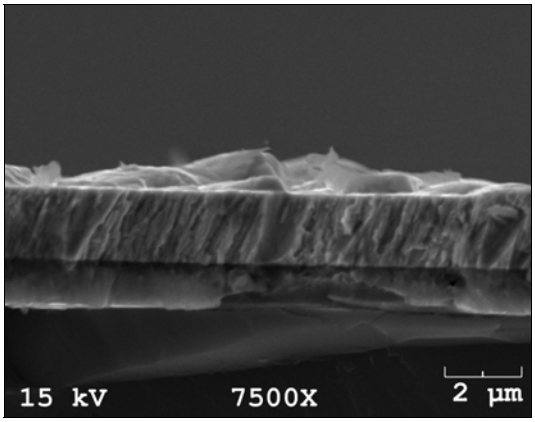


Figure 5.9: Cross-section of Re300-0.5

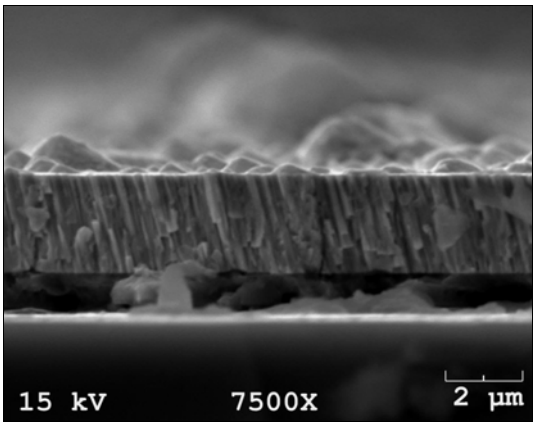


Figure 5.10: Cross-section of Re300-1.5

Also the microstructure of W-Re film seen on the cross-section image shown in Figure 5.11 is nearly the same as pure rhenium coatings. The microstructure again belongs to the Zone 1 of Thornton's model for this coating.

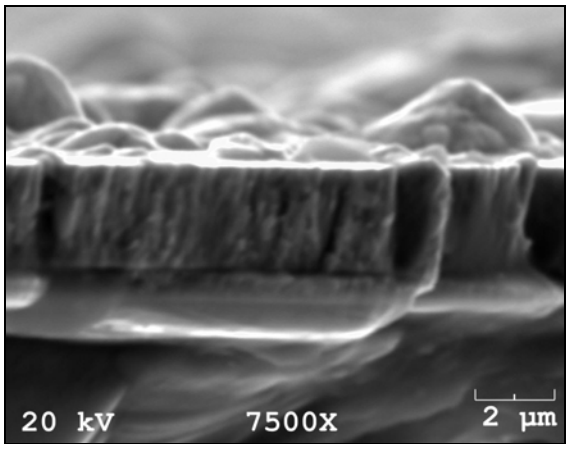


Figure 5.11: Cross-section image of W-Re300-1.0 coating

5.6. Composition of W-Re Coatings

The EDS analysis result for W-Re coating deposited on Si wafer substrate is shown in Table 5.2. The analysis showed that the film has a very similar composition to the W-Re target. Therefore, coating of W-Re alloy was proved to be successfully achieved.

Table 5.2: EDS analysis of W-Re coatings on Si wafer substrates

Element	Line	Intensity (c/s)	Error 2-sig	Atomic %	Conc.
W	Lα	28.33	1.093	75.600	75.363 wt.%
Re	Lα	8.61	0.602	24.400	24.637 wt.%
				100.000	100.000 wt.%
kV		20.0			

5.7. Surface Roughness Measurements

The average surface roughness values measured by optical profilometer for all coatings with different coating parameters were given in Table 5.3. The result for W-Re alloy coatings was very similar to the Re metallic coating, thus no effect of tungsten could be mentioned on the surface roughness of the film. The reason for the high roughness value of the surfaces is mainly the cathodic arc evaporated Ti layer. If a material of high melting point with a high vapor pressure was used during ion bombardment, macro droplet formation could be minimized in this way (PalDey and Deevi, 2002). Anyway Schwaller et al., suggest that the macroparticle contamination often encountered in cathodic arc PVD deposited coatings, is not an issue in wear protection since these minority inclusions are of lower hardness than the matrix

material, and their protruding parts are worn away in the first few contacts of their application (Schwaller et. al., 2005). Thus no the effect of surface roughness on tribological behavior of the coatings was taken into account and they were not investigated.

Table 5.3: Average surface roughness values of the films deposited under various parameters

Sample	**Re200-1.0**	**Re300-1.0**	**Re400-1.0**	**Re300-0.5**	**Re300-1.5**	**W-Re300-1.0**
Ra (nm)	*77.67*	*77.48*	*110.02*	*104.15*	*73.10*	*81.32*

5.8. X-Ray Diffraction Analysis

The XRD patterns of all pure rhenium samples are given in Figure 5.12. All the peaks fully correspond to the reference peaks of pure rhenium. Also in Figure 5.13, the diffractograms of W-Re coatings are seen comparing to the peaks of 80% W – 20% Re and Re_3W.

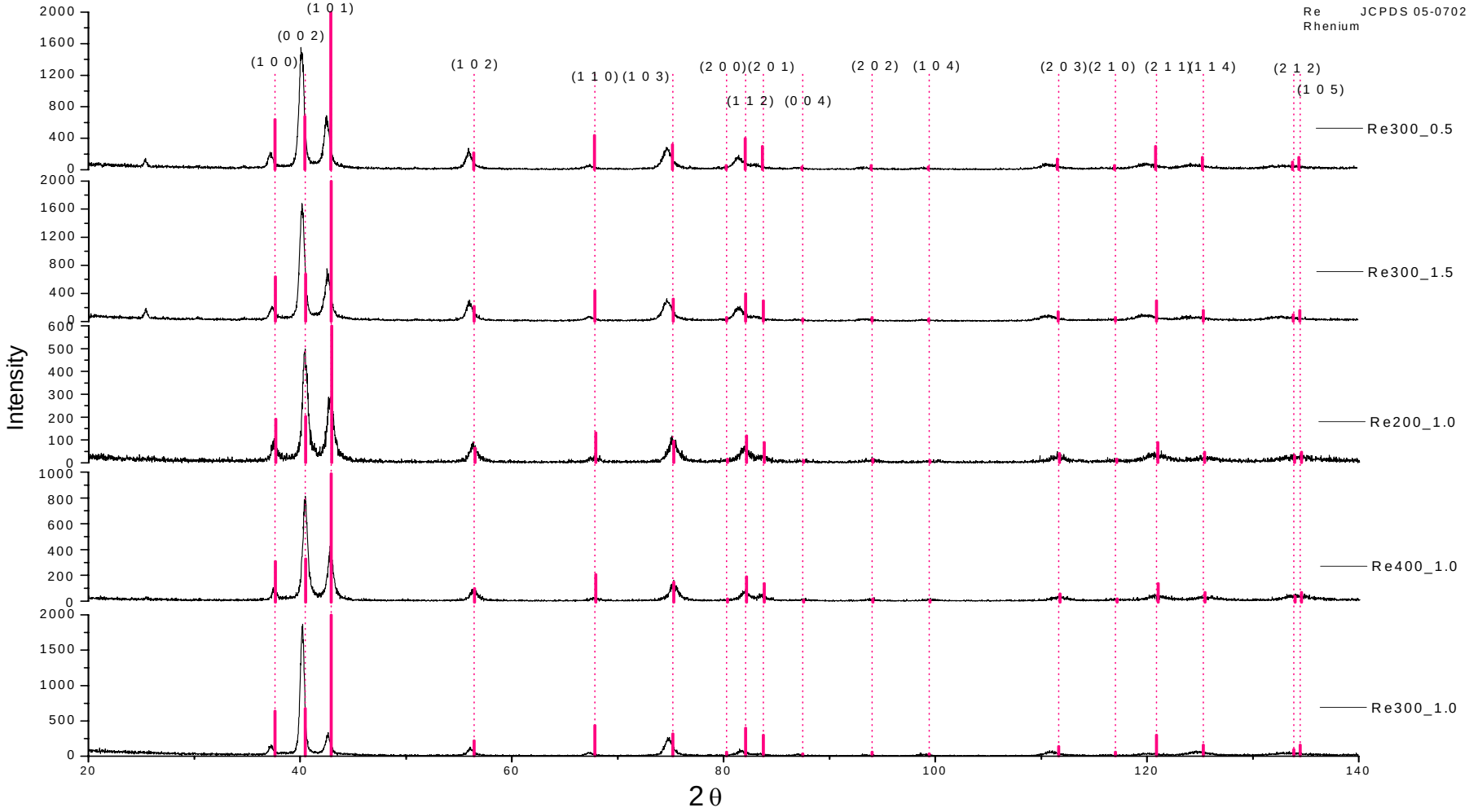


Figure 5.12. XRD analysis results for pure rhenium samples coated with different coating parameters

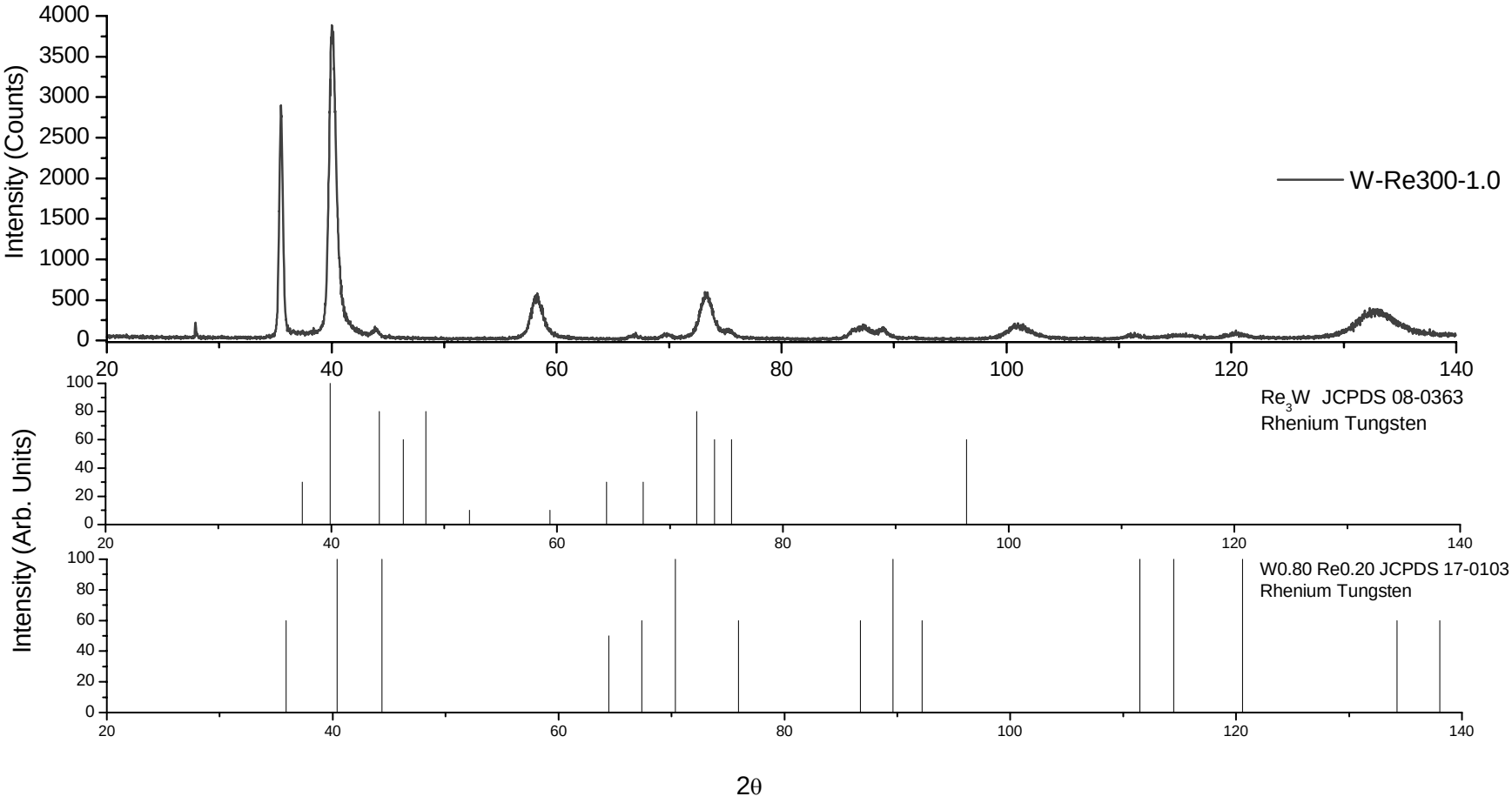


Figure 5.13. X-ray diffractograms of the W-Re coatings (on top), compared to those containing the most prevalent reflection peaks of the Re_3W (middle) and 80% W – 20% Re (bottom).

5.9. Characterization of Tribological Behavior

The results of the wear tests were classified according to the temperature they were conducted. Thus the results were evaluated separately for room temperature and for high temperatures. Also the results of both W-Re and Re coatings were investigated comparatively.

5.9.1. Tests at Room Temperature

Room temperature tests were done with using both fretting and ball-on-disc techniques. For fretting tests just alumina counter-body was used while for ball-on-disc tests both 440C steel and alumina balls were used. All of the tests were conducted two times for proving reproducibility.

5.9.1.1. Ball-on-Disc Tests

Two counterface materials, 440C steel ball and alumina ball were used for ball-on-disc tests. The effect of rotating speed was also investigated within the scope of these tests. In Table 5.4 the parameters used in the tests are given.

Table 5.4: Parameters chosen for room temperature ball-on-disc tests

	Re				**W-Re**			
Rotating speed (cm/s)	10		20		10		20	
Counterface material	Alumina	440C steel	Alumina	440C steel	Alumina	440C steel	Alumina	440C steel
Temperature (°C)	23	23	25	24	20	21	18	19
Humidity (%RH)	56	50	45	46	45	37	47	48
Radius (mm)	3.93	5	4.44	3.68	2.22	3.24	5	6.5
Distance (m)	500				500			
Normal load (N)	2				2			

The variation of coefficient of friction values of pure rhenium ball-on-disc test against alumina ball with two different rotating speeds are given in Figure 5.14. The

ball-on-disc tests against alumina ball done on pure rhenium coating were enough to prove the unique tribological behavior of rhenium. Coefficient of friction starts with a relatively higher value of about 0.22. Then for both of the rotating speeds it goes on a lowering trend and become stable after 100 meters. Through the remaining of the test, it maintains an average value of 0.13. Also it was seen that the variance in rotating speeds did not reflect a noticeable difference in coefficient of friction.

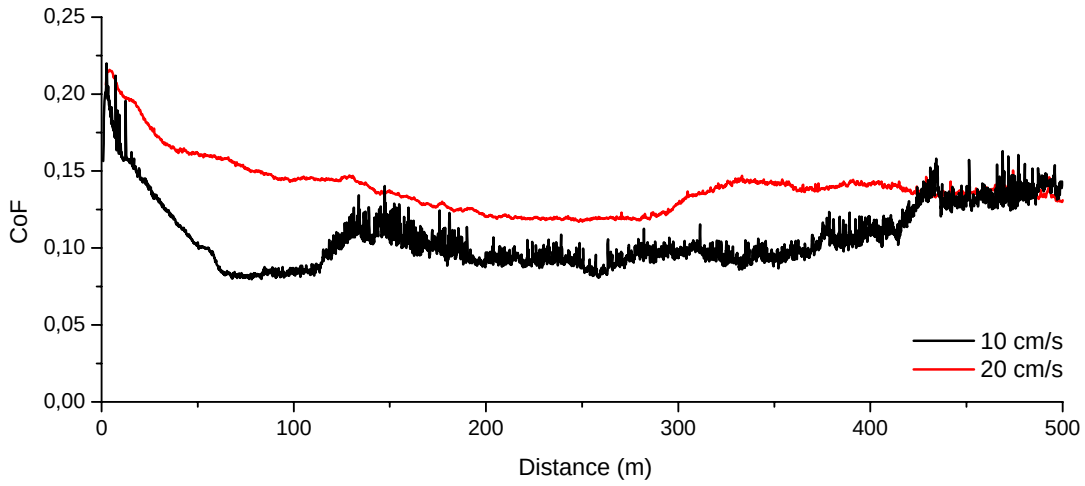


Figure 5.14: The variation of coefficient of friction values for pure rhenium tested at room temperature against alumina ball with two different rotating speeds

The examinations of contact surfaces of the samples showed that the wear tracks were composed of just shallow traces having a maximum depth of 0.135 µm. This value is less than 4 % of the total thickness of the coating. Similarly the alumina balls did not show a sign of wear. The 3D images of the sample surfaces and the related 2D profiles are shown in Figure 5.15 and Figure 5.16.

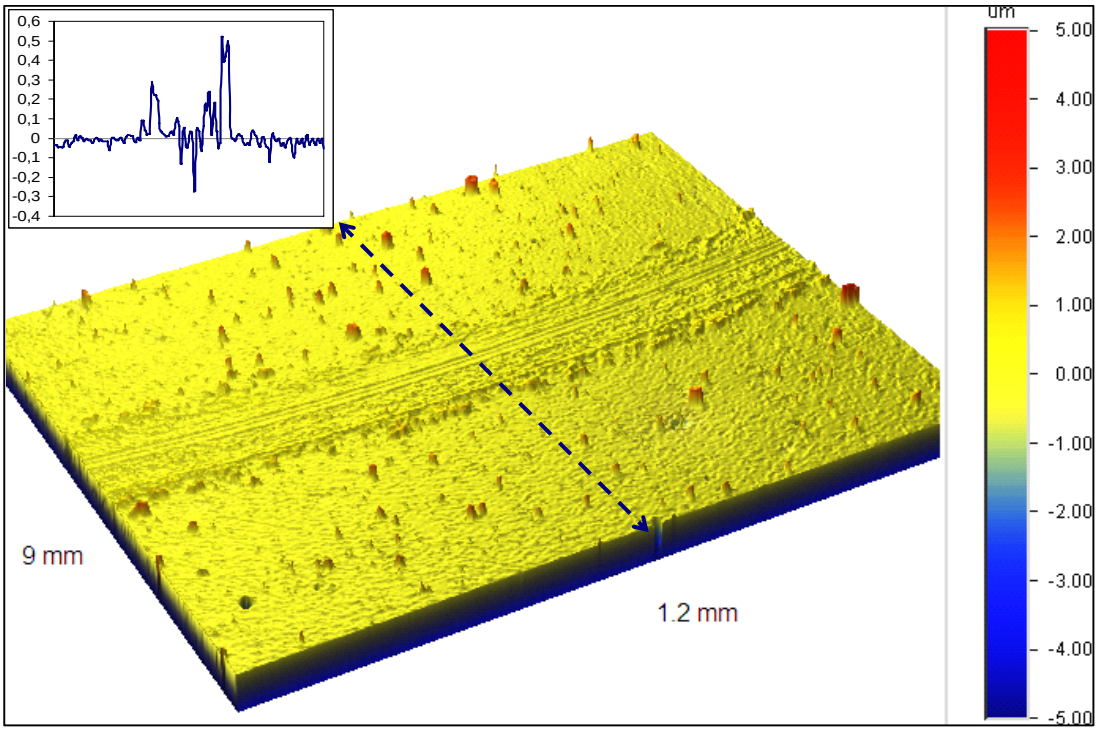


Figure 5.15: Wear track of the Re coated sample after ball-on-disc test against alumina ball at 20 cm/s rotating speed

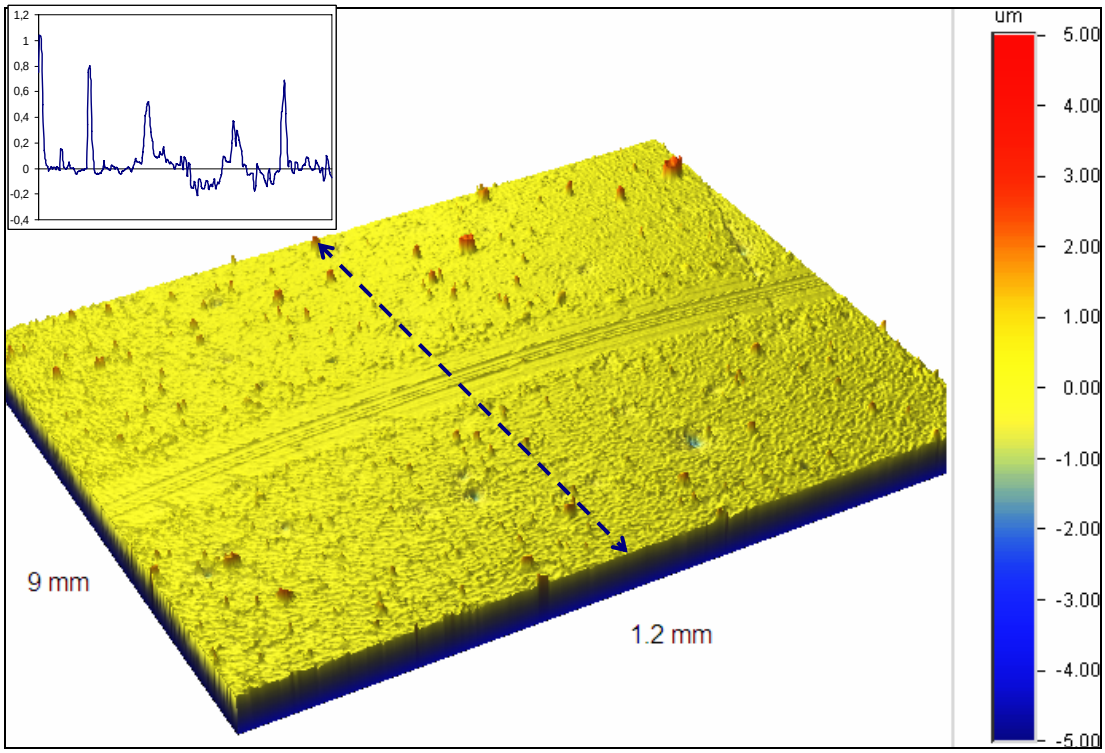


Figure 5.16: Wear track of the Re coated sample after ball-on-disc test against alumina ball at 10 cm/s rotating speed

The coefficient of friction variations of the tests against 440C steel ball are given in Figure 5.17. Again no difference between the two different rotating speeds could be distinguished. This time the coefficient of friction is higher than the tests done

against alumina ball. The average values are found to be about 0.5. But the wear tracks on the samples were much less apparent. This time the wear on the ball was catastrophic. The radius of the formed disc on the worn surface is around 850 µm. That much wear corresponds to a worn volume of 0.0833 mm^3 from the steel ball. The relevant images of the coated sample and the counterface material with the bal-on-disc tests against steel ball are given in Figure 5.18 and Figure 5.19.

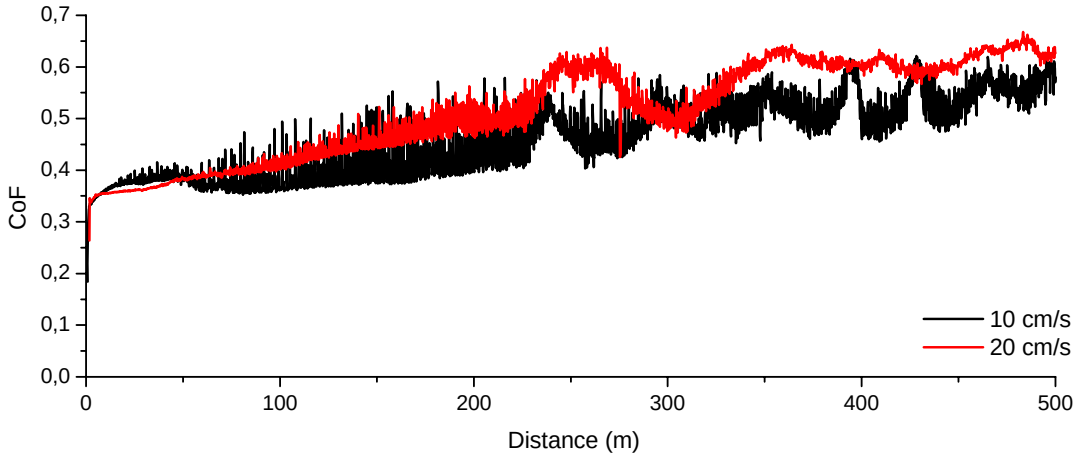


Figure 5.17: Variation of coefficient of friction values of pure rhenium ball-on-disc tests against 440C steel ball

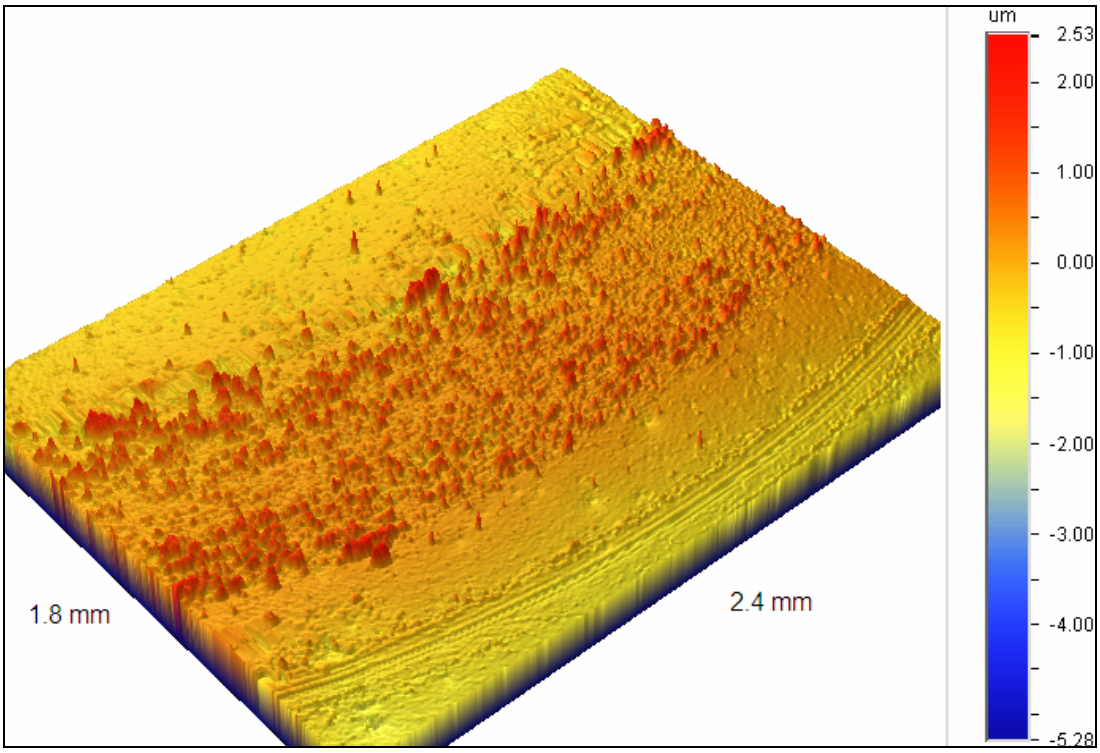


Figure 5.18: Wear track of the Re coated sample after ball-on-disc test against 400C steel ball

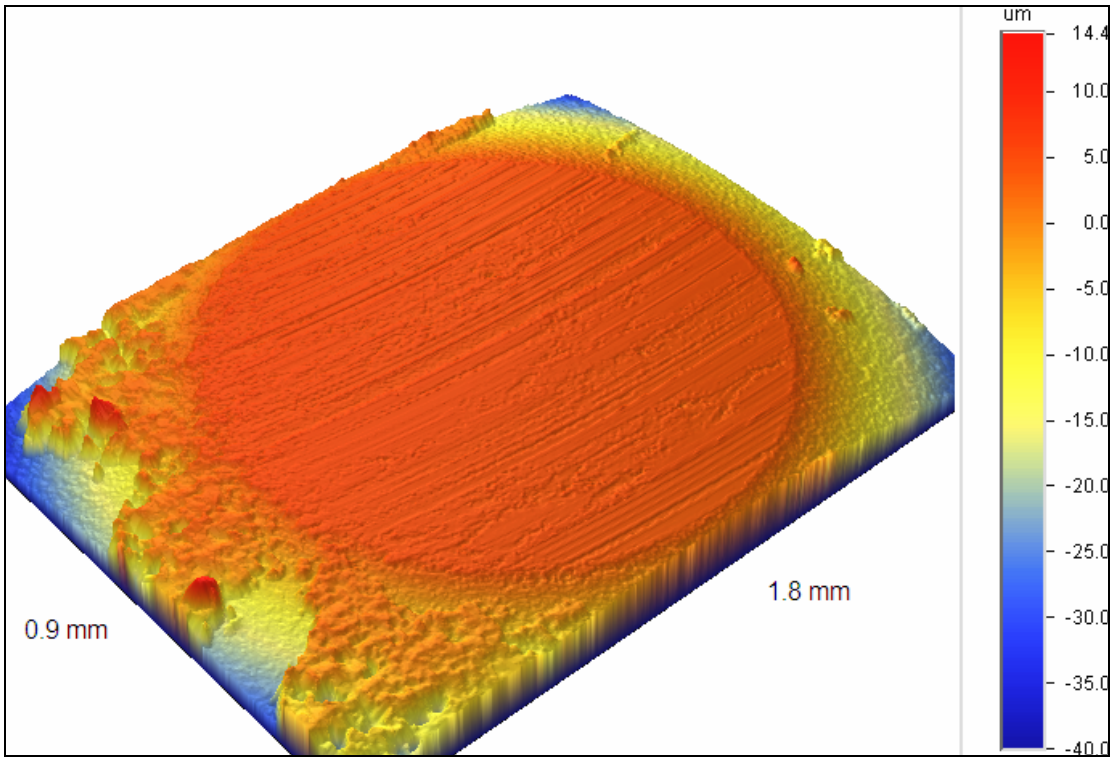


Figure 5.19: Wear scar of the steel ball ran against Re coated sample in ball-on-disc test

The results of the ball-on-disc tests over W-Re alloy coatings were much more interesting than the already brilliant findings about friction behavior of pure rhenium. W-Re alloy with a composition of 25 % Re and 75 % W, gave reasonable coefficient of friction values. The coefficient of friction values are shown in Figure 5.20 comparing two different rotating speeds. Therefore addition of rhenium to tungsten as an alloying element can also give low coefficients and producing this alloy will be much more economical than a pure rhenium coating.

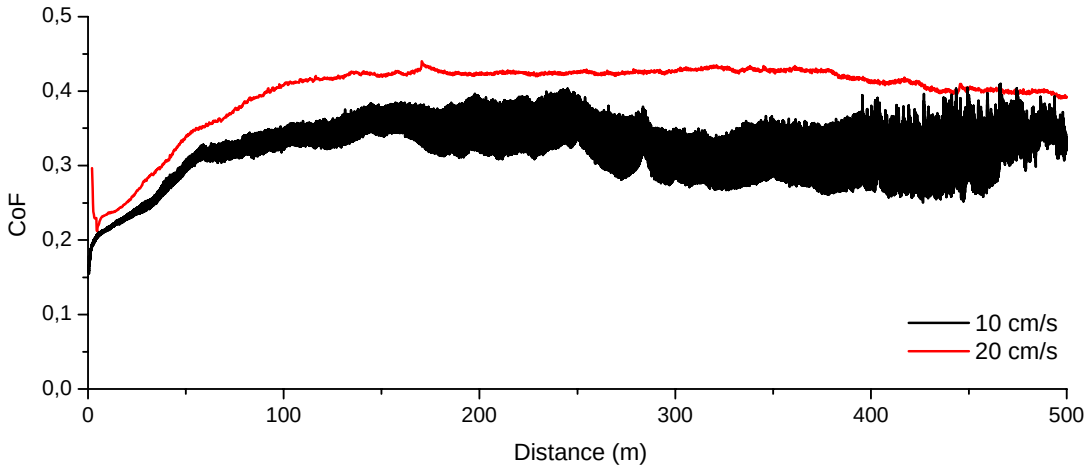


Figure 5.20: The variation of coefficient of friction values for W-Re alloy films tested at room temperature against alumina ball with two different rotating speeds

The starting friction coefficient values of the ball-on-disc tests on W-Re coatings were very similar with the beginning values for Re coatings. But this time contrary to the Re coatings, the progressing of coefficient of friction values showed an increasing trend. But in a short period, the values became stable at around 0.35. The relevant 3-dimensional images and 2-dimensional profiles of the wear tracks are shown in Figures 5.21 and 5.22.

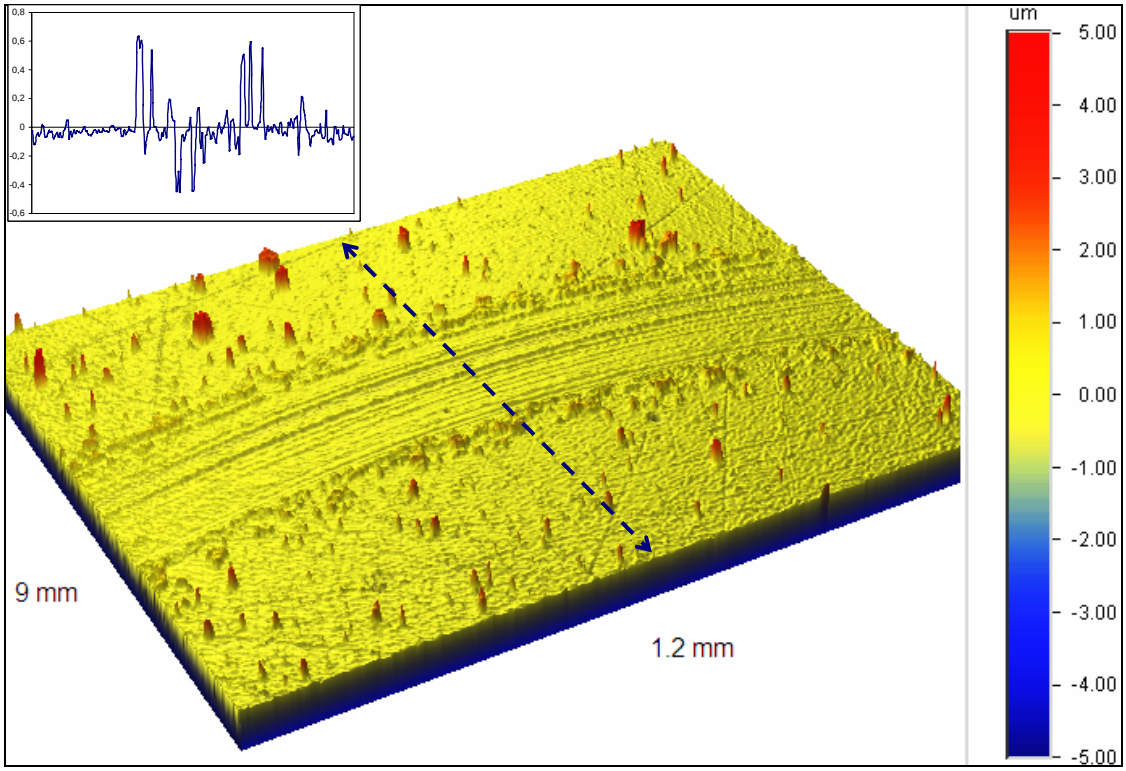


Figure 5.21: Wear track of the W-Re coated sample after ball-on-disc test against alumina ball at 10 cm/s rotating speed

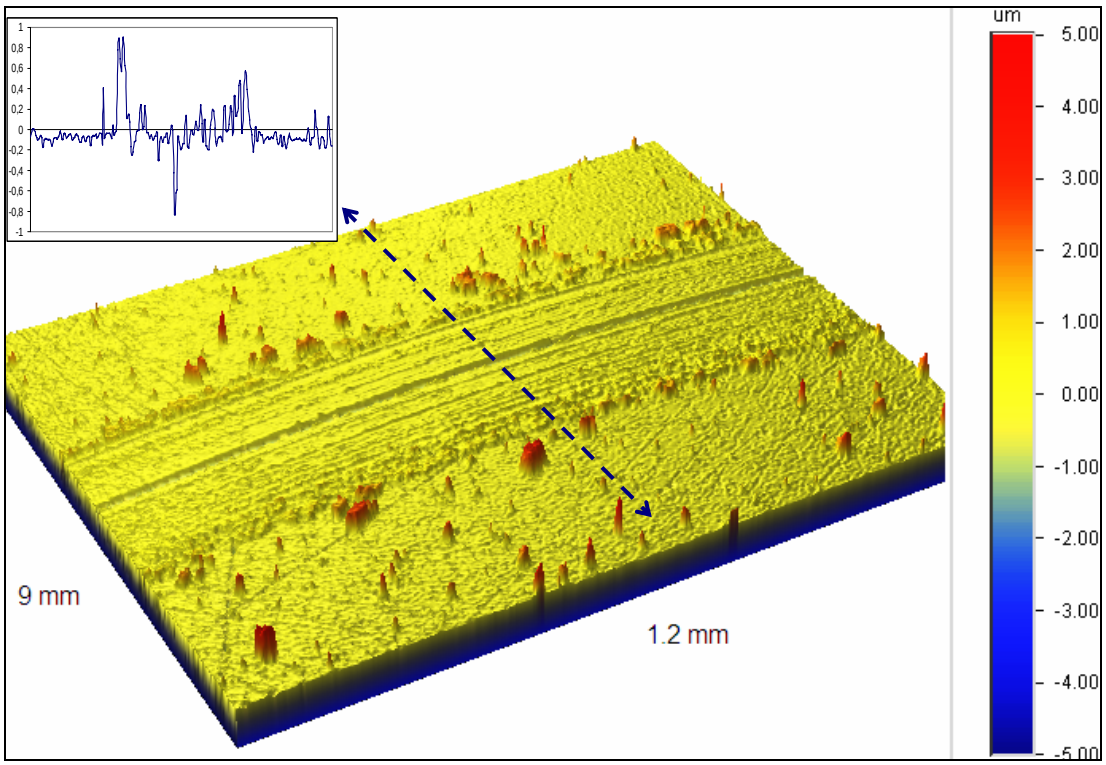


Figure 5.22: Wear track of the W-Re coated sample after ball-on-disc test against alumina ball at 20 cm/s rotating speed

The wear track of the test with 10 cm/s rotating speed had a width of 239 µm. Maximum depth within this track was 0.426 µm. Also there were other shallow traces within the track with different depths. For the case of the test with 20 cm/s rotating speed, the wear track on the sample was 316.2 µm wide. This time maximum depth was 0.750 µm and there were no other deep traces within the track. The slight difference in the width of wear tracks could also be seen again from the slight difference in the coefficient of friction values.

The ball-on-disc tests against 440C steel ball were also conducted for W-Re coated samples. The variation of friction coefficient values with distance for two rotating speeds is seen in Figure 5.23. Again as it was for the tests with alumina ball, the coefficient of friction starts with a relatively lower value of 0.33. Then again like the test with alumina ball, it progresses increasingly until it becomes stable at a mean value of 0.65. If we compare this value to the tests done with 440C steel ball on pure rhenium coatings, we see that it is higher than the rhenium coated sample by 0.65 to 0.50. This much difference is just like it was for the tests against alumina ball. Also again no noticeable difference between the two rotating speeds was distinguished.

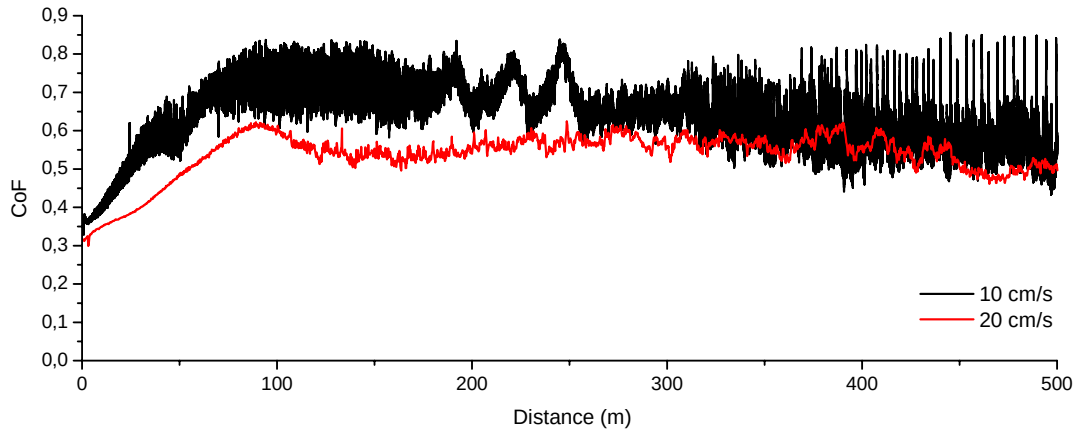


Figure 5.23: The variation of coefficient of friction values for W-Re alloy films tested at room temperature against 440C steel ball with two different rotating speeds

The relevant 3-dimensional images of the wear track for both the sample and the steel ball for two different rotating speeds are seen in Figure 5.24 and Figure 5.25. While the tracks on the samples were just like slight wear traces, the contacting surfaces of the balls were considerably worn off. The circular shape of the worn surface had a value of ~600 µm which is similar to the wear track on the sample.

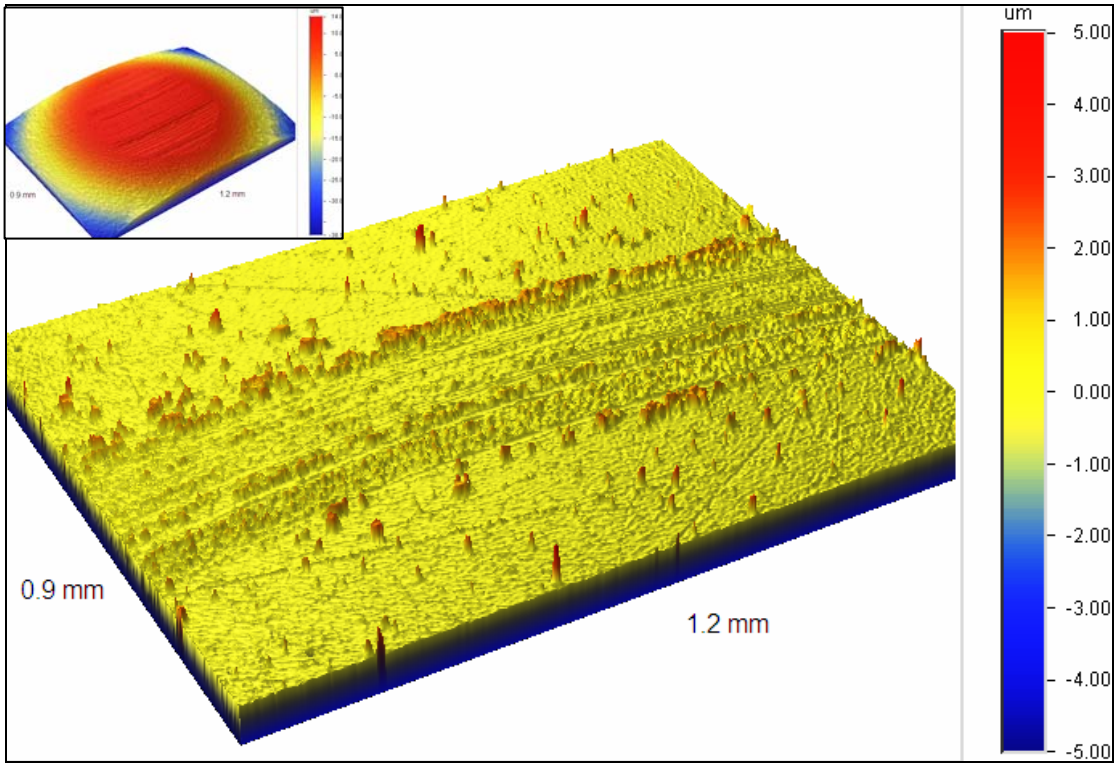


Figure 5.24: The wear tracks on W-Re coated sample and 440C steel ball of test with 10 cm/s rotating speed

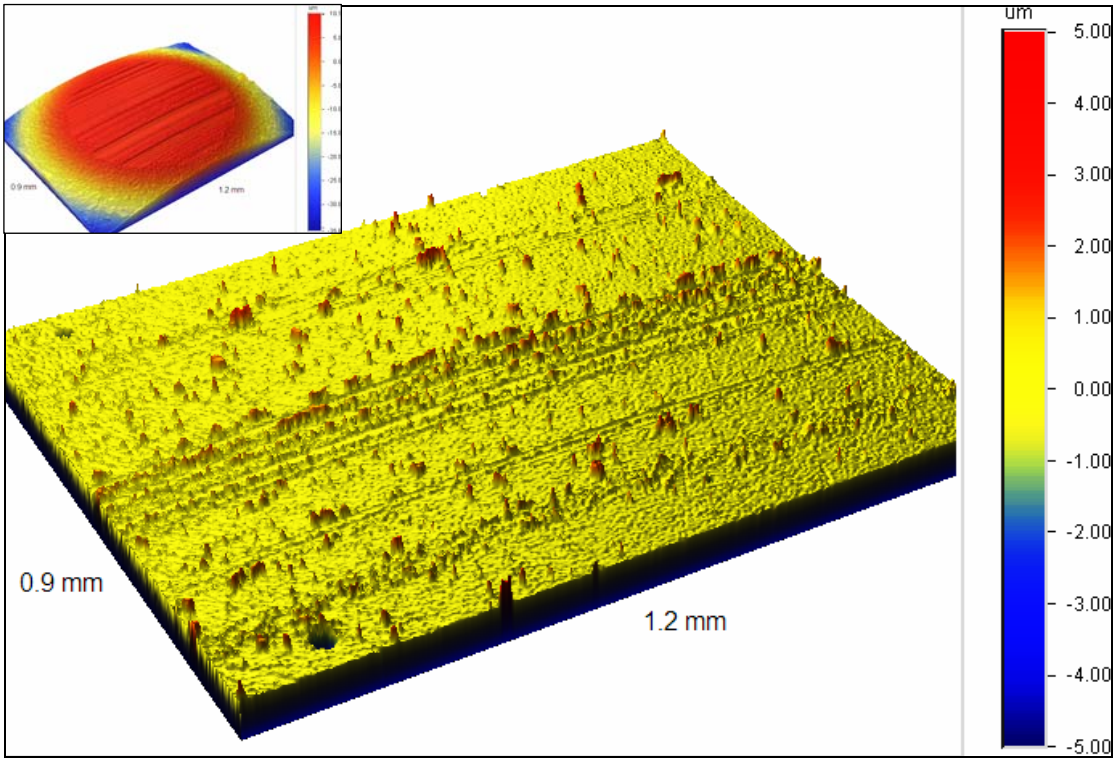


Figure 5.25: The wear tracks on W-Re coated sample and 440C steel ball of test with 20 cm/s rotating speed

5.9.1.2. Fretting Tests

All the fretting tests done on pure rhenium and W-Re coatings are conducted with an alumina counter-body. The parameters applied during the tests are given in Table 5.5.

Table 5.5: Parameters chosen for room temperature fretting tests

	Re	**W-Re**
Temperature (°C)	21	19
Humidity (%RH)	45	44
Frequency (Hz)	10	
Stroke length (µm)	100	
Number of cycles	20400	
Counterface material	Alumina	
Normal load (N)	2	

The evaluation of friction coefficients for pure Re and W-Re coatings are given in Figure 5.26. Both of the coatings gave the same average coefficient of 0.33. Also the

repeated tests' results were very similar, indicating that the tests have reproducibility. It is a very positive and useful result that W-Re alloy coating gave the same coefficient of friction values as pure rhenium as it meets the expectations. Therefore its possibility has been proved that rhenium's unique tribological properties can be carried to an alloy with an amount of 25% rhenium addition.

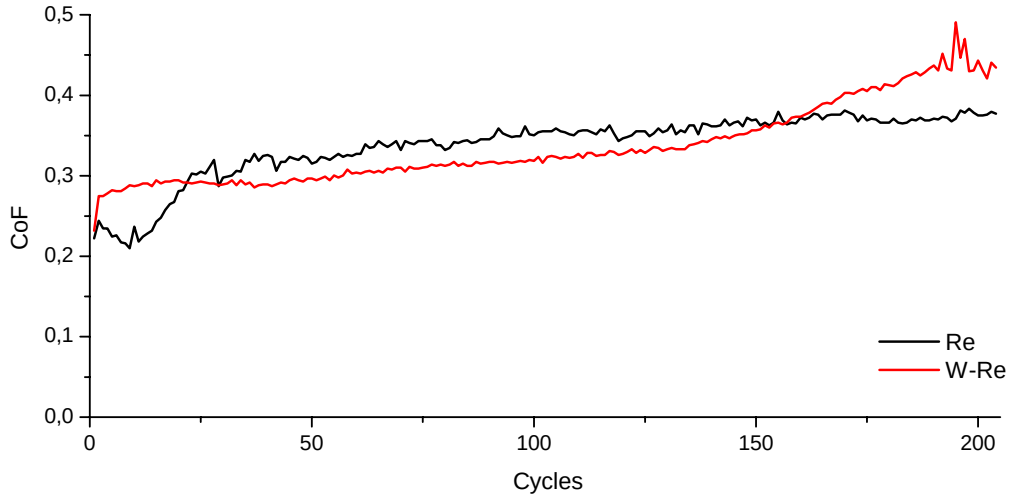


Figure 5.26: Evolving of the friction coefficients for pure Re and W-Re coatings in fretting tests at room temperature

For comparison, the relevant 3-dimensional images and corresponding 2-dimensional profiles of pure rhenium and W-Re coatings are given alternatively in Figure A.1 and Figure A.5, respectively. For pure rhenium coated sample, the wear scar consists of a circle shaped region with a diameter of 90 µm. The same shaped wear scar exists on W-Re coated sample with a 111 µm diameter. Both of the surfaces do not have a worn depth, just the debris particles are seem to be built up around the wear scars.

5.9.2. High Temperature Tests

High temperature tests were only able be conducted with fretting wear testing system. Thus the fretting tests at 50°C, 100°C and 150°C against alumina ball were done over both pure rhenium and W-Re coatings. The testing parameters are given in Table 5.6.

Table 5.6: Parameters chosen for high temperature fretting tests

	Re			**W-Re**		
Temperature (°C)	50	100	150	50	100	150
Humidity (%RH)	39	39	42	45	36	54

Frequency (Hz)	10
Stroke length (µm)	100
Number of cycles	20400
Counterface material	Alumina
Normal load (N)	2

The friction coefficients of high temperature fretting tests for pure rhenium and W-Re coatings are given in Figure 5.27 and Figure 5.28 respectively. For pure Re coatings the friction coefficient at 50°C has an average value of 0.5. Then it increases to 0.6 at 100°C. When the temperature was increased to 150°C, then the friction coefficient evolves in a different fashion. First it seems to stable at a constant value of 0.5. But as the tests progresses, friction shows tendency to decrease a couple of times for 20 – 30 cycle periods. But if it's to be considered generally, it would be seen that the coefficient of friction values are much higher for high temperatures compared to room temperature tests. But for the case of W-Re coatings the variation of friction coefficient with temperature showed a different characteristic. First at 50°C, it reaches a top average of 0.59. Then at 100°C it drops down to 0.46. But after the test at 150°C it shows a further decrease to a slightly higher value than room temperature to 0.34. Because of this interesting decrease in the friction coefficient, an extra test was conducted at a higher temperature than 150°C, at about 200°C. The result was very hopeful, because this time the friction coefficient decreased further to an average of 0.2. This result clearly introduced that for W-Re coatings, the friction was decreasing with increasing temperature.

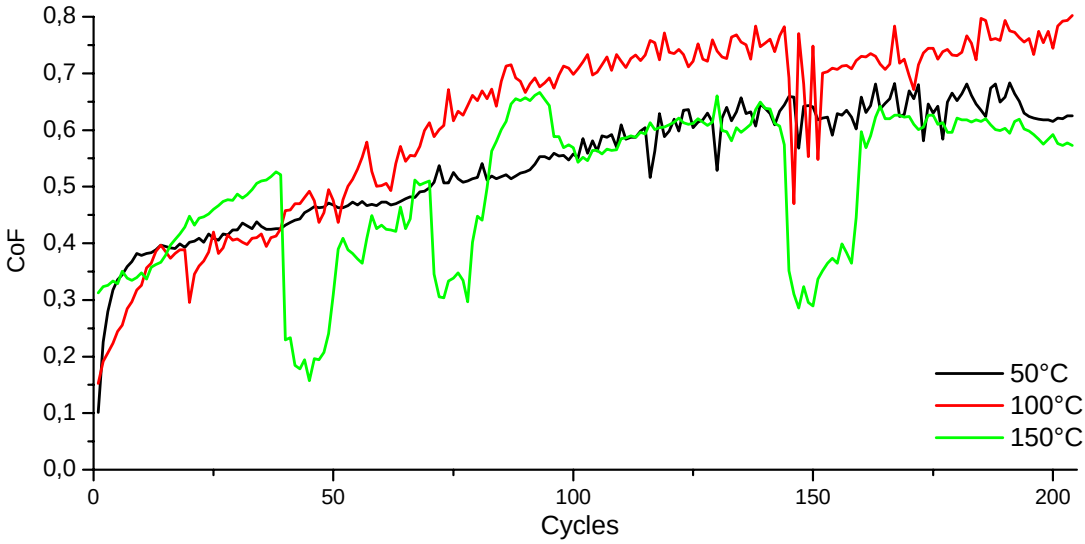


Figure 5.27: Coefficient of friction values for pure Re coating at high temperature fretting tests

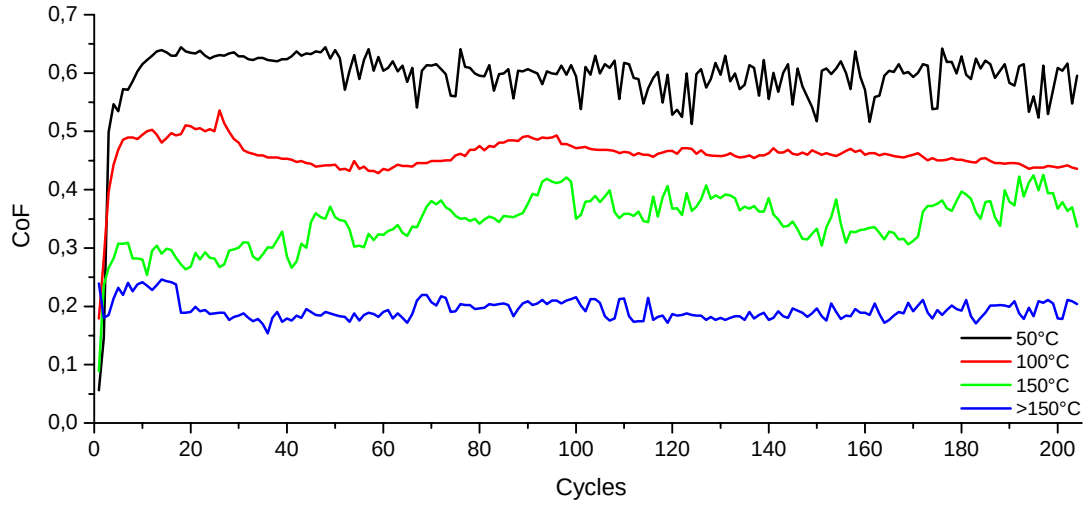


Figure 5.28: Coefficient of friction values for W-Re coating at high temperature fretting tests

The 3-dimensional images and corresponding 2-dimensional profiles of high temperature fretting test results for pure rhenium and W-Re coatings are given alternatively in Figures A.2-A.4 and Figures A.6-A.8, respectively. For 50°C tests no indication of wear can be mentioned for both of the coatings. A slight trace with a 100 µm diameter but without depth through the coating can be seen on Re coated samples surface. Only the debris particles were built up around this trace. The same situation seems to be valid for the W-Re coated sample. As a result of 100°C test, a spherical shaped worn surface was observed on the surface of Re coated sample. This spherical trace has a diameter of 180 µm parallel to the surface and a depth of 0,15 µm. This much wear corresponds to a worn volume of 1.93×10^{-6} mm^3. On the other hand no wear could be observed on the W-Re surface. Again there were only

debris particles built up around the contact surface. For the case of 150°C tests, the wear damage was more noteworthy for the Re coating. There was a rectangular shaped trace with dimensions of 200 μm x 151 μm on the surface. Within this huge trace there were two deep slits with depths of 0.768 μm and 1.011 μm. the total volume of this worn region is approximately $9.38x10^{-6}$ mm^3. Contrarily there was no indication of wear or worn depth on the surface of W-Re coating. This result totally corresponds with the low friction coefficient obtained at 150°C fretting test for W-Re coatings.

This behavior of friction coefficient helped to introduce the tribological character of rhenium alloyed with tungsten. The question to be answered was why friction was decreasing with temperature for W-Re coatings. The highly volatile oxides of rhenium caused low friction coefficients at high temperatures. At high temperatures the oxides in the system were probably boiled away because of the high flash temperatures at the contact area or were being removed from the wear track away because of their softness and little adhesion to the surface. That's because why the friction was increasing with temperature for rhenium coatings. But for the case of W-Re coated samples, it was something else than the volatile rhenium oxides that lowering the friction coefficient. The answer suggested in this work is about the contribution of tungsten to the unique tribological behavior of rhenium as it helped rhenium oxide particles to be held at the surface. Therefore rhenium oxide particles haven't removed away from the contact area and tungsten helped highly lubricious oxides of rhenium achieve lubricity and made the coatings give lower friction coefficients at high temperatures.

6. CONCLUSION

1. This study has showed the possibility of successfully producing pure Re and W-Re coatings with magnetron sputtering physical vapor deposition technique. The adhesion of the films to the HSS substrates was supported with Ti interlayer which was produced by cathodic arc evaporation PVD technique.

2. The effects of magnetron power and chamber pressure were observed on the mechanical properties of rhenium coatings. It was seen that increase in magnetron power resulted in a direct increase in the thickness of the films and the thickest film was obtained at 400 W magnetron power. Also throughout the three different chamber pressures, the thickest of the films was achieved at 1.0 Pa depending on the optimum ionization efficiencies and collisional scattering inside the chamber.

3. According to the micro-hardness tests, the coatings produced at three different chamber pressures had the similar hardness value of about 22 GPa; while the coatings of different magnetron powers exhibited varied results. The hardness of the films of 200 and 400 W were similar at around 17 GPa but the hardness of the film coated at 300 W was 22 GPa. Depending on the x-ray diffraction analysis, higher hardness of this coating was attributed to the internal stress observed over the x-ray diffraction patterns.

4. Friction and wear properties of Re and W-Re coatings were investigated with both ball-on-disc and fretting test methods, ran against alumina and 440C steel counterfaces and at room and high temperatures. The lowest coefficient of friction value with 0.13 was reached by the ball-on-disc test of rhenium running against alumina counterbody at room temperature. In the ball-on-disc test of W-Re coated sample with the same parameters the coefficient of friction value was about 0.35. In none of these tests the alumina counterbodies were worn out. The coefficient of friction results of the tests ran against 440C steel counterbody were higher than alumina as 0.5 and 0.65 for pure Re and W-Re coated samples respectively. The wear on the samples were composed of only slight traces while

the wear on the steel balls were very high causing spherical traces with diameters up to 850 μm.

5. Room temperature fretting tests resulted in similar coefficients of friction as ball-on-disc tests. There was not any considerable wear on both coated samples and the counterbodies. Piled up debris was observed around the contact area on the samples.

6. Fretting wear behavior of the coatings was also investigated at 50, 100 and 150°C for both pure Re and W-Re coatings. At high temperatures, higher wear rates and coefficient of friction values were obtained for pure Re coatings than at room temperature. But for W-Re coatings the coefficient of friction reached a top at 50°C and then lowered at higher temperatures down to 0.2. There was no wear on the W-Re coated samples and similarly none of the alumina counterbodies was worn out at the end of the tests.

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APPENDIX A

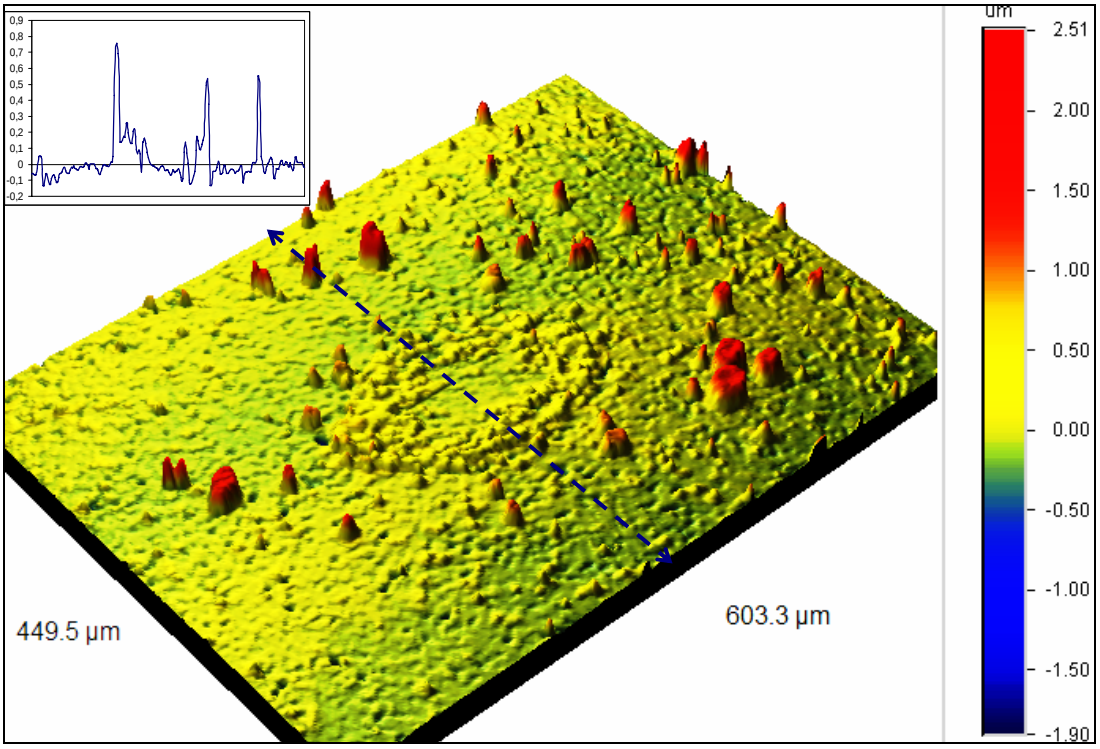

Figure A.1: Wear scar of pure Re coating at room temperature fretting test against alumina

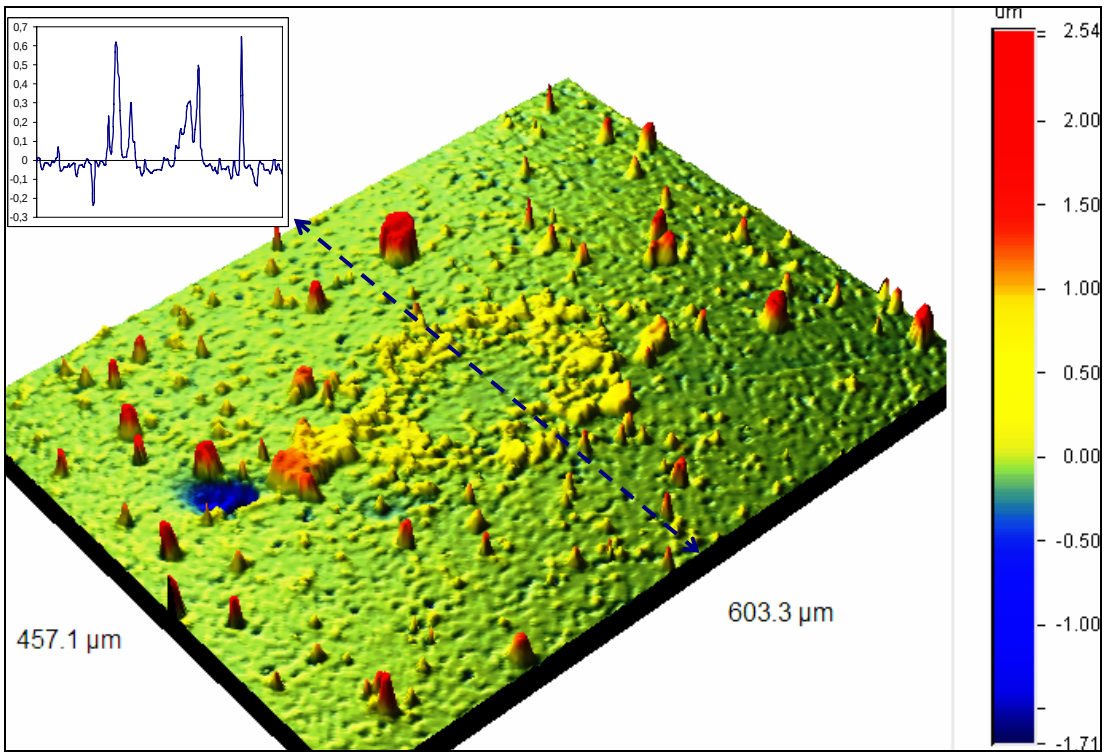

Figure A.2: Wear scar of pure Re coating at 50°C fretting test against alumina

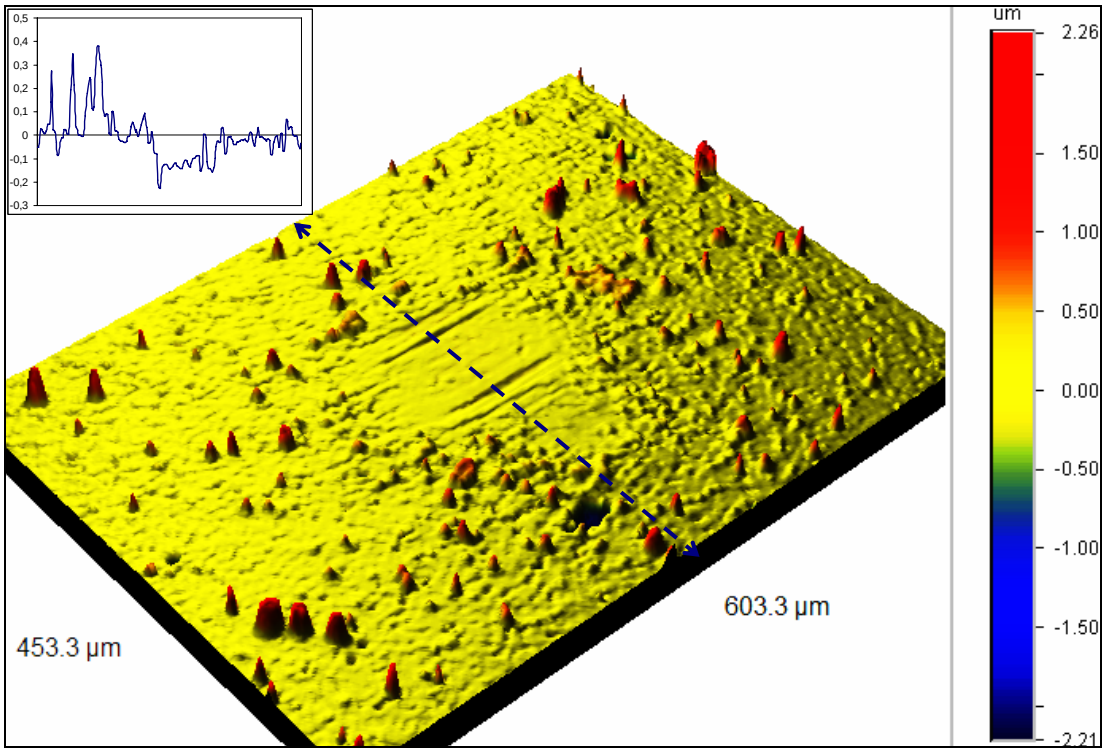

Figure A.3: Wear scar of pure Re coating at 100°C fretting test against alumina

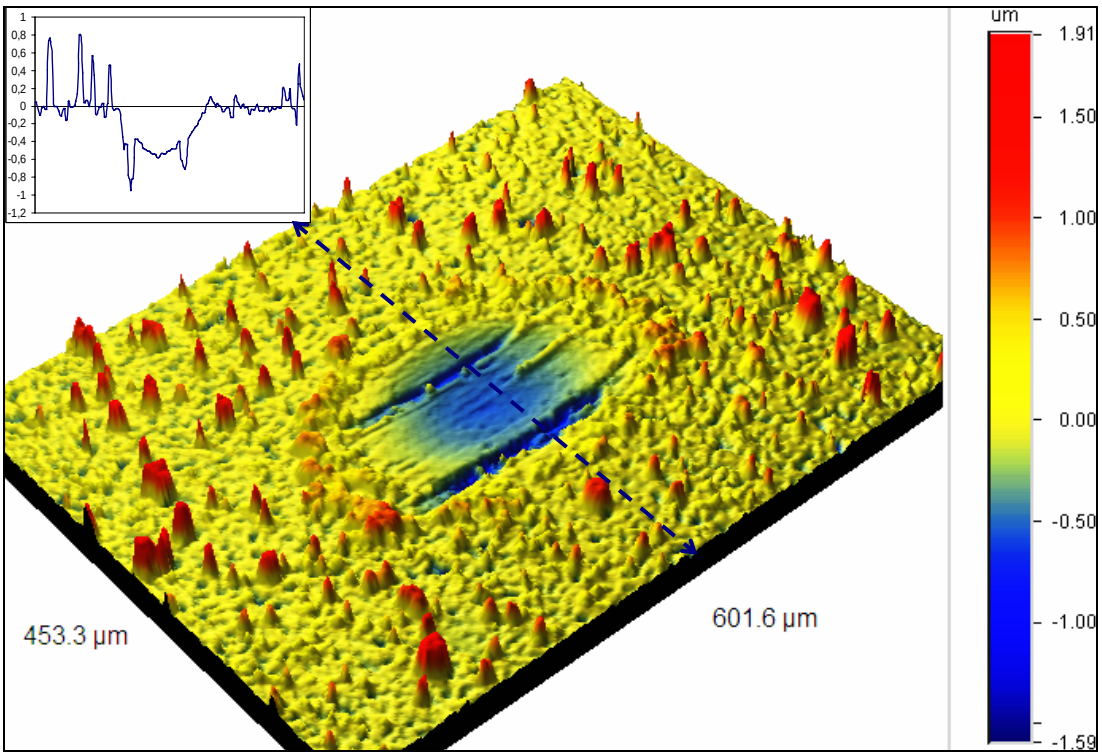

Figure A.4: Wear scar of pure Re coating at 150°C fretting test against alumina

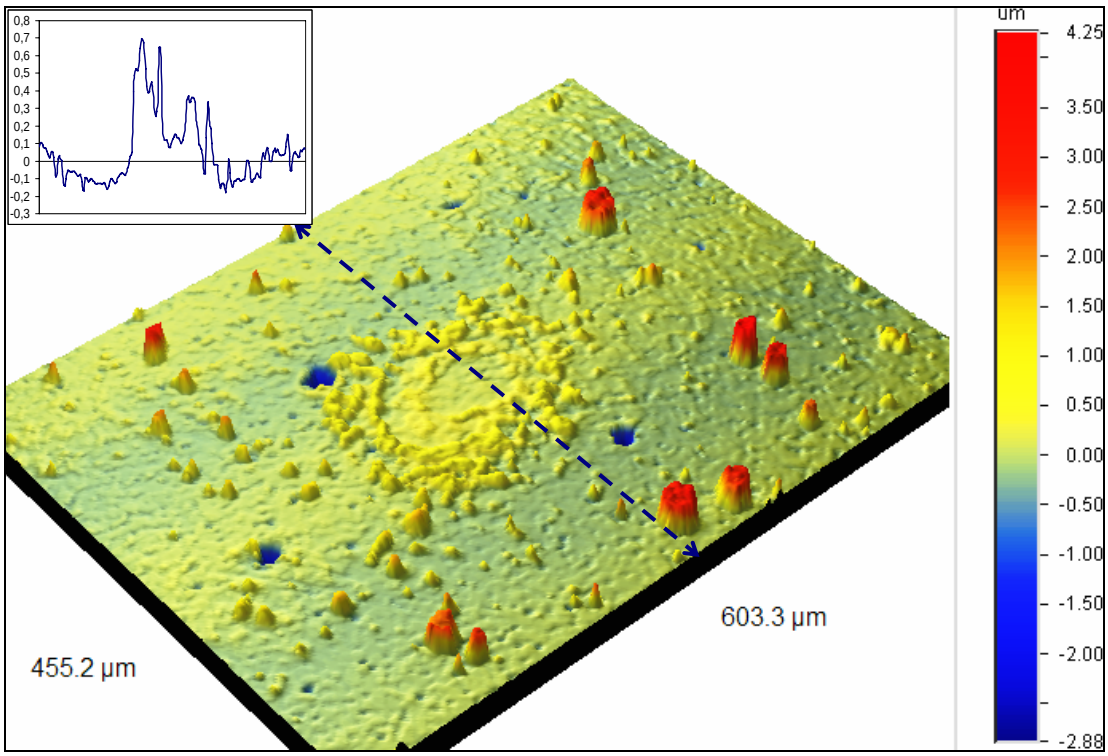

Figure A.5: Wear scar of W-Re coating at room temperature fretting test against alumina

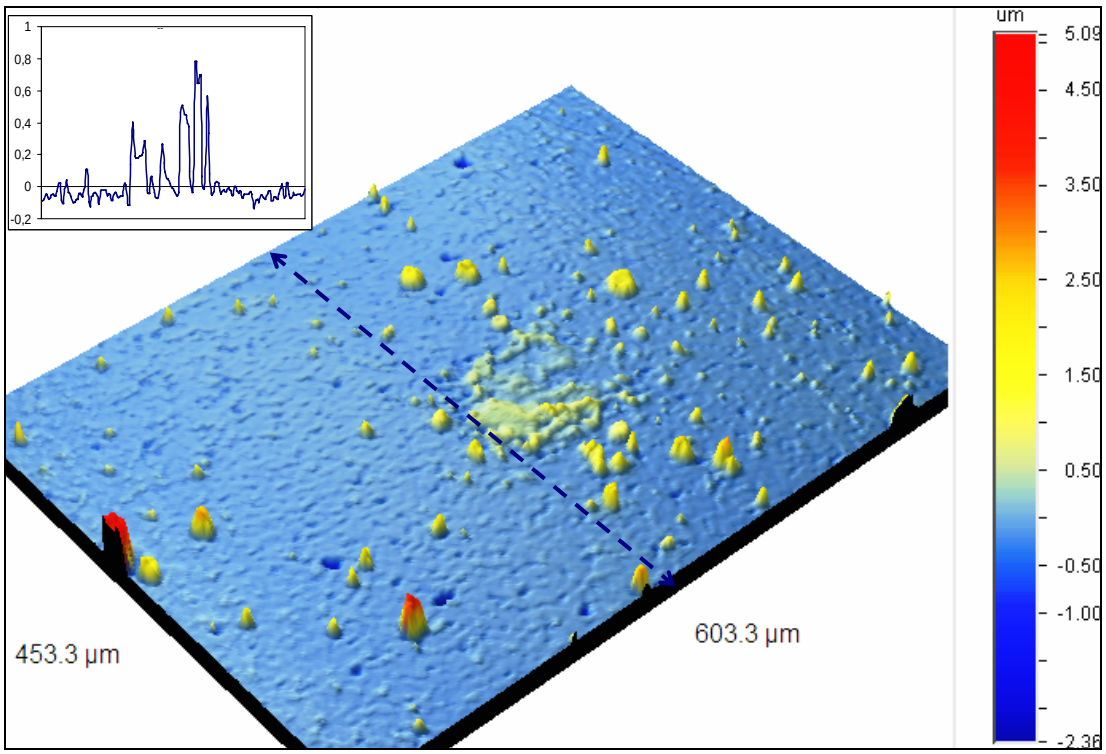

Figure A.6: Wear scar of pure Re coating at 50°C fretting test against alumina

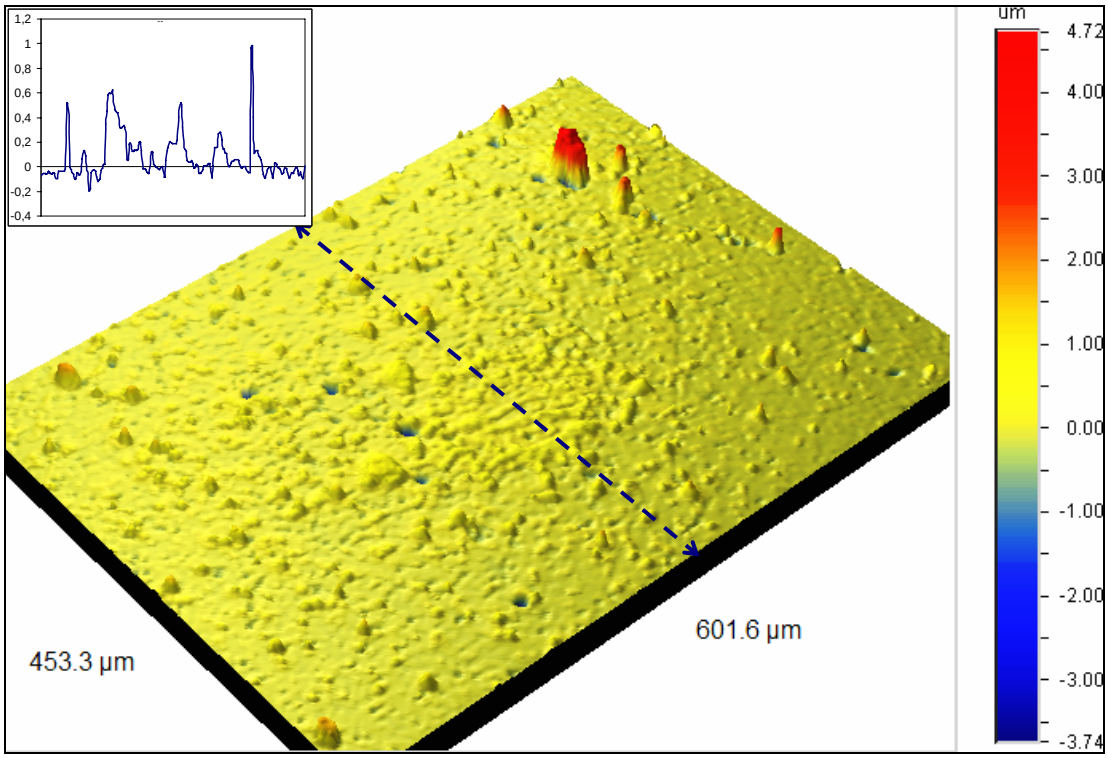

Figure A.7: Wear scar of pure Re coating at 100°C fretting test against alumina

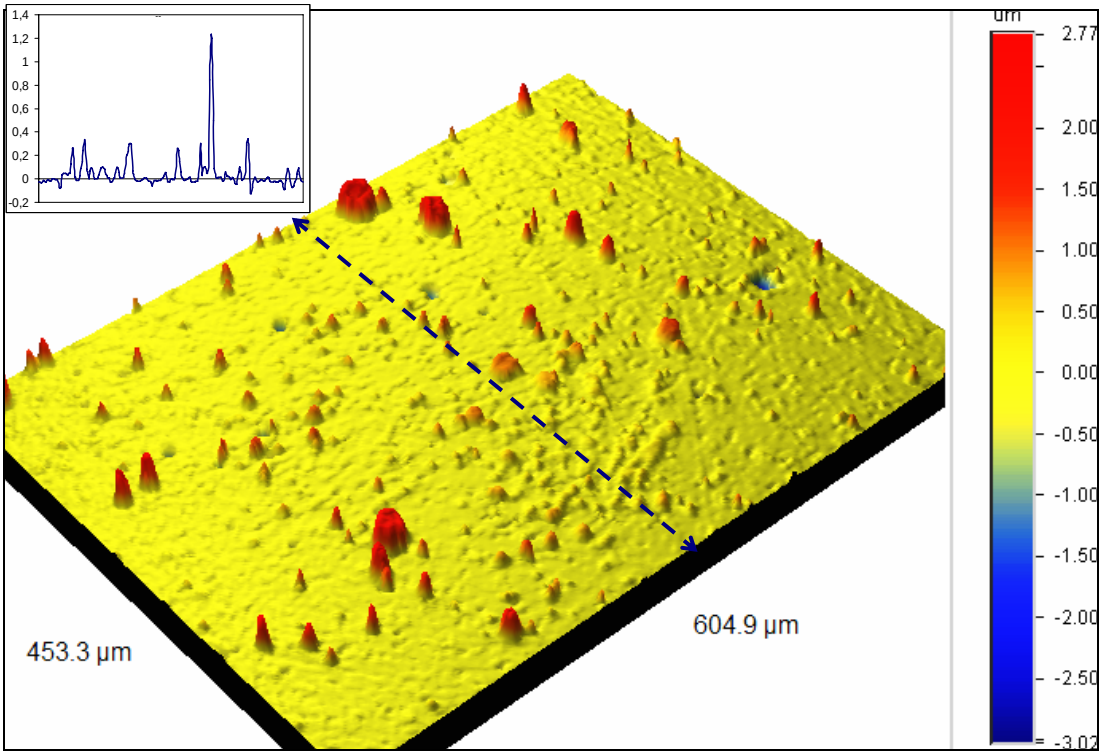

Figure A.8: Wear scar of pure Re coating at 150°C fretting test against alumina

RESUME

Nazem Göçkan was born in Istanbul, in 1983. She completed her elementary education in Özel Taş İlkokulu, in 1994. Then in 2001, she graduated from Beşiktaş Atatürk Anatolian High School. The same year she began her university education in Istanbul Technical University, Metallurgical and Materials Engineering department. She graduated there in 2005 and the same year she began her graduate education in Materials Science and Engineering program in ITU. For one year between 2005-2006, she worked as an assistant researcher in the framework of the TUBITAK supported project "Development of High Performance Rhenium Based Hard Nano-Composite Coatings for Tribological Applications". In 2006 she was accepted as an Erasmus Exchange Student by the EU Center of ITU, and now within this exchange program she continues her studies in Katholieke Universiteit Leuven, Belgium.