

**SYNTHESIS OF HIGH TEMPERATURE WEAR RESISTANT WC
AND WN COATINGS**

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By

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July, 2012

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ABSTRACT

SYNTHESIS OF HIGH TEMPERATURE WEAR RESISTANT WC AND WN COATINGS

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In this study, WC and WN thin films were synthesized using reactive magnetron sputter deposition in order to develop promising alternatives to the well known wear-resistant coatings such as CrN, TiN, TiAlN and TiB₂ etc. For this purpose, WC and WN coatings were deposited on Si(100) and steel (100Cr6) substrates by a Direct Current (DC) reactive magnetron sputtering system. X-ray Diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS) were used to uncover the atomic structure of the films and the change in the chemical bonding states of the atoms. Also, the hardness measurements were performed using a nano-indentation tester on as-deposited films and after the films were subjected to 500°C for two hours. A pin-on-disc tribometer was used to investigate the wear-rates of these coatings at room temperature (RT) and 500°C under ambient atmosphere conditions using 6 mm in diameter Al₂O₃ balls. Scanning electron microscopy (SEM) was used to investigate the microstructure and measure the thickness of the coatings. Also, for chemical analysis energy dispersive spectroscopy (EDS) was used.

Two sets of experiments were designed and performed for the preparation of WN coatings. In the first set, effect of N₂ flow rates during deposition was investigated on the

structure and properties of coatings deposited. The N_2 flow rates were varied between 17% - 66% of the total flow ($Ar+N_2$). The results of these experiments exhibited a significant drop for the hardness and wear rates of WN coatings deposited with increasing N_2 flow rates when tested after 500°C treatment. On the contrary, RT wear test results indicated an improvement in the wear rates with increasing N_2 flow rates. XRD data for the samples subjected to 500°C. XRD analysis indicated the presence of a soft tet- WO_3 layer over the coatings treated at 500°C which is found to be the main culprit for the degradation of the tribological properties. In order to prevent the formation of this soft oxide layer on WN coatings, W/WN multilayer coatings were synthesized in the second set of experiments where the W layers were used as diffusion barriers for oxygen. After the optimization of deposition parameters for synthesizing W/WN multilayer coatings, subsequent tribological examinations indicated the multilayer coatings to be comparably wear resistant at both RT and 500°C. Furthermore, hardness of the multilayer coatings with optimized parameters were found to be around 20-25 GPa at RT and 15-20 GPa at 500°C and their corresponding wear resistances were measured to be $\sim 2.0 \times 10^{-6} \text{ mm}^3/\text{Nm}$ at RT and $\sim 4.0 \times 10^{-6} \text{ mm}^3/\text{Nm}$ at 500°C.

As the second challenge, WC thin films were synthesized within the framework of this study. The first set of synthesis experiments was done using acetylene (C_2H_2) as the carbon source. It was found that increasing relative amount of C_2H_2 flow during sputter deposition resulted in the degradation of tribological properties of coatings due to amorphous carbon build-up in the films. To overcome this degradation of properties, alternative solid sputter targets such as B_4C (as an alternative C source for 2nd set), W/ B_4C (composite targets) and W_2C targets (for co-sputtering experiments of 3rd set) were used for the deposition of WC films. The results of the structural and chemical analysis indicated the presence of well-crystallized WC phases (WC and W_2C) in the coatings sputter deposited from B_4C targets. Comparatively, coatings deposited using solid WC and W_2C targets resulted in coatings with the same phases. Tribological testing of these coatings indicated that WC films synthesized using B_4C targets to have better mechanical performance after 500°C treatment while coatings co-sputtering from compound targets worked better at RT.

Keywords: Tungsten Nitride, Tungsten Carbide, Thin Films, Reactive Magnetron Sputtering, Multilayer Coatings, B₄C, Co-sputtering, Hardness, Wear Resistance

ÖZET

YÜKSEK SICAKLIKTAKİ AŞINMAYA DİRENÇLİ WC VE WN KAPLAMALARIN SENTEZLENMESİ

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Bu çalışmada, CrN, TiN, TiAlN ve TiB₂ vb. gibi iyi bilinen aşınmaya dirençli kaplamalara umut vadeden alternatifler geliştirmek amacıyla reaktif magnetronlu saçtırma biriktirme tekniği kullanılarak WC ve WN ince filmler sentezlenmiştir. Bu amaçla, tek kristal silisyum (Si(100)) ve çelik (100Cr6) alttaşlar üzerine bir Doğru Akım (DC) Magnetronlu Saçtırma sistemiyle WC ve WN kaplamalar biriktirilmiştir. Filmlerin atomik yapısını ve atomların kimyasal bağlanma durumlarındaki değişiklikleri açığa çıkarmak için X-ışını Diffraktometresi (XRD) ve X-ışını Fotoelektron Spektroskopisi (XPS) kullanılmıştır. Ayrıca, kaplandıktan hemen sonra ve 2 saat boyunca 500°C'ye maruz bırakıldıktan sonra filmler nano-indentasyon (nano boyutta kontrollü iz/çukur oluşturma) testi kullanılarak sertlik ölçümleri yapılmıştır. Bu kaplamaların oda sıcaklığında (RT) ve 500°C'de, normal atmosfer koşulları altında ve 6 mm çapında Al₂O₃ toplar kullanılarak aşınma hızlarının incelenmesi için bir disk üzerine yüklemeli (pin-on-disc) tribometre (kontrollü aşındırma cihazı) kullanılmıştır. Mikroyapı incelemesi ve kaplamaların kalınlığını ölçmek amacıyla Taramalı Elektron Mikroskopisi (SEM) kullanılmıştır. Ayrıca, kimyasal analiz için Enerji Ayrıcı Spektroskopi (EDS) kullanılmıştır.

WN kaplamaların hazırlanması için iki deney seti dizayn edilip ve uygulanmıştır. İlk deney setinde, N₂ (azot) gazı akış hızının elde edilen kaplamaların yapı ve

özelliklerine etkisi araştırılmıştır. N₂ akış hızları, toplam akışın (Ar+N₂) %17-%66'sı arasında değiştirilmiştir. Artan N₂ akış hızıyla birlikte WN kaplamaların 500°C uygulaması sonrasında ölçülen sertlik ve aşınma performanslarında belirgin bir düşüş olduğunu bulunmuştur. Bunun aksine, oda sıcaklığında yapılan aşınma testinin sonuçları artan N₂ akış hızlarıyla birlikte aşınma hızlarında gelişme olduğunu gösterilmiştir. XRD analiziyle, 500°C'de tutulmuş kaplamaların tribolojik özelliklerindeki zayıflamanın temel sorumlusunun kaplamaların üzerinde oluşan yumuşak tet-WO₃ tabakası olduğu belirlenmiştir. WN kaplamalar üzerinde bu yumuşak oksit tabakasının oluşumunu engellemek için ikinci deney setinde, oksijen difüzyon bariyeri olarak ince bir W tabakasının kullanıldığı W/WN çok-tabakalı kaplamalar sentezlenmiştir. W/WN çok-tabakalı kaplamaların sentezlenmesi için biriktirme parametrelerinin optimize edilmesinden sonra yapılan tribolojik incelemelerde, çok-tabakalı kaplamaların hem oda sıcaklığında hem de 500°C'de kıyaslanabilir ölçüde aşınmaya dirençli oldukları belirlenmiştir. Buna ek olarak, optimize edilmiş parametrelerle sentezlenen çok-tabakalı kaplamaların sertlikleri oda sıcaklığında yaklaşık 20-25 GPa ve 500°C'de 15-20 GPa olarak bulunmuş ve bunlara karşılık gelen aşınma dirençleri oda sıcaklığında $\sim 2.0 \times 10^{-6}$ mm³/Nm ve 500°C'de $\sim 4.0 \times 10^{-6}$ mm³/Nm olarak ölçülmüştür.

İkinci geliştirme uğraşı olarak, bu çalışma çerçevesinde WC ince filmleri sentezlenmiştir. İlk sentez deneyleri seti, asetilen (C₂H₂) gazının karbon kaynağı olarak kullanılmasıyla yapılmıştır. Saçtırmayla kaplama işlemleri sırasında artan C₂H₂ akış miktarının, kaplamaların tribolojik özelliklerinde, filmlerdeki amorf karbon miktarındaki artış nedeniyle, zayıflamalar olduğu keşfedilmiştir. Özelliklerdeki bu zayıflamanın önüne geçilmesi için, WC filmlerin kaplanması, B₄C (2. sette alternatif C kaynağı olarak), W/B₄C (kompozit hedef) ve W₂C hedefleri (3. setteki eş-zamanlı saçtırma deneyleri için) gibi alternatif katı saçtırma hedefleri kullanılmıştır. Yapısal ve kimyasal analiz sonuçları B₄C hedeflerden saçtırma yapılarak elde edilen kaplamalarda iyi kristalize olmuş WC fazlarının (WC ve W₂C) bulunduğunu göstermiştir. Benzer olarak, katı WC ve W₂C hedefler kullanılarak yapılan kaplamalar neredeyse aynı fazlarla sonuçlanmıştır. Mevcut kaplamalara yapılan tribolojik testler, B₄C hedef kullanılarak sentezlenen kaplamaların 500°C'de tutulması sonrasında, bileşik hedeflerden eş-zamanlı

saçtırmayla yapılan kaplamaların ise oda sıcaklığında daha iyi mekanik performansa sahip olduklarını göstermiştir.

Anahtar Kelimeler: Tungsten Nitrür, Tungsten Karbür, İnce Filmler, Reaktif Magnetronlu Saçtırma, Çok-tabakalı Kaplamalar, B_4C , Eş-zamanlı Saçtırma, Sertlik, Aşınma Direnci

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1 INTRODUCTION

1.1 Wear and Wear Mechanisms

In general terms, wear can be defined as a failure mechanism resulting from continuous loss of material from a solid surface, stemming two solid surfaces in contact with each other and in relative motion (1). Wear is an inevitable part of industry, causing significant costs through loss of labor and time. Furthermore, waste of material through parts exchange, yield loss and substandard quality in the production lines are also part of the problem. Recently, another aspect of wear due to conservation of energy has been raised. Overall, it is stated that wear related problems together with inefficient use of energy can easily amount to 7% of GNP (Gross National Product) for industrialized countries according to The Jost Report (2). It is not unexpected that wear related problems led to the establishment of a new field of study in science and technology termed “tribology”. As a general definition, tribology deals with contacting surfaces in relative motion (3).

There are four main mechanisms of wear, namely; abrasive, adhesive, corrosive and erosive wear. Abrasive wear occurs when a hard surface or hard particles move along a softer surface and remove material from this soft surface with plastic (permanent) deformation or fracture. Deformation of the softer surface can be observed in three different modes. Presence of parallel grooves (see Figure 1.1.1) and ridges formed by the removed material are observed after deformation similar to the ploughing of soil (Figure 1.1.2).

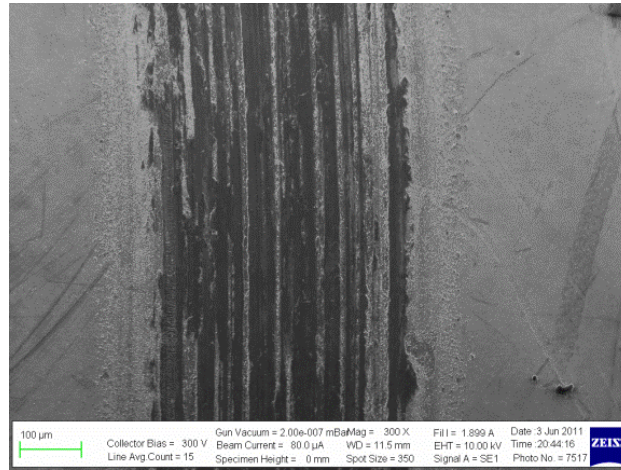


Figure 1.1.1: SEM image of 100Cr6 steel surface after abrasive wear. Sliding direction is along vertical axis.

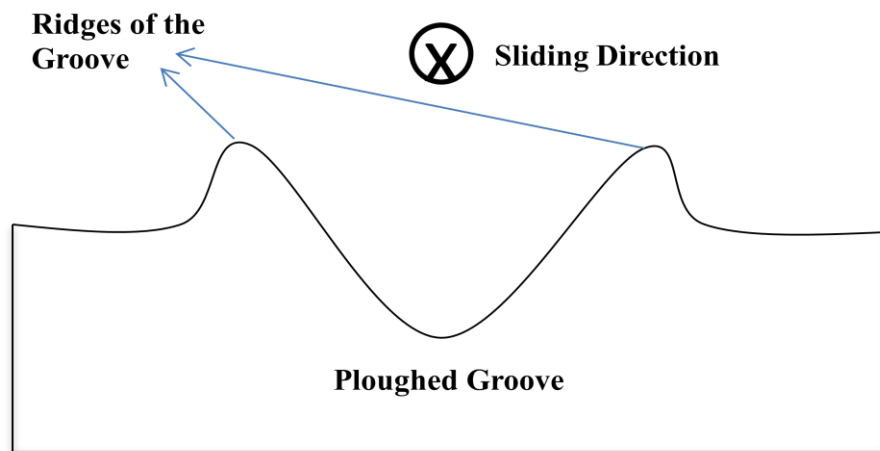


Figure 1.1.2: An idealized abrasively worn section of a material.

Another typical feature of abrasive wear is the wedge formation. Wedges are formed by the abrasive tip carrying the deformed material and pushing them to the sides (ridge formation). Finally, this continuous action creates wedges at the end of the wear scar. In the cutting form of abrasive wear, abrasive tip strips off the material in the shape of continuous or discontinuous chips. Abrasive wear also induces surface and subsurface cracks which results with further removal of material from the abraded surface together with the different wear modes described above (4).

The second important wear mechanism is adhesive wear that is mostly seen in metals. Adhesive wear occurs when two surfaces in contact (especially at the tips of the surfaces) adhere to each other, causing the permanent detachment of small parts or particles from one of these surfaces leading to further material removal. Metals and other materials generally have contaminants on their surface like surface oxides or carbonaceous molecules; hence these contaminants prevent adhesion of surfaces to each other. However, removal of these surface contaminants or under certain conditions such as ultra high vacuum creates the possibility of these surfaces sticking to each other. Especially, during sliding action of counter-acting surfaces adhesive wear causes severe problems on these surfaces. Generally, lubricants are used to counteract this particular mechanism of wear.

Corrosive wear is a result of chemical reaction between a surface and corrosive substances that is in contact with the mentioned surface. This particular mechanism is different from the others on the basis that the attack on the surface is by means of chemical reaction rather than the sliding motion of two contact surfaces. There is no plastic deformation and any other mechanical failure mechanisms are involved. The corrosive medium can be a chemical reagent, lubricant, water film and even air. If the reaction product is strong enough to bear the applied loads and strongly adhere to the surface, it may prevent further wear of the materials surface. On the other hand, a weakly bonded reaction product can cause more severe wear of the materials surface due to loss of mass (5).

The last wear mechanism that will be mentioned in this work is the erosive wear. Erosion is another mechanism of wear that does not need the contact of two surfaces. In this type of wear, the loss of mass stems from the strike or impingement of the liquid drops, solid particles or fluids (containing gas bubbles or abrasive particles) to the solid surface. As a result of the impact mentioned, a certain amount of momentum (energy) is transferred to the surface and this momentum transfer causes removal of material fragments from the surface of the materials. The removed material fragments also add to the abrasive particles and causes further material loss from the surface. Furthermore, if this wear mechanism takes place at high temperatures, it causes further increase in the

material removal due to the increase in the momentum transfer. This type of wear gains significant importance specifically for such cases as ship propellers, valves, pipes, turbine blades, radar domes of aircrafts etc (6, 7).

In this work, mainly the abrasive wear mode was addressed and taken into account for finding an appropriate solution. In that sense, wear resistance and some of the related mechanical properties of materials will be discussed here. Wear resistance can be defined as the ability of a material to withstand the gradual material removal from the surface caused by abrasion. This property is generally evaluated with standard wear tests such as pin-on-disc testing and the test results are termed as “wear rate” for this specific material. Wear rates for materials (with the units g/Nm or mm^3/Nm) are calculated as the ratio of the total weight (or volume) loss to the product of applied load (N) and total distance (m) worn. It should be noted that the lower the calculated wear rate the more wear resistant is the material.

The second important property is called hardness and it is defined as the resistance of a material to surface penetration or permanent deformation at the surface. Hardness is strongly related with the strength of the interatomic bonds of the materials. As a result of this, covalently bonded and some ionically bonded materials have very high hardness values among others. This property of materials is generally tested with an indentation method. The indenters are generally made out of very hard materials such as diamond. During an indentation test, the indenter is pressed against the surface of the tested material. Then, either the vertical indentation depth, or the imprint size left on the surface is measured against the indentation load. The resultant data is then processed according to the type of hardness measurement, and the hardness of the material is either reported in some kind of hardness scale (e.g. VHN for Vickers hardness) or in kgf/mm^2 or GPa.

There is not a general agreement on the relation between wear rate and hardness of materials because of the complexity of the wear phenomena. There is no direct formula proposed by the researchers studying on this relation as well, but simulative and experimental results from some of the studies show that wear rates are inversely proportional to the hardness of the materials in question (8, 9). This means that harder

materials generally have lower wear rates (or better wear resistance). But, yet this relation does not provide sufficient data for exact evaluation of wear rates. Materials always contain various kinds of defects such as dislocations, vacancies and cracks in their structure resulting from production and/or shaping processes. Furthermore, loads applied on the surfaces of the materials during real time processes emerge as impact loads (rather than applying the same load slowly) which can also generate similar defects in the structure of the given materials. These defects may cause abrupt failure of the materials as a result of events like crack propagation even though they have high hardness values. This explanation leads us to another important material property which is called toughness. Toughness is the ability of a material to absorb energy and deform plastically without fracturing. Materials with high toughness can absorb more energy before failure and can bear loads for longer times before being fractured. Toughness is generally measured with Charpy and/or Izod impact tests. The resulting values are simply given as the amount of energy per volume or area (Joule/m^3 , Joule/m^2 or $\text{MPa.m}^{1/2}$) (10). Therefore, a material with very high resistance to wear should be both tough and hard.

Anti-Wear Approaches

Three main approaches can be taken into account for the solution of the abrasive wear problem. These are:

1. Appropriate selection of materials
2. Surface modification processes
3. Surface coatings

First approach includes use of the selection and application of the right engineering materials for the conditions in question. Generally, most of these materials are either ceramic or one of the ferrous grade alloys. Among these, diamond is one of the oldest materials known to mankind and has the highest hardness known although, there has been several claims to the otherwise, which has been refuted recently (11, 12). Diamond has a significantly high resistance against the majority of wear mechanisms

(abrasive, adhesive and erosive) but due to its high production costs, people have always been searching for cheaper alternatives.

Another important example for hard and wear resistant materials is the cubic-BN (cBN). CBN is a very attractive material due to its relatively good wear performance, chemical inertness and high temperature stability but it suffers from the similar problems with diamond. It is an artificial material, and unlike diamond it cannot be mined which increases the cost of production (13). Additionally, high speed steels (especially that are produced by powder metallurgy), aluminum oxide (Al_2O_3), silicon carbide and nitride (SiC , Si_3N_4), and tungsten carbide (WC) ceramics can be given as further examples for the wear resistant materials used in the industry (14–19). On the other hand, while these wear resistant ceramics have superior hardness, they suffer from their brittle nature and high production costs. Furthermore, application areas for these materials in the industry are also limited relative to ferrous and other metallic alloys significantly suppressing the investments for larger production facilities that may decrease the cost of production. In this study, amongst these examples, special attention will be given to tungsten carbide and tungsten nitride. These two will be discussed in more detail in the following sections.

Second and third anti-wear approaches listed above are generally termed as “surface engineering”, that is surface based techniques are used to counter mechanisms causing wear (7). In Figure 1.1.3 a chart is provided which summarizes the methods used.

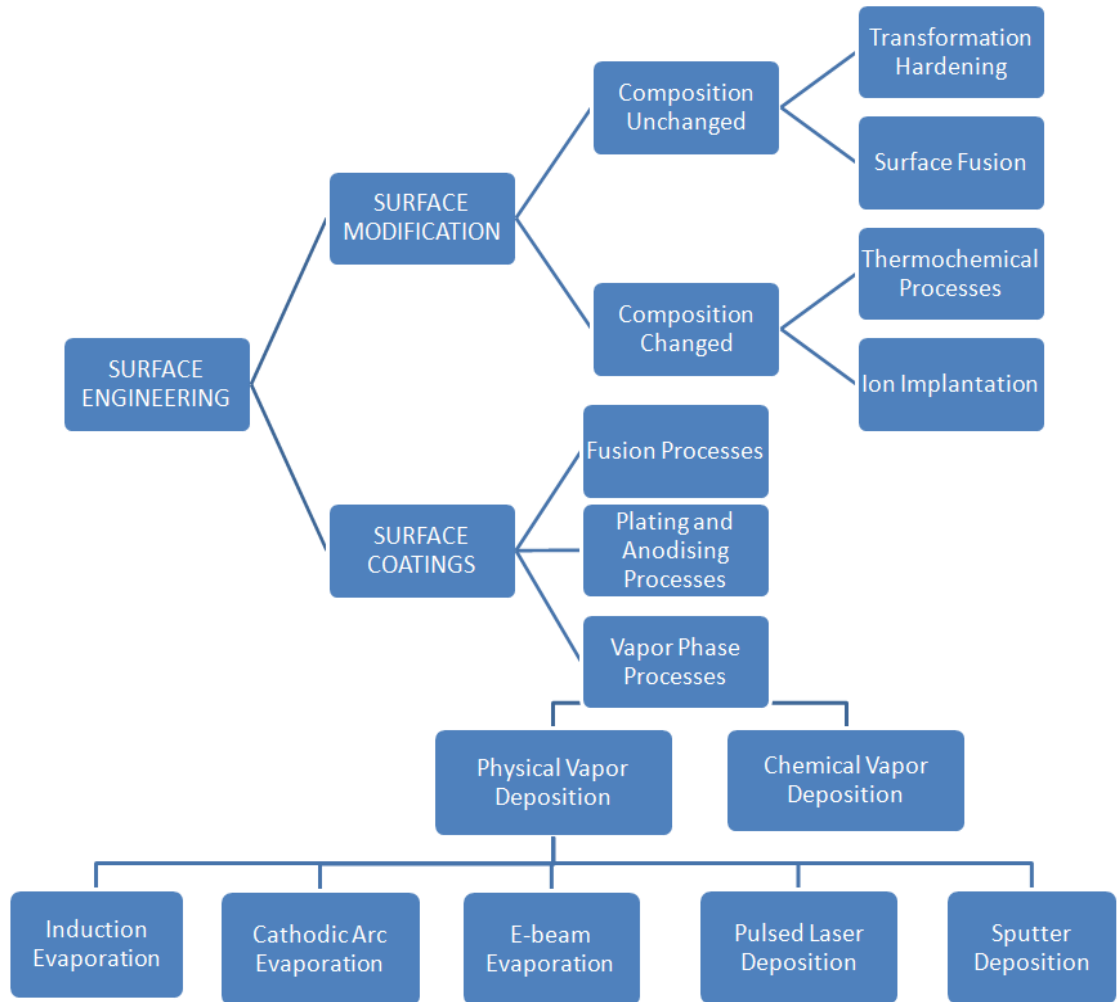


Figure 1.1.3: A general chart of the methods of surface engineering.

Considering the techniques listed in this chart, Surface Modification is accomplished by either changing the surface composition or without modifying the composition. For the case of ferrous alloys, improvement in the surface properties can be accomplished by transformation hardening, where surface of low carbon steels are rapidly heated to above austenite transformation temperature ($> 727^{\circ}\text{C}$) and then quenched in order to obtain the harder and wear resistant martensite phase on the surface of the steels. The rapid heating of the surfaces can be achieved by four different sources used; flame heating (20), induction heating (21), laser (22) and e-beam hardening (23). Surface melting is a similar process which can also lead to transformation hardening. However, in this technique more heat is used and mainly aims to cause hardening

through grain-size reduction (Hall-Patch relationship) on the surface. This technique is mainly used for cast steels containing 0.4% to 0.9% carbon (24).

The second group of surface modification techniques involves compositional changes on the surface of the material to be protected from wear. The first group of these techniques can be termed as thermochemical processes due to the heating of the surface to enhance the diffusion and bonding processes. Small atoms such as C and N are diffused into the surface of the material at high temperatures in order to create an interstitial solid solution region at the top surface which improves the mechanical strength of the surface against wear. Carburizing (22) and carbonitriding (25) are the basic examples for this type of process. In the second class, diffusion induces the formation of a chemically and physically distinct new layer on the surface. A compound with a distinct chemical composition is formed on the top layer of the bulk. Nitriding (26) and boronizing (27) can be given as example for this process.

The last technique that will be mentioned under surface modification techniques is ion implantation. In this process, energetic charged particles of the desired atoms for implantation ($C \Rightarrow C^+$, $N \Rightarrow N_2^+$) are generated and accelerated towards the surface to be modified with an energy level sufficient to penetrate through the surface of the material. Implantation finds a wide application field in the electronics industry for device fabrication (28) and can be considered as a good candidate for the case of anti-wear studies as well. The basic mechanism behind implantation is the improvement of the mechanical properties of the surface by the zero-dimensional defects created during implantation.

Techniques utilized for preparing surface coating form another branch of the surface engineering methods. While, coating and deposition techniques are closely related with the main framework of this thesis, they will be covered in detail in the following chapter under the title of “Thin Films”.

1.2 Thin Films

1.2.1 Thin Film Synthesis Techniques

Today's technological advances partially owe their progress and success to the technologies enabling the synthesis materials in a cost effective fashion. The word “thin film” generally refers to a layer of material with a thickness less than 10 μ m. The idea of thin films for the case of tribological applications is based on the application of a resilient thin layer over the surface of a bulk material surface (substrate) to enhance its surface properties keeping its bulk properties intact. Through this concept, the tribological properties (including corrosion resistance) of a relatively cheaper bulk material can be improved immensely. Furthermore, most of the time manufacturing the whole system using the bulk format of the thin film material is either technologically or economically not viable. Generally, the substrate material is chosen that it can be easily shaped, and is relatively tougher and ductile. Understandably, substrate materials are often chosen from appropriate metal alloys. In general for tribological applications, thin film materials are ceramics such as transition metal nitrides, carbides and borides which are significantly harder but yet lack the ductility and toughness of the substrate metals. In some cases, diamonds like carbon (DLC) coatings are also used. Therefore, it should be apparent that it is usually cost prohibitive or technologically ill advised to manufacture the whole system from the wear resistant ceramic thin film material.

The synthesis methods for thin films can be simply be grouped into three classes, namely, plating, fusion (or molten state) and vacuum deposition processes. Shortly, plating processes include coating of metallic surfaces by dipping them in an electrolyte solution (solution state). This process can be used to produce ions for the desired coating material (generally another metal) either by an external source (an electrical field in the case of electroplating or electrodeposition) or by a reducing agent without a current source (electroless deposition). Then, these ions are directed toward the substrate metal surface (cathode) by the effect of the electrical field for deposition. Generally, chrome and nickel are deposited onto the ferrous alloy surfaces for increasing their wear and corrosion resistance. If the metal to be coated is aluminum, the process is generally called anodizing (29). Molten state processes can be considered under two classes. The

first one is welding which uses essentially the same concept as in welding process for joining dissimilar materials. During this technique, the coating material in powder form is melted on the surface that is to be coated limiting the range of materials for the coating layer. However, thermal spraying is a further improvement on this application where the coating material is melted away from the surface and then sprayed onto the surface where it quickly cools down. Thickness control is also in thermal spraying process. Together with the relatively good adhesion properties of the produced coatings, thermal spraying is attracting considerable attention in the field of wear resistance coatings (30).

Vapor deposition processes involve coating setups that are operated under vacuum conditions. Vapor phase of materials can be achieved either by a chemical reaction or by energy transfer through various physical means. The first method that uses chemical reaction is called chemical vapor deposition (CVD). In CVD processes, gaseous compounds of the desired material are synthesized and flow over a heated substrate. The compilations of techniques in the latter one are termed generally as physical vapor deposition (PVD) techniques.

During CVD processes, thermally activated chemical reactions in the gas phase and/or on the substrate surface results in the formation of the building blocks of the coating material which then condenses on the substrate surface and incorporates to the formation of a film. The chemical reactions required for the film formation can be activated either direct heating, plasma generation or a laser beam in the CVD chamber. CVD has the advantage of synthesizing a homogenous coating on all over the substrate, while the high temperatures required for film formation can induce undesired phase changes and embrittlement of the substrate materials. This disadvantage limits the use of CVD techniques severely for wear resistant coatings application (31). On the other hand, PVD techniques are often operated at lower temperatures. The main principles of PVD are based on using physical activation means to create the vapor phases of the materials to be coated on a surface. Thermal activation in the case of resistive, laser-, arc- or electron-beam heating is used to evaporate the a source material which is then allowed to condense on a desired substrate. Furthermore, it is also possible to cause ejection of

atoms from a surface into vapor phase via momentum transfer, e.g. by using another energetic particle such as an electrons or ions. This process is called sputtering.

In general, to perform a sputtering process, generation of a gaseous glow discharge is required. In order to generate a discharge, a sufficient amount of electrical potential is applied between two electrodes (cathode and anode) at a low pressure chamber (~ 0.1 -10 torr). Applied potential causes electron emission from cathode surface and these electrons are accelerated towards anode with the effect of the electrical field present. Noble gases such as Ar or Kr are used in this chamber and ionized due to the collision between these atoms and accelerating electrons. Similarly with the effect of the electrical field, Ar^+ ions begin to accelerate towards the cathode (32). The material to be coated is placed on the cathode and from hereof it will be called the target. Ions impinging on the target material transfer their energy as a result of collisional processes on the surface. Due to these interactions some of the atoms on the surface are transferred enough energy to break bonds with the surroundings and are removed from the surface. This is called sputtering and the coating process proceeds with the arrival of the sputtered atoms onto the substrate surface and condensation of those atoms over this surface (i.e. deposition) (33).

As an attractive coating method that can be used at lower temperatures, sputter deposition has been through further improvements in order to become more cost effective and versatile. One of these advances is the use of magnetrons with a magnetic field extending to the front of the cathode surface which allows for the trapping of the emitted electrons close to the material's surface increasing the ionization yield in the plasma formed on the cathode. This results in an increase in the sputter rate of the target coating materials. This is known as magnetron sputtering. Another enhancement is the use of pulsed-dc and radio frequency power supplies from generating the plasma discharge over the cathode for sputtering. This improvement enables the deposition of non-conducting and semi-conducting materials through sputtering without charge accumulation on the surface of dielectric or insulating target materials such as many oxides and nitrides. Furthermore, with the use of co-sputtering of the individual elements or sputtering from compound materials, different compounds can be coated on

desired substrates. In addition to that, further use of reactive gases such as C_2H_2 (as C source) and N_2 (as N source) helps deposition of various nitride and carbide compounds which are hard and wear resistant. This particular technique is called reactive sputtering (34).

1.2.2 Wear Resistant Thin Film Applications

There are numerous coating systems studied for applications requiring wear-resistance such as TiN, Ti(X)N (X: C, Al, Si etc.), CrN, CrC, TiB₂, diamond-like carbon (DLC) and their combinations through nano-composite and multilayer approaches(35). The scope of this study is going to be over two promising alternative materials, namely tungsten nitride (WN) and tungsten carbide (WC).

1.2.3 Tungsten Nitride (WN) and Tungsten Carbide (WC) Thin Films

Transition metal nitrides and carbides are frequently used in industry due to their outstanding properties such as high hardness, wear resistance, chemical and thermal stability and thermal conductivity. As a promising one, tungsten nitride (WN) is finding various applications especially in the electronics industry. There are several reports based on the use of WN in integrated circuits as a diffusion barrier in between copper and silicon layers (36–38). There are also other reports where WN-based coatings are employed as a barrier coating for resistive switching memory cells (or resistive random access memory-ReRAM) in order to enhance the switching properties of such structures (39).

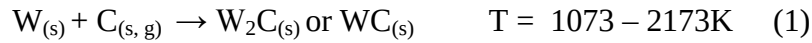
Other potential uses of WN thin films are related to micro-injection mold inserts (for CD, DVD, etc. production) as a contamination resistant material (40), polymer electrolyte fuel cells (PEFCs) as an alternative to expensive platinum catalysts (41), photoelectrochemical hydrogen production as photocatalyst material (42) and in phase change memory cells as a thermal boundary resistance material (43). For the applications that are mentioned above, WN thin films have been synthesized by metal-organic chemical vapor deposition (MOCVD) (44), plasma enhanced chemical vapor deposition (PECVD) (45), pulsed laser deposition (PLD) (46), atomic layer deposition (ALD) (47) and ion beam assisted deposition (IBAD) (48).

It is clear from the information provided above that none of these applications mentioned actually take advantage of the promising mechanical properties of WN such as its high hardness (exceeding 30 GPa). Nevertheless, there have been noteworthy attempts for the development of WN based materials as potential candidates for wear resistant coatings (49). In fact, several researchers examined the properties of coatings in the W-N system by investigating the effect of synthesis parameters (N_2 partial pressure, temperature, bias voltage etc.) on the wear properties of the resulting films (50–53). Also, there are other researchers interested in the influence of several alloying components on W-N based films such as Co, Ni, Ti, Si, Cr, Ge, O and C (54–58). Another important point that should be mentioned is that for tribological applications generally reactive magnetron sputtering is the major synthesis technique used (59–65). Contrary to the efforts mentioned above, oxidation problem of WN coatings at temperatures above 450°C (66) is the major problem keeping the wide-spread use of WN-based coatings in the cutting tool and related industries.

The second important candidate that will be mentioned here is tungsten carbide (WC). WC is a rather well known material due to its high hardness (24-30 GPa), melting temperature (2870°C), Young's Modulus (670 GPa) and chemical inertness. It was considered as an alternative to diamond when it was first synthesized in the early 19th century. After the important developments over the last century, as a bulk ceramic, WC (aka cemented carbide) began to enjoy the intense attention of the metal cutting, forming and shaping industry (67). Also, there are some other potential applications where WC is studied being a strong candidate, such as anode material for fuel cells (68) and core material for armor piercing ammunitions (69). On the other hand, as a wear resistant coating, WC has not received a similar interest. There are some applications in the microelectronic circuits (70) and some aircraft components (71). As for tribological applications, WC is generally used in multilayer diamond like carbon (DLC) based coatings as a reinforcement phase or oxidation resistant layer (72). In fact, DLC coatings are known to have remarkably low coefficient of friction and wear rates at room temperatures while they suffer from poor adhesion, oxidation resistance, low hardness and chemical inertness (73). Therefore, for demanding applications DLC coatings are synthesized together with supporting W or WC (74–76). Synthesis of high-

quality WC coatings through sputter deposition route is not an easy task to achieve at low temperatures (77, 78). An overview to the related literature exhibits that WC coatings are generally synthesized through sputter deposition method by either using W or WC targets with the help of a carbonaceous gas such as methane (79), acetylene (80), benzene (81) or even C₆₀ (buckminster fullerene) (82). There are studies where graphite targets were used as the carbon source as well (83).

Analysis of the results from various studies on the synthesis of WC coatings indicates that at low substrate temperatures coatings were either poorly crystallized or contained β -WC_{1-x} and/or α -W₂C phases (77). The hexagonal α -WC phase, which is the main constituent of the favorable bulk tungsten carbides, requires significantly higher substrate temperatures ($\geq 500^{\circ}\text{C}$), or annealing of the as deposited coatings under controlled gas flow conditions (78, 82). Another issue regarding the WC coatings is that often the coatings that are synthesized using gaseous carbon sources were found to contain large amounts of amorphous carbon in their microstructure (84, 85). Below is the well-known reaction between W and C that leads to the formation of WC compounds(72):



In this thesis, anti-wear properties of two W-based coatings were investigated and reported; tungsten nitride and tungsten carbide. Deposition parameters used during the synthesis for both of the coatings were optimized in order to improve the wear properties at room temperature as well as at 500°C. For this purpose, unique concepts were developed and applied. For WN, the first step taken was to scrutinize the effect of the amount of N₂ gas flow into the deposition chamber during deposition and following this W/WN multilayer coating concept was applied during the synthesis for improved wear resistance at high temperatures. As for the WC coatings, first of all, the effect of the amount of acetylene (C₂H₂) gas flow during deposition was examined similarly to the deposition experiments for WN coatings. It was observed that synthesis of crystalline WC coatings was not possible using graphite targets or C₂H₂ flow as for the carbon

source. An alternative approach was developed where a B_4C target was used for the C source resulting in the formation of well-crystallized WC phases. Furthermore, co-sputtering experiments with several combinations of WC, WB_4C (composite target; 1:1 molar ratio) and W_2C targets in order to compare the resultant coatings to the ones synthesized with B_4C .

2 EXPERIMENTAL

2.1 Deposition System and Deposition Procedure

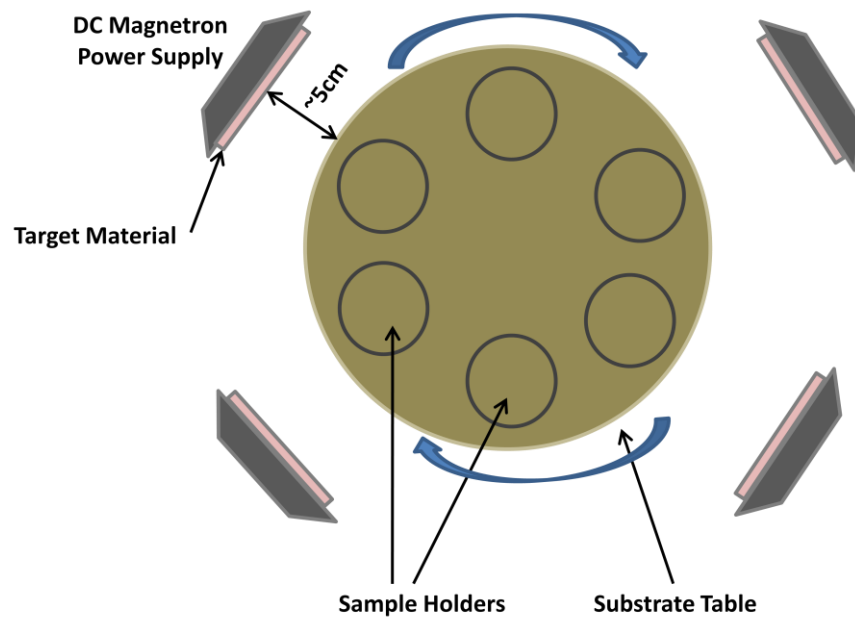
The synthesis of the coatings were performed on a CemeCon CC 800/9 Physical Vapor Deposition (PVD) system (CemeCon AG) which houses four planar dc powered magnetrons. A general look of the system can be seen in the following figure (Figure 2.1.1).



(a)



(b)



(c)

Figure 2.1.1: A general image of (a) the deposition system, (b) the deposition chamber of the given system, and (c) a simple illustration showing the simple arrangement of the deposition chamber from the top view

2.1.1 Deposition Parameters for WN Experiments

For the deposition of WN series, two tungsten targets (> 99.9%) and two Cr targets (> 99.9%) were installed onto the magnetrons. Polished AISI 100Cr6 steel discs of 6 mm thickness and 50 mm diameter and cleaved pieces of Si(100) wafers were used as substrate materials. Before deposition, the chamber was evacuated to a base pressure level of 3 mPa. In order to further clean the chamber and remove the contaminant gaseous molecules (i.e. adsorbed species such as CO₂ gas and water vapor) from the chamber-walls, the chamber was heated to a temperature of ~450°C for 30 minutes. After that, Ar gas was sent into the system until the chamber vacuum reached 350 mPa. A bias voltage is applied to the substrate table with respect to ground in order to create a plasma on the substrate surface. As a result, the substrates were sputter cleaned with the help of an intense Ar⁺ ion bombardment for 45 minutes prior to deposition process. As the last step before the main deposition, a thin Cr layer (<500 nm) was deposited on the substrates as a buffer layer improving the adhesion of the main coating to the substrate. The pressure in the chamber was kept at 600 mPa levels while the bias voltage given to the substrates was set at 120 V dc during the main deposition step.

In the first set of experiments, the amount of N₂ gas flow and its effect on the properties of WN coatings were investigated. For this purpose, W targets were operated with a power density of 7.5 W/cm². The N₂ gas flow ratio (N₂/(Ar+Kr+N₂)) during main deposition experiments were controlled and adjusted by using three separate mass flow controllers (MFCs); one for each gas used. This ratio was changed within a range of 17-66% during this set of experiments. In the second set of experiments, multilayer concept was applied on the deposition conditions. During multilayer coating synthesis subsequent layers of W and WN were deposited on top of each other. For the W layers, MFC for N₂ was set to zero flow. Two separate N₂ flow rates were used for the WN layer in the multilayer deposition experiments; 66% and 25% N₂ flow. A summary of the deposition parameters for WN experiments is given below Table 2.1.1:

Table 2.1.1: A summary of the deposition parameters for WN experiments.

	Targets	Table Rotation	N₂ Flow N₂/(Ar+Kr+N₂)	Comments
SET 1	W (x2) Cr (x2)	1 RPM	17% 20% 25% 33% 50% 66%	Single layer WN coatings were produced using varying N ₂ flow rates.
SET 2-1	W (x2) Cr (x2)	1 RPM	66%	Multilayer coatings were produced with: 3 bilayers, 4 bilayers, 6 bilayers, 8 bilayers, 11 bilayers using a constant N ₂ flow of 66%.
SET2-2	W (x2) Cr (x2)	1 RPM	25%	Multilayer coatings were produced with: 4 bilayers, 11 bilayers using a constant N ₂ flow of 25%.

2.1.2 Deposition Parameters for WC Experiments

For the deposition of WC series, two W targets (> 99.9%) together with a graphite (C) target (> 99.9%) and a B₄C target (> 99.9%) were installed in the first set. In the second set of experiments, one W target, a B₄C target and two Cr targets (> 99.9%) were used. In the third set of experiments, WC targets with WB₄C or W₂C targets (>99.9%) were replaced with the other targets. Details for the deposition parameters are given in Table 2.1.2. Similarly, polished AISI 100Cr6 steel discs of 6

mm thickness and 50 mm diameter and cleaved pieces of Si(100) wafers were used as substrate materials. The procedure prior to the main deposition step was the same with the one applied to the WN experiments. During main deposition step for WC series, the substrate bias was kept at 100 V dc different than the WN series.

In the first set of experiments, the amount of acetylene (C_2H_2) gas sent through the chamber during depositions was varied between 0 and 20 ml C_2H_2 . In the second set, samples were positioned in front of W and B_4C targets after buffer layer deposition substrate table was stopped during the main deposition. In the third set of experiments, three different target configurations were used. One of them was performed only with WC targets and on other two experiments two of the WC targets were replaced with WB_4C and W_2C targets, respectively. The table was rotated with 1 RPM during these second set of experiments. 10% N_2 flow ($N_2/(Ar+Kr+N_2) \times 100$) was sent to the chamber during all the deposition experiments.

Table 2.1.2: A summary of the deposition parameters for WC experiments.

	Targets	Table Rotation	C_2H_2 Flow (ml/min)	N_2 Flow ($N_2/(Ar+Kr+N_2)$)	Comments
SET 1	W (x2) B_4C Graphite (C)	1 RPM	0 5 8 15 20	NO	Effect of C_2H_2 flow on the coatings was investigated.
SET 2	W B_4C Cr (x2)	OFF	NO	10%	B_4C was used as the C source.
SET 3	WC (x2) WB_4C (x2) W_2C (x2) Cr	1 RPM	NO	10%	Co-sputtering experiments were performed for comparison.

2.2 Thin Films Characterization

2.2.1 X-ray Diffraction (XRD)

The crystal structures of the coatings were examined with an X-ray Diffractometer (Rigaku Corporation, Miniflex Model). The source of X-rays was Ni-edge filtered Cu K α radiation (1.5405 Å). Samples were scanned in the 2 θ range of 20-100°. Step size for the data collection was 0.05°, while the scan speed was kept at 1°/minute.

2.2.2 X-ray Photoelectron Spectroscopy (XPS)

For the analysis of the coating chemistry, samples were analyzed using an XPS system (Specs GmbH) in which a monochromatic Al K α radiation (1480 eV) was used as the X-ray source. Before taking the spectra from individual samples, all the films were sputter etched using Ar⁺ ions (1keV for 5 minutes) in order to clean the surfaces and remove the contamination layer due to atmosphere exposure after the deposition. During survey and the detailed scans of W 4f, B 1s, C 1s, N 1s and O 1s binding energies, a flood electron gun was also operated ($I_{\text{emission}} = 30 \mu\text{A}$) in order to prevent charge accumulation on the film surfaces. The detailed data was collected with 25 eV pass energy and 0.05 eV step size.

2.2.3 Scanning Electron Microscopy (SEM)

An SEM system (Zeiss-EVO 40) was operated in order to take images of the deposited films. The lanthanum hexaboride (LaB₆) gun filament was operated under vacuum conditions in which pressure was below 1.0×10^{-4} mBar levels for the main chamber that the sample is loaded, while the gun chamber was separated from the main chamber and gun chamber was always in vacuum below 5.0×10^{-7} mBar levels. Cross-sectional and 45° tilted surface images were taken from each sample with 10kV source voltage with a working distance of 10 to 12 mm.

2.3 Testing of the Wear and Related Mechanical Properties

Hardness and Young's Modulus of the coatings were measured with a Nano-indentation Tester (CSM Instruments) with a diamond indenter tip (Figure 2.3.1). The maximum load applied to the samples was in the range between 10 to 70 mN. Load

selection was made according to the indentation depth and the load was chosen in such way that this indentation depth did not exceed 1/10 of the actual film thickness, so possible effect of the substrate material to the measurements was minimized. Wear tests of the coatings were operated using a High-Temperature Tribometer (CSM Instruments) which was a pin-on-disc type wear testing instrument and during the test samples can be heated up to 800°C. The coated disc samples were rotated and worn against a 6 mm diameter alumina (Al_2O_3) ball under ambient atmosphere conditions. During wear testing in this study, a constant 5 N load was applied onto the samples. Rotation speed was set at 10 cm/s and samples were worn for a total distance of 180 m. Calculation of the wear rates was performed with the help of another instrument called surface profilometer (Sloan DEKTAK 3030ST). These wear tests were conducted both at room temperature and 500°C for each sample, a schematic for the wear test is given in Figure 2.3.1). For further comparison of the high temperature performance of the coatings, nano-indentation tests were repeated after 500°C heat treatment for 2 hours.

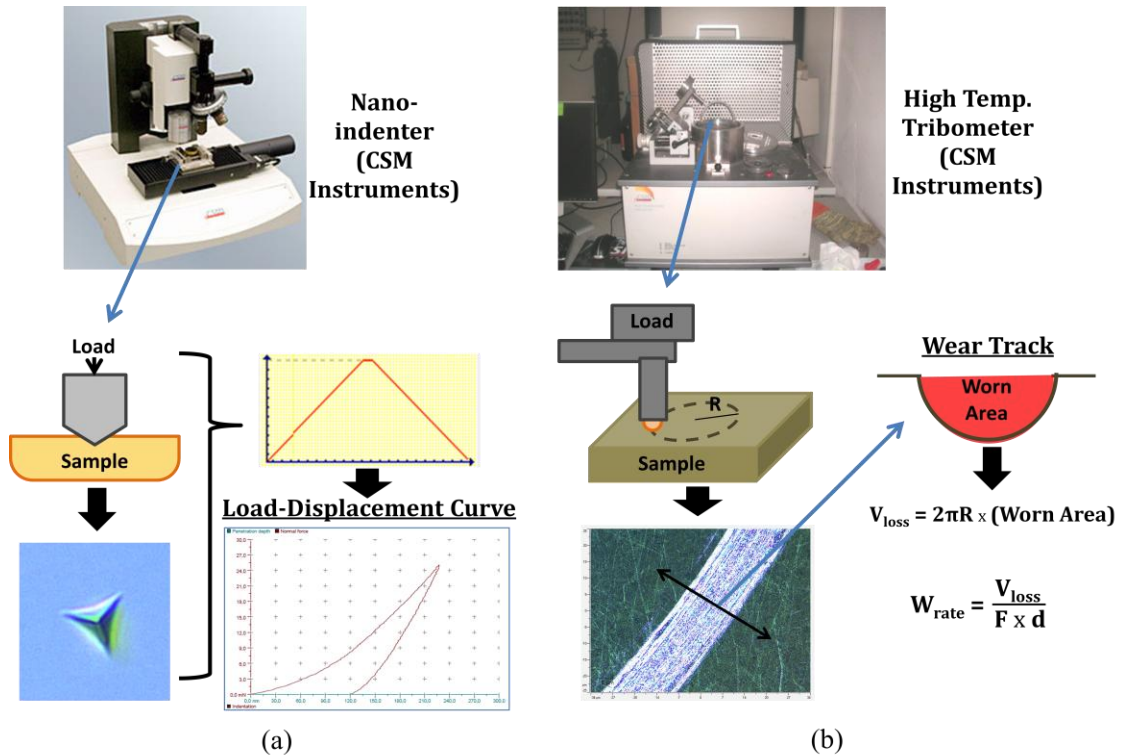


Figure 2.3.1: Testing equipments and procedures for (a) hardness and (b) wear rate measurements.

3 RESULTS AND DISCUSSION

3.1 Deposition of Tungsten Nitride Thin Films

WN synthesis experiments start with the first set of trials where N_2 flow ratios were investigated. The X-ray diffraction (XRD) data acquired from the WN coatings synthesized in set 1 are given in Figure 3.1.1. From the θ - 2θ scans of the coatings it is clear that until 50% N_2 flow ratio, metallic-W (BCC, JCPDS=02-1058) seems to be the dominant crystalline phase in the coatings. Diffraction peaks originating from the metallic-W phase exhibits a broadening behavior following the increase in the N_2 flow. Starting with the 50% N_2 flow ratio, two other peaks appear around the d_{110} peak ($2\theta = 39.8^\circ$) at $2\theta = 36.5^\circ$ and 42.5° which are most likely related with the peaks for (111) and (200) planes in the α -WN (JCPDS #65-2898) and β - W_2N (JCPDS #07-9962) phases. Thus, by itself XRD data is considered inadequate to identify the phase structure in these coatings. However, in the related literature nearly all XRD data obtained from WN coatings displaying the previously mentioned two peaks at $2\theta = 36.5^\circ$ and 42.5° are interpreted as originating from β - W_2N phase (59, 60, 86–89). Another point that should be mentioned regarding these plots (Figure 3.1.1) is that the two WN based peaks were found to be shifted towards lower 2θ values which could be due to poor crystal quality of the phases and/or the stress generated in the films during synthesis. Nevertheless, a similar shift was not observed for the peaks from the metallic-W phase.

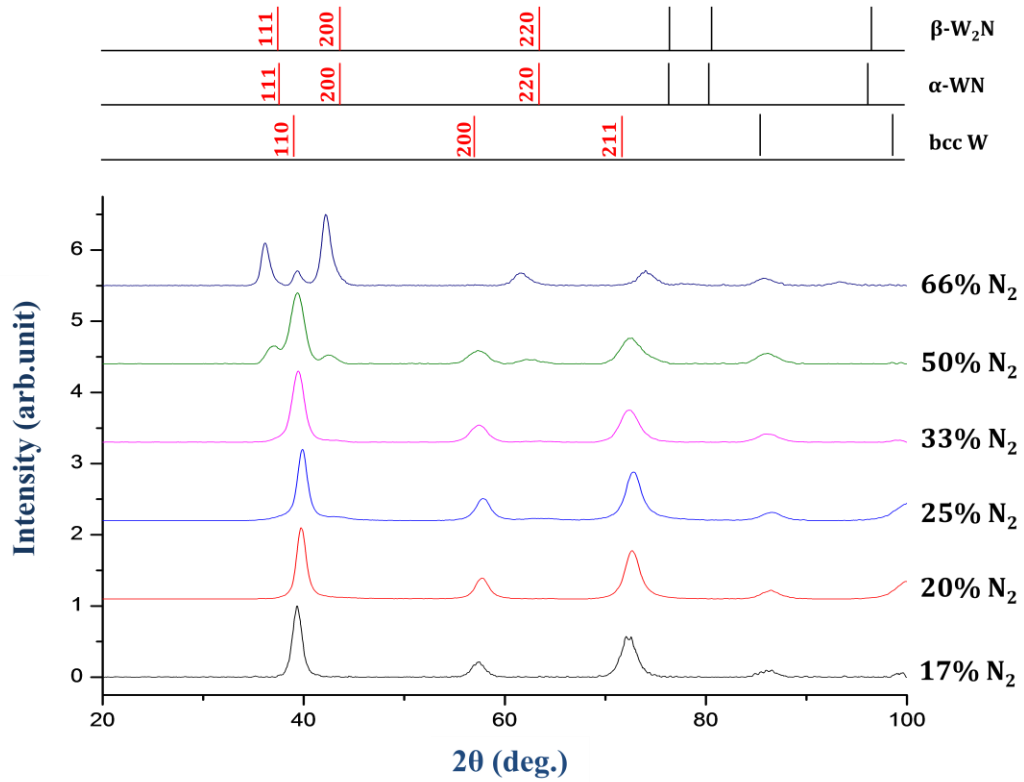


Figure 3.1.1: X-ray diffraction patterns from coatings deposited with varying N₂ flow rates.

A structural change in the WN coatings during the N₂ flow series samples is also evident in the representative SEM micrographs given in Figure 3.1.2. As it is seen in the images, WN coatings display a rather dense structure until 50% N₂ flow with a hint of nano-crystalline structure. Then, abruptly at 66% N₂ flow (Figure 3.1.2d), the microstructure of the WN films start indicating a definite columnar microstructure.

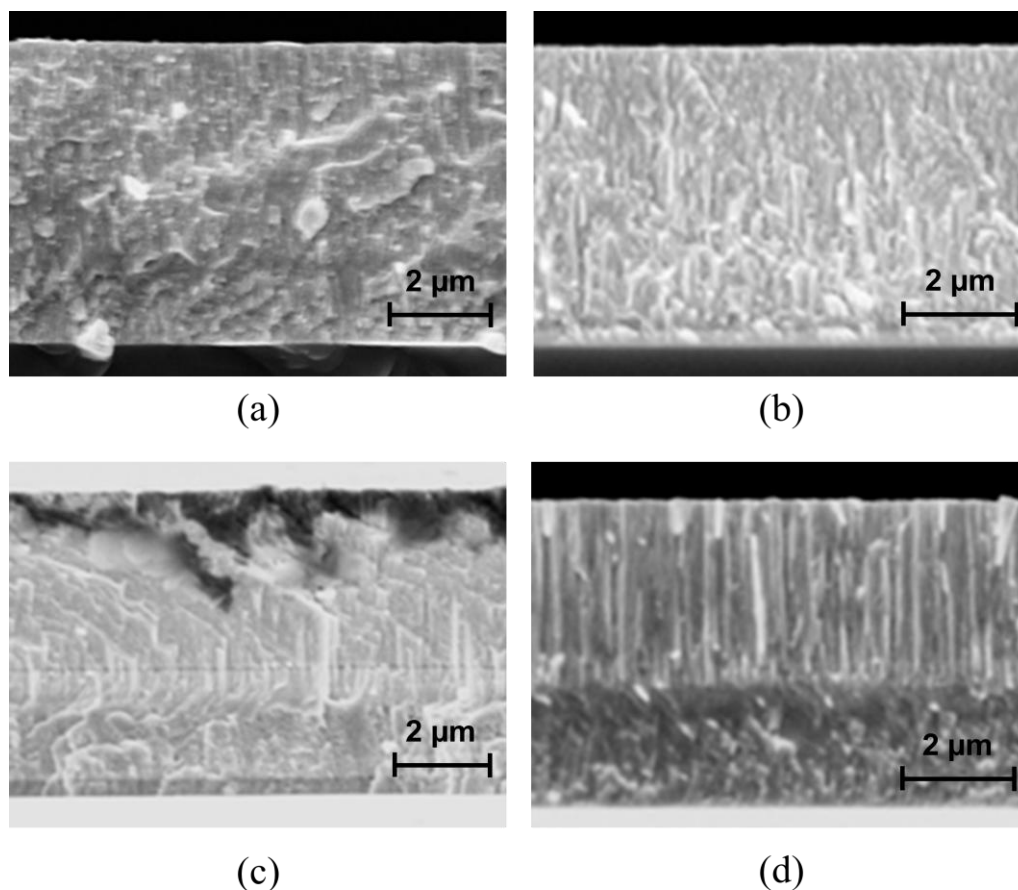
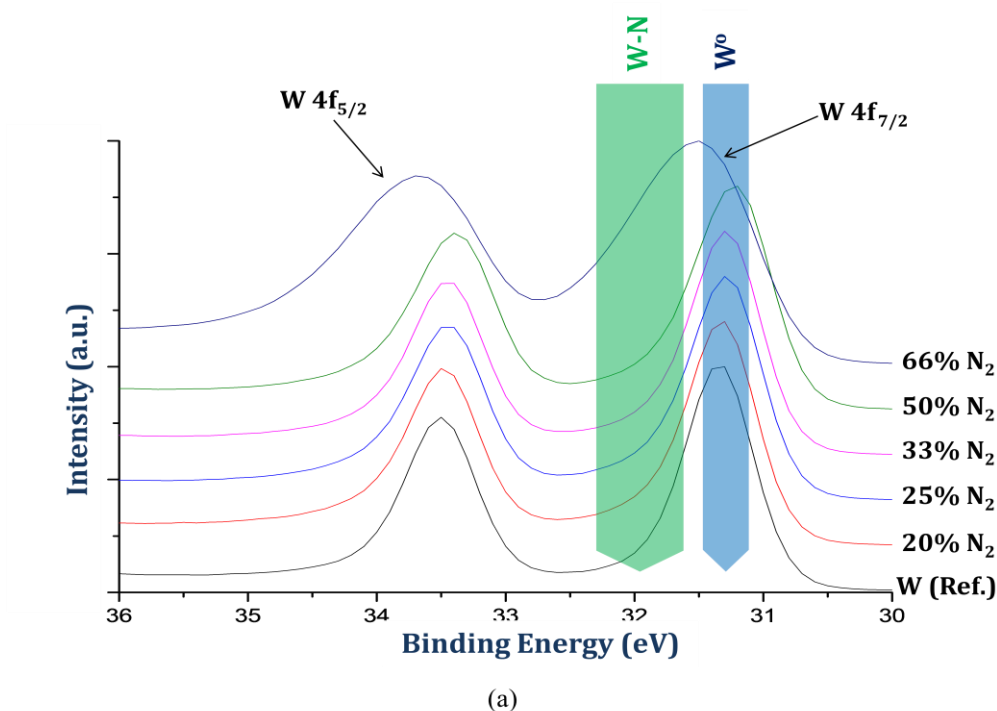


Figure 3.1.2: SEM cross-sectional images of the N_2 gas series with (a) 25%, (b) 33%, (c) 50% and (d) 66% N_2 flow rates.

W-N coatings deposited at different N_2 flow rates were further examined by XPS and the changes in their chemical environment is monitored from the W 4f and N 1s binding energy spectra obtained from these coatings (Figure 3.1.3). The binding energy for W 4f_{7/2} and W 4f_{5/2} doublets remains almost unchanged centered around 31.3 eV and 33.5 eV, respectively while the N_2 flow rate increases. At 66% N_2 flow rate, a shoulder at higher binding energy side appears, as seen in Figure 3.1.3a. A similar shift can also be seen in the spectra of N 1s region at 66% flow rate (Figure 3.1.3b). In order to resolve this structure and find out the reason for this abrupt shift, the W 4f and N 1s peaks of the coating with 66% N_2 flow rate were further deconvoluted. The deconvolution of the wide W 4f_{7/2} doublet at 31.5 eV using symmetric Gauss-Lorentz functions yields three separate peaks at the following binding energy positions; 31.3, 31.8 and 32.4 eV (Figure 3.1.4a). The component at 31.3 eV clearly indicates W-W bonding, while the one at 31.8

eV implies W-N coordination. Finally, the one at 32.4 eV suggests a stronger electron transfer away from tungsten. The oxygen content on the surface of this film is found to be around 6.7 % which is too small for explaining this relatively larger component. In the literature, W $4f_{7/2}$ peaks positioned at above 32 eV are also associated with richer nitrogen coordination. A similar result can also be interpreted from the N 1s spectrum from the same coating, as is shown in Figure 3.1.4b. The two peaks at 397.3 and 398.0 eV in the N 1s spectrum probably belong to two different W-N bonding schemes for the same crystal structure with different nitrogen stoichiometries (90, 91). The last component at 399.8 eV could probably be a result of preferential sputtering during cleaning of the surfaces of the coatings (92, 93).



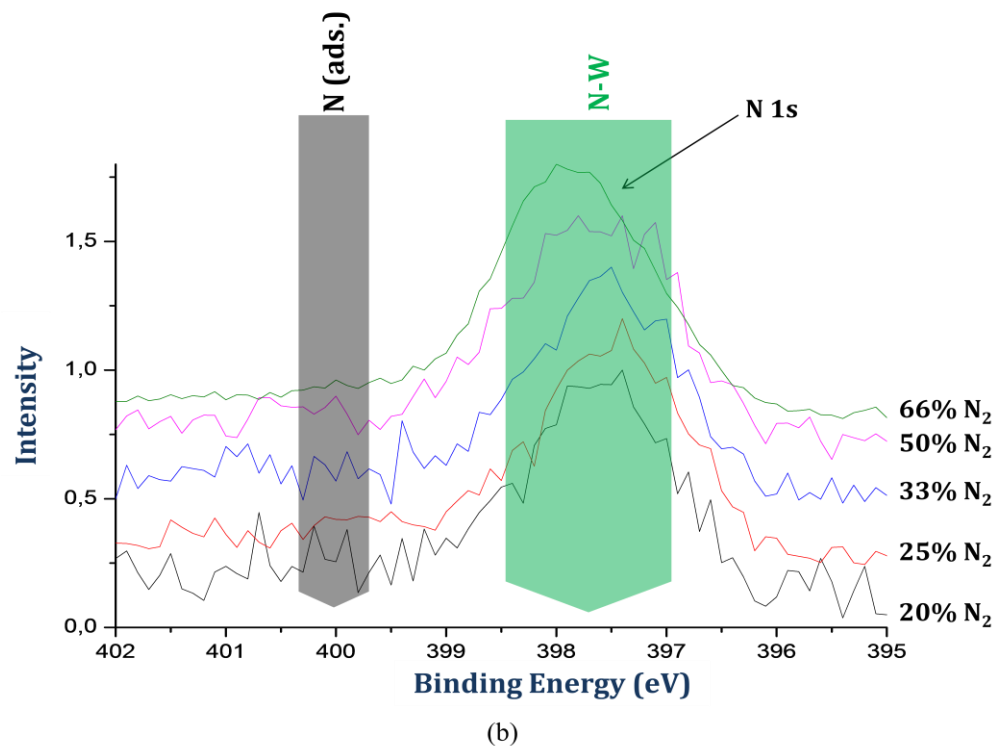


Figure 3.1.3: (a) Detailed XPS spectra depicting 4f binding energy region of W and (b) 1s binding energy region of N in waterfall format for coatings deposited with changing N_2 flow rates. Assigned W and N coordination schemes are depicted on the plot.

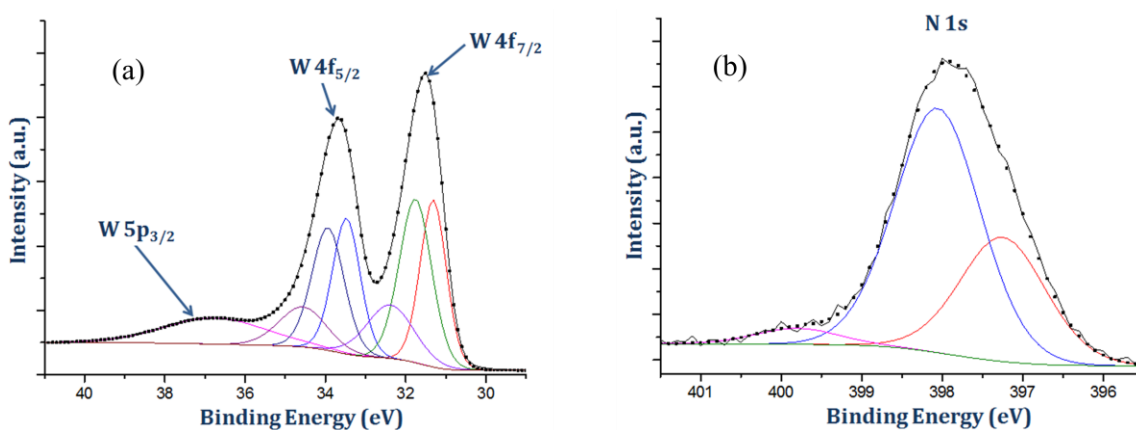
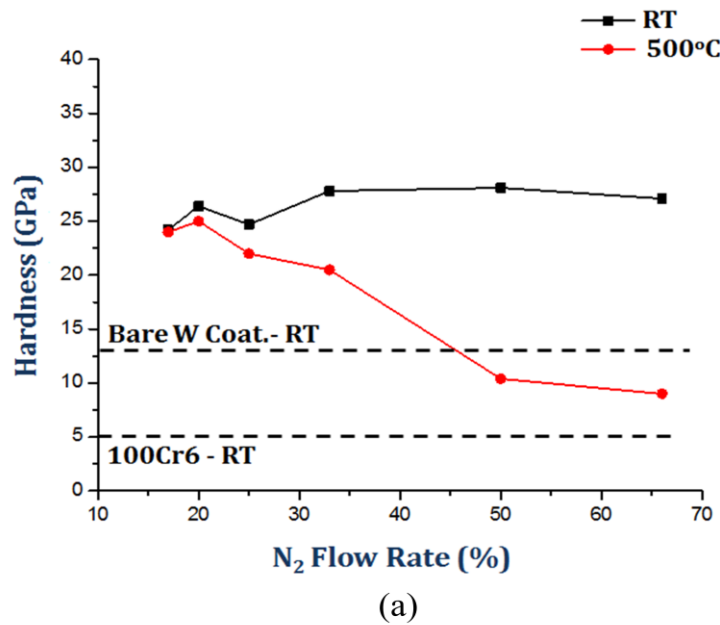


Figure 3.1.4: (a) Deconvoluted W 4f binding energy spectrum for 66% N_2 flow showing a fit with three peaks and, (b) deconvoluted N 1s peak for 66% N_2 flow indicating a fit with two peaks.

Further interpretation of the XPS spectra from WN coatings point toward another important result; until 66% N₂ flow rate, on W 4f detailed analysis, there is no clear transition from metallic-W to W-N coordination. However, N 1s peak is always in the W-N coordination region plausibly implying that metallic tungsten has an appreciable nitrogen solubility that has not been discussed in the earlier literature regarding the W-N binary system. The phase diagram for W-N system proposed by Schmidt et al (94) does not suggest any appreciable solubility of N in W. Furthermore, this phase diagram also suggests WN to assume a liquid phase at room temperature and pressure. On the other hand, the model proposed by some other researchers (95) for the nucleation of β -W₂N phase clearly involves distortion of the BCC lattice of metallic-W due to the gradual incorporation of interstitial N which suggests appreciable solubility of N in the host matrix.

Wear-related properties, hardness and wear rate, were measured for the coatings synthesized at varying N₂ flow rates. The hardness measurements obtained were plotted against the N₂ flow rates used during the deposition as shown in Figure 3.1.5a. The hardness values obtained from the polished surface of 100Cr6 steel and from a sputter deposited tungsten coating were also given as a reference for further comparison. At room temperature, hardness of the coatings was found to be independent of N₂ flow rate used for deposition; between 25 and 28 GPa. Overall, these values were very well matching the ones reported in the literature (in the 25-30 GPa range), while Polcar et al. reported WN films having higher hardness almost reaching 40 GPa (51) using similar nitrogen flow ranges during deposition. Moreover, there are several other reports pointing out that nitrogen content is an important factor determining the hardness of such coatings (62, 96). Besides, in order to better understand the effect of nitrogen incorporation into the coatings, hardness measurements were repeated after the coatings were subjected to 500°C for 2 hours at ambient atmosphere. A significant decrease in the hot hardness of the coatings is observed after 33% N₂ flow rate. Similarly, wear rates for these coatings are plotted at both room temperature and 500°C as seen in Figure 3.1.5b. Wear rates of these coatings seemed to be slightly improved with increasing N₂ flow rates at room temperature, while an important drop was observed for wear rates measured at 500°C for films deposited with N₂ flow rates above 33% (Figure 3.1.5b).

Polcar and his colleagues also reported a similar drop in their reports on dropping wear rates of WN coatings with respect to increasing nitrogen content measured in the coatings. Furthermore, at 500°C, they measured the lowest wear rate for the coating with the highest nitrogen content (at. 58%), as low as $\sim 2.4 \times 10^{-6} \text{ mm}^3/\text{Nm}$ (52). The decrease in the hardness and wear rates with increasing temperature was related with the formation of a soft oxide phase (tet-WO_3) in the coatings (51–53). Similarly, in Figure 3.1.6 the XRD pattern obtained from film synthesized using 50% N_2 flow after 500°C treatment is provided in comparison with the as-deposited pattern showing several diffraction peaks belonging to WO_3 phase in the 2θ range between 20-to-35. This data is inline with the reports in literature indicating a softening behavior as a result of oxide phase formation on WN coatings.



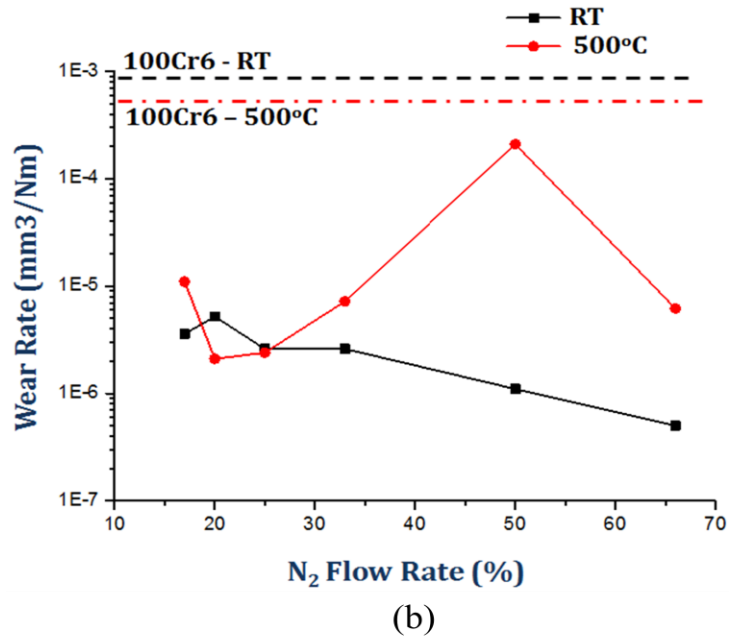


Figure 3.1.5: (a) Nano-hardness and (b) wear rate results of WN coatings sputter deposited with varying N₂ flow rates measured at room temperature and 500°C.

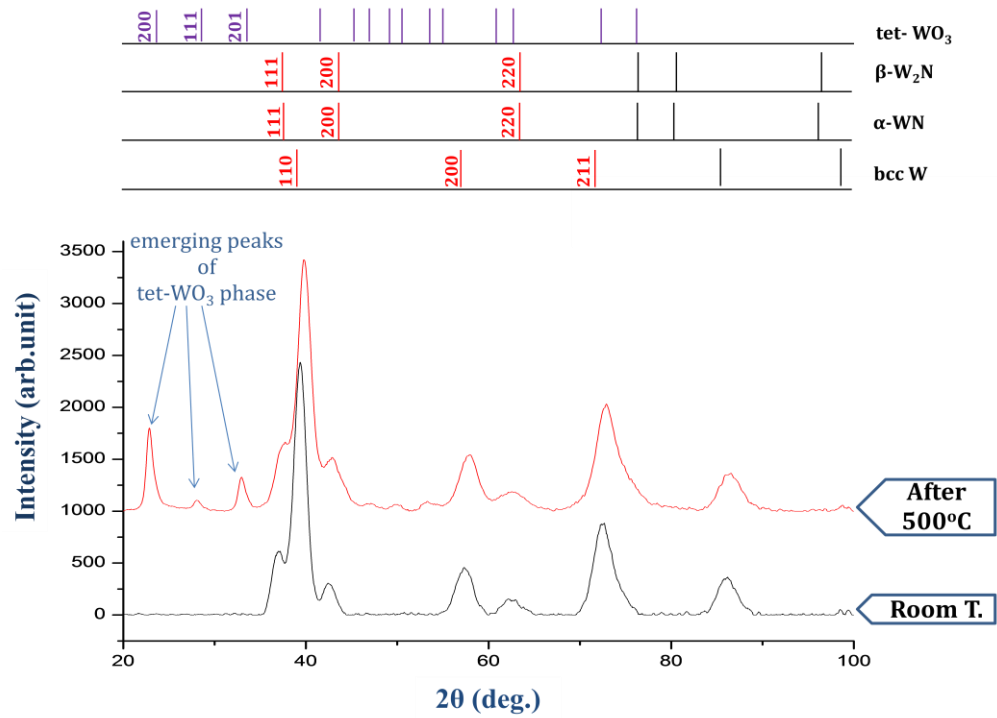


Figure 3.1.6: XRD scan of the WN coating deposited with 50% N₂ flow rate before and after heat treatment at 500°C for two hours.

The main concept that has been used for improving the wear performance of the coatings was the synthesis of the coatings as W/WN multilayers. In the multilayered W/WN depositions, initially a N₂ flow rate of 66% was utilized and kept constant during the deposition of WN layers. The number of W/WN bilayers was used as the main variable between separate runs. A total of five coatings with 3-, 4-, 6-, 8- and 11-bilayers of W/WN were deposited in the first multilayer series. For each film, the bilayer thickness was kept constant, thus films with more bilayers were thicker. Thicknesses of the films were measured from cross-sectional SEM analysis and the thickness of each individual bilayer (W+WN) was adjusted to be approximately 700 nm with W-to-WN thickness ratio approaching 1:1 (Figure 3.1.8). The deposition periods for these coatings were arranged such that the final/top layer would be WN, except for the film with 6 bilayers that was terminated with a W layer. In Figure 3.1.7b, XRD patterns from the multilayered films are shown. These given plots clearly show the formation of coatings with two co-existing phases; namely W and β -W₂N.

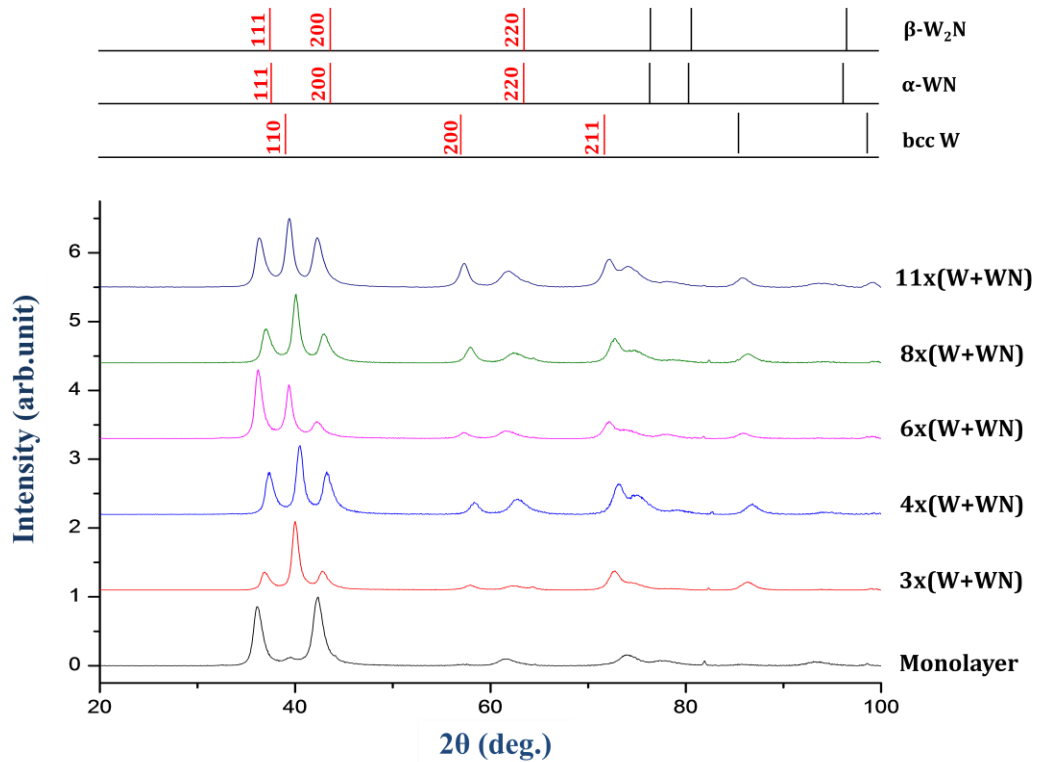


Figure 3.1.7: X-ray diffraction patterns from multilayer W/WN coatings deposited with 66% N₂ flow rate.

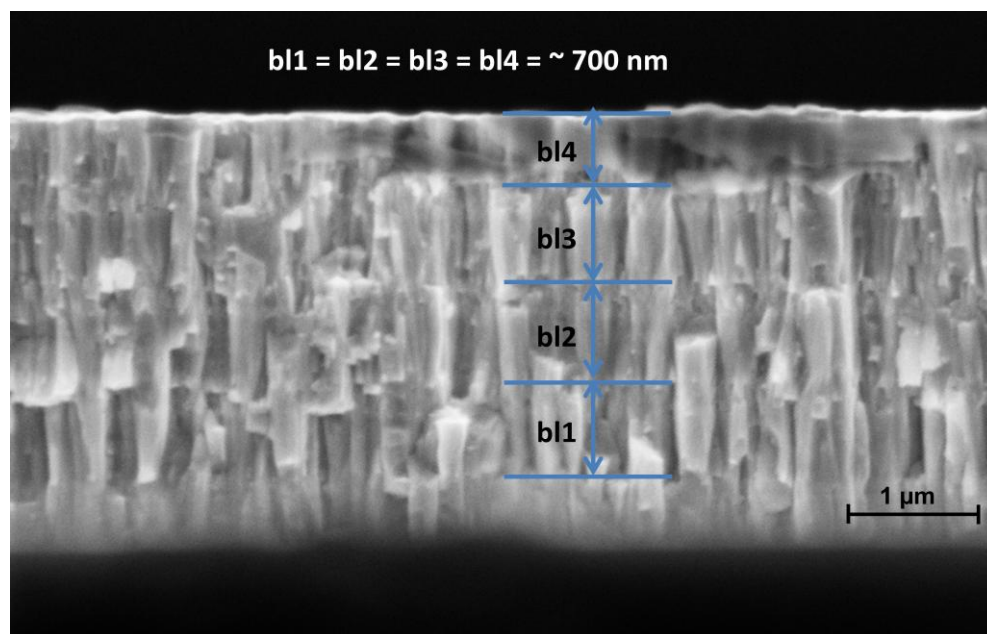
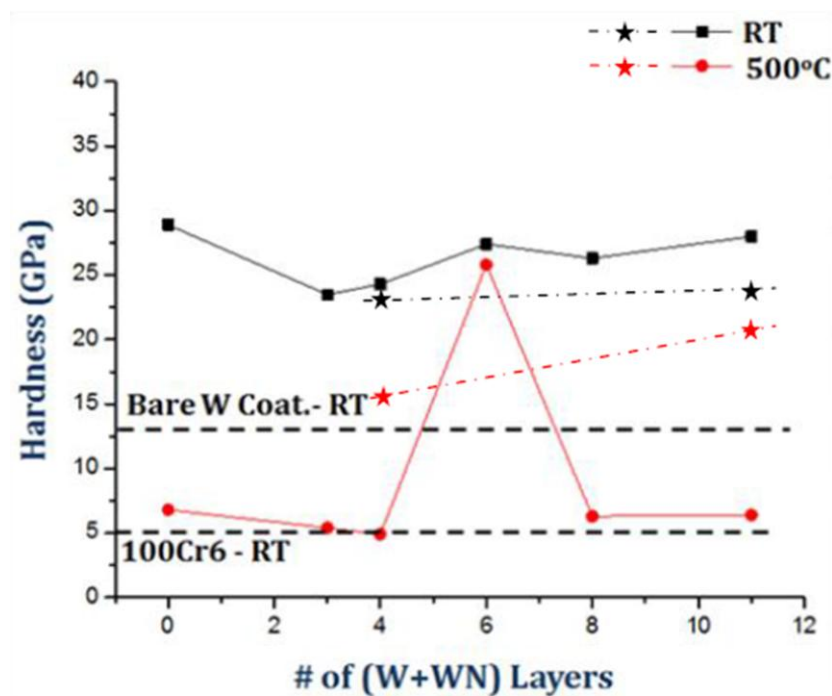


Figure 3.1.8: Representative SEM image for the multilayered W/WN coatings with 4 bilayers.

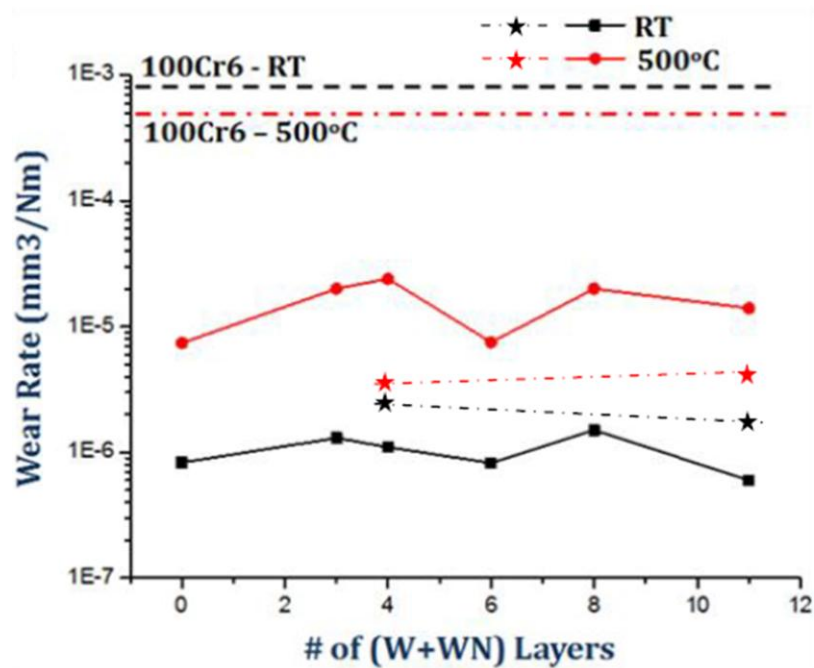
The coatings deposited with the aforementioned multilayer concept were subjected nano-indentation and pin-on-disc tests at RT and 500°C. The resultant hardness and wear rate data are given in Figure 3.1.9a and Figure 3.1.9b, respectively. It is clear that the use of W/WN bilayers immediately influenced the hardness of the coatings after the heat treatment at 500°C as shown in Figure 3.1.9a. Hot hardness values measured for these coatings were all around 6 GPa except for the coating with 6 bilayers. This significant decrease in the hot hardness is very similar to the drop encountered for the N₂ gas flow series. Thus, it is very likely as result of the formation of WO₃ on the top of the coatings. Furthermore, the wear rates measured were almost independent of the number bilayers and stable around $\sim 10^{-6}$ and $\sim 10^{-5}$ mm³/Nm for RT and 500°C, respectively.

The noteworthy exception regarding the 6-bilayer film exhibiting a markedly different hot hardness data was most probably a result of the WN termination layer for this 6 bilayer film having a lower nitrogen content different than the rest of the other multi-layer coatings. The thin W-rich (or N-deficient) layer was apparently protecting the underlying WN layer from oxidation better than the top layers of the other multilayer coatings. However, this layer was easily worn out during 500°C wear testing exposing

the underlying WN layer to ambient atmosphere and allowing for the formation of softer WO_3 . These results required a revisit of the N_2 flow rate experiments, in order to further improve the wear rate of multilayer W/WN coatings. From the analysis of the wear rate data in Figure 3.1.5b, when the flow rate for N_2 gas was set at values less than 33%, the wear rate of the WN coatings measured at 500°C and RT were almost equal to each other. Therefore, two multilayer W/WN deposition experiments, 4 bilayers and 11 bilayers, were repeated by setting the N_2 flow rate at 25% during WN layer synthesis. The results of the hardness and wear tests on these coatings are marked by solid stars on the plots shown in Figure 3.1.9a and Figure 3.1.9b, respectively. It can be easily seen that lowering the N_2 flow rate induced a significant improvement in the wear rates, and almost no considerable performance losses at 500°C. Even though, the hardness of the coatings suffered some drop at 500°C for the 4-bilayer case, the improvement over 66% N_2 flow rate case is clearly noteworthy.



(a)



(b)

Figure 3.1.9: (a) Nano-hardness and (b) wear rate results of multilayer coatings sputter deposited with 66% N₂ flow rate measured at room temperature and 500°C. (The hardness and wear performances of the coatings (4- and 11-bilayered) deposited with 25% N₂ flow rate were represented as black and red solid stars connected with dashed-dot lines on the plots)

3.2 Deposition of Tungsten Carbide Thin Films

The X-ray Diffraction (XRD) data obtained from WC coatings synthesized in SET 1 (see Table 2.1.2) were plotted in Figure 3.2.1; peaks due to the substrate are indicated with “S”. The films synthesized in SET 1 display a sharp peak (110) peak for the metallic-W phase overlapping with a very wide peak. It is hard to identify the source phase for this wide peak. Due to its width, it is possible that this peak is a convolution of multiple peaks from the both carbide phases of W. Hence, in order to figure out the phase in these coatings, further analysis of the as-deposited specimens were done using XPS analysis.

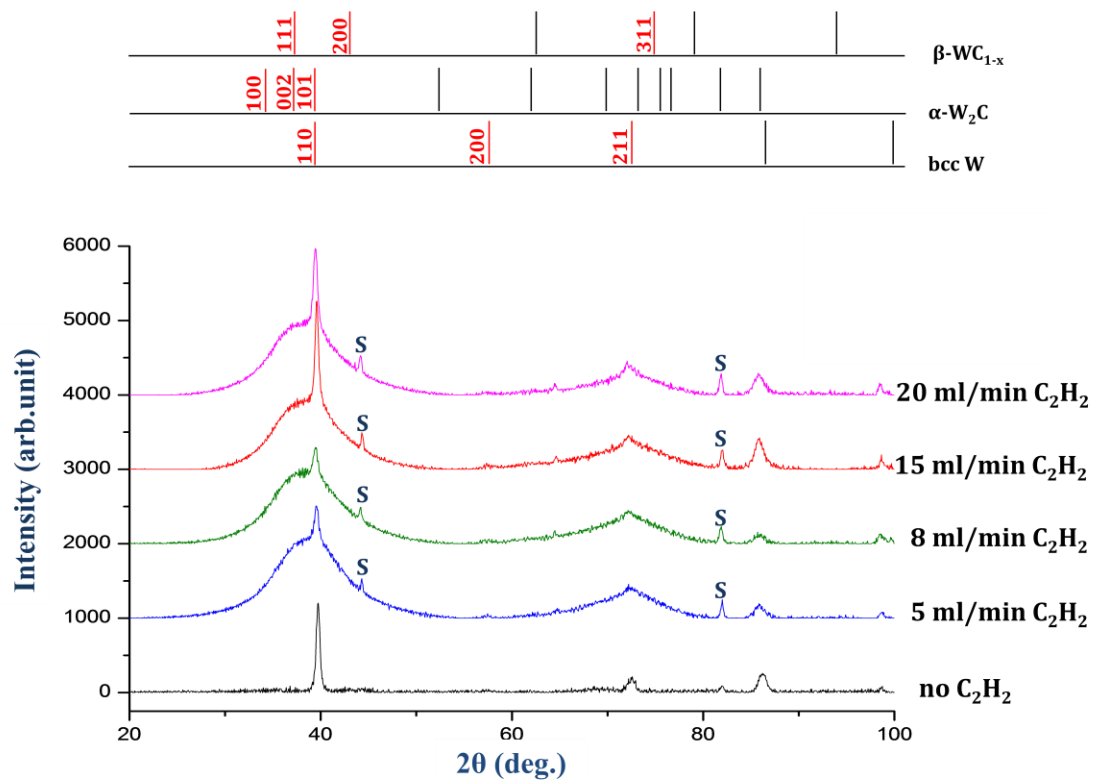


Figure 3.2.1: X-ray Diffraction Data for samples with varying C_2H_2 flow amounts (1st set).

SEM analysis of the acetylene gas series shows that (Figure 3.2.2) without any acetylene supply the coating structure is rather dense with equiaxed grains. As the acetylene flow is increased, the microstructure of the films became less dense with columnar grains in majority. This finding can indicate that the reaction that proceeds during the deposition becomes diffusion controlled with the increase in the number of C atoms reaching to the surface of the growing film.

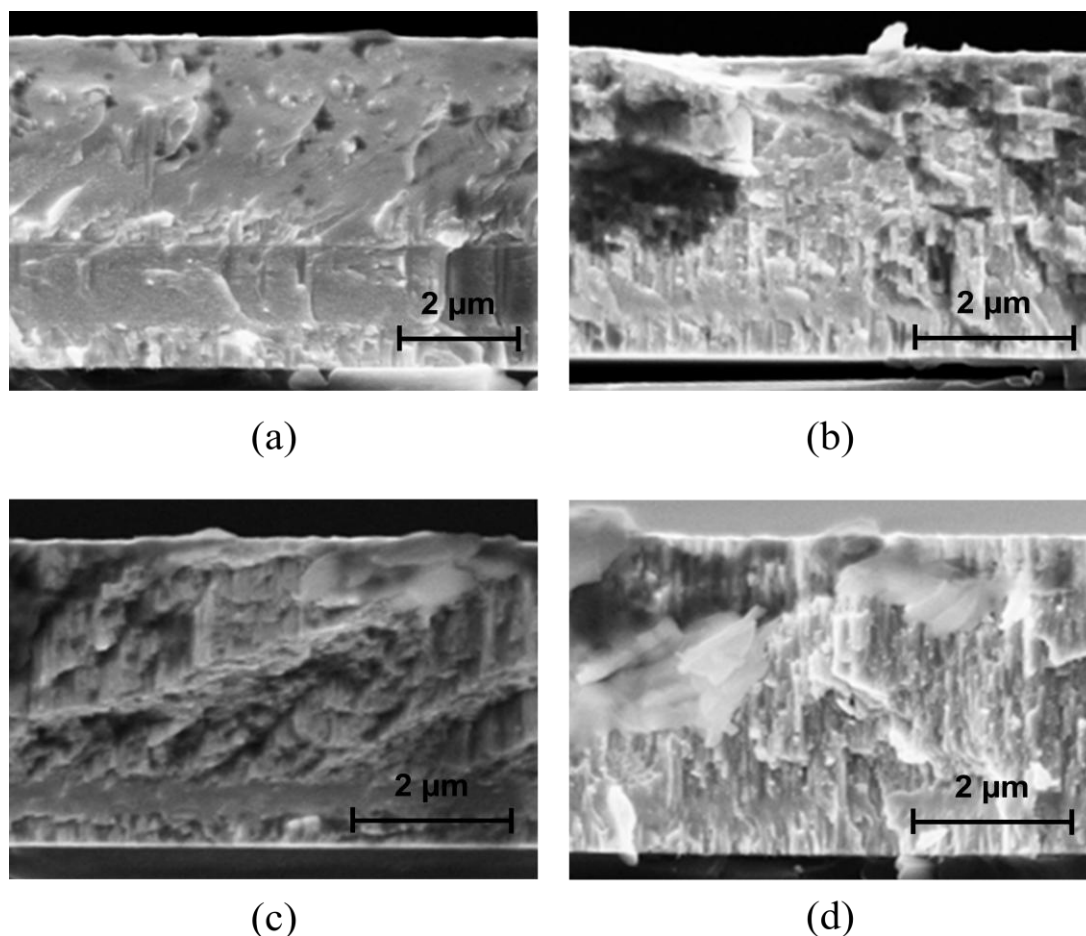
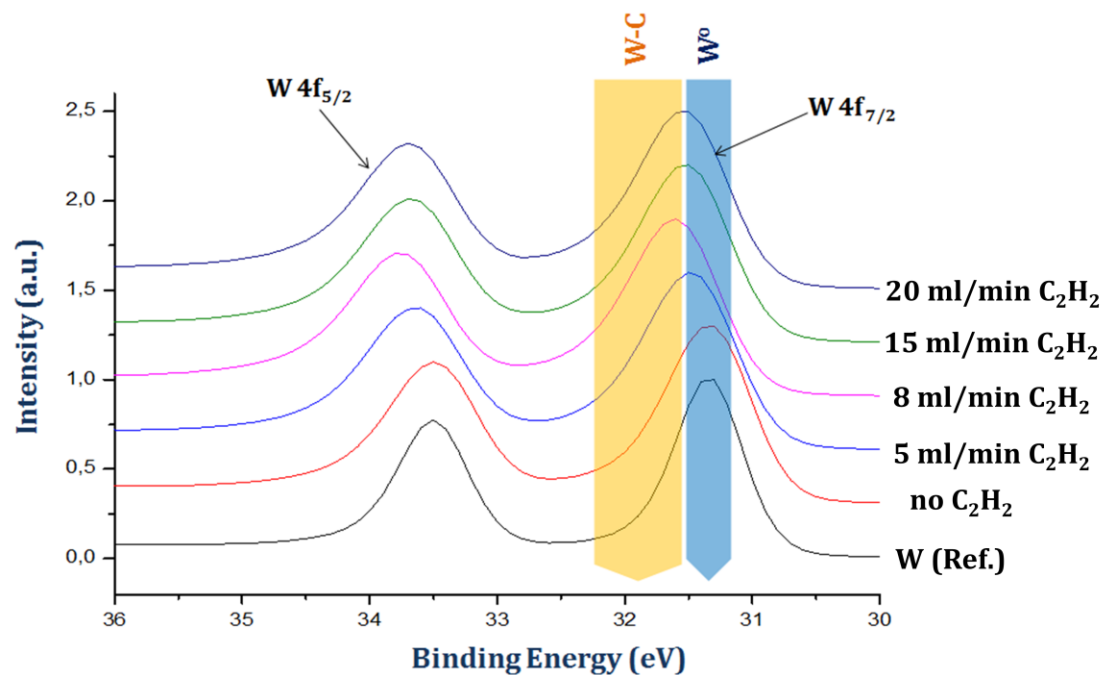


Figure 3.2.2: SEM cross-sectional images of the C₂H₂ gas series (1st set) with (a) no C₂H₂, (b) 8 ml/min, (c) 15 ml/min and (d) 20 ml/min C₂H₂ flow.

To gain more information about the phase content coatings, samples were further examined using X-ray Photoelectron Spectroscopy technique. The resulting detailed analysis of the XPS data for the four main peaks, namely, W 4f, C 1s, and B 1s were plotted in Figure 3.2.3 a, b, and c, respectively. As a reference, W 4f peak of metallic W was plotted together with that obtained from the coatings. As it is seen in the W 4f plots (Figure 3.2.3 a), there is a gradual shift towards higher binding energies until 8 ml C₂H₂ flow. The maximum shift is observed for coatings deposited with 8 ml C₂H₂ flow or higher suggesting W-C bonding to be the dominant bonding. The C 1s region (Figure 3.2.3 b) similarly shows that most C atoms to be coordinated with W, but there is a clear rise on the high energy side of the main peak which is a result of increasing unreacted C amount with increasing C₂H₂ flow. These results may suggest that beyond a certain

amount of C_2H_2 flow, arrival rate of carbon atoms to the surface of the growing film is faster than the combined rate of the diffusion of C atoms into W metal and the formation of WC phase. Finally, B 1s peak (Figure 3.2.3c) shows that all the B atoms are coordinated with W atoms.



(a)

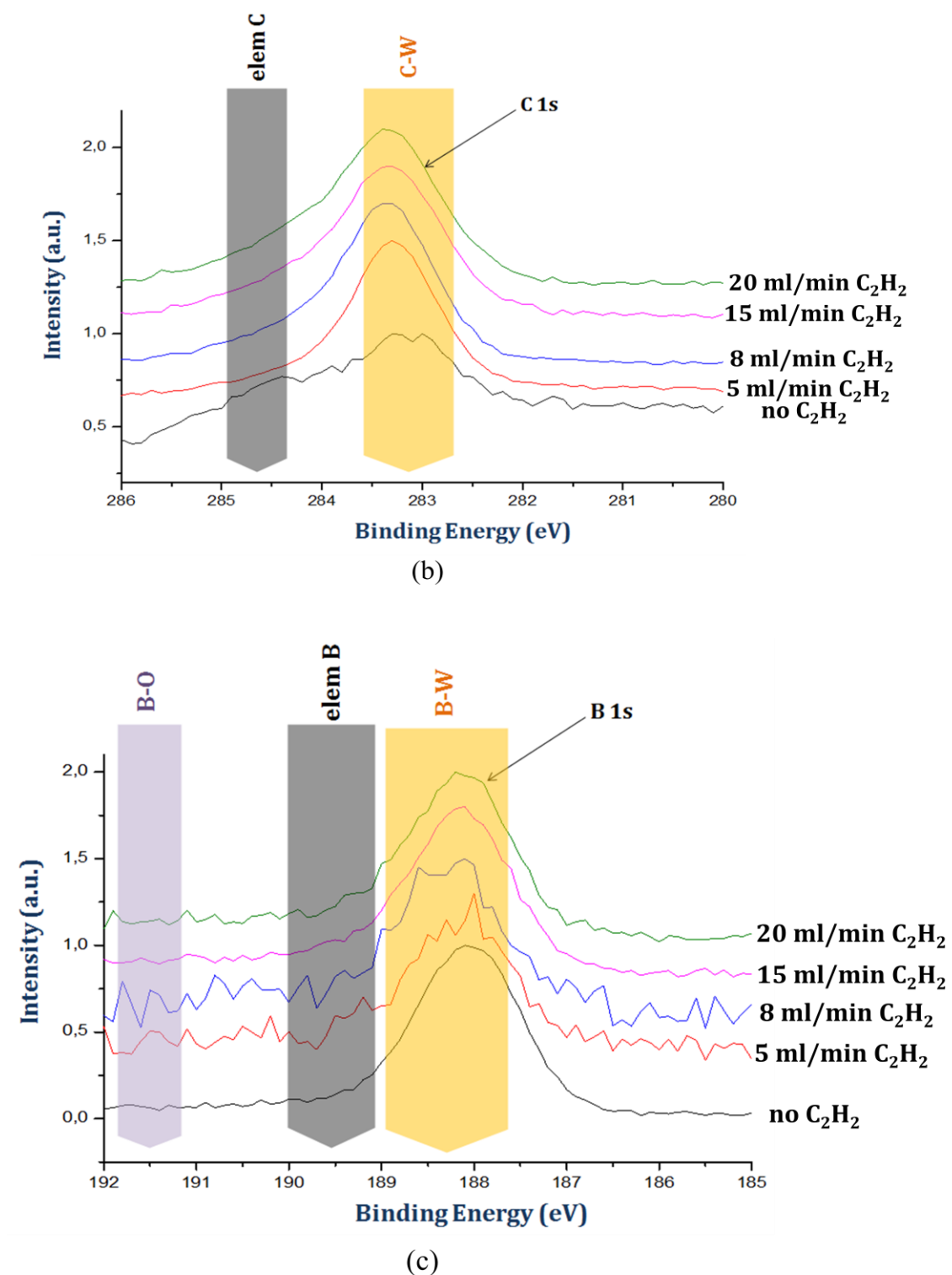
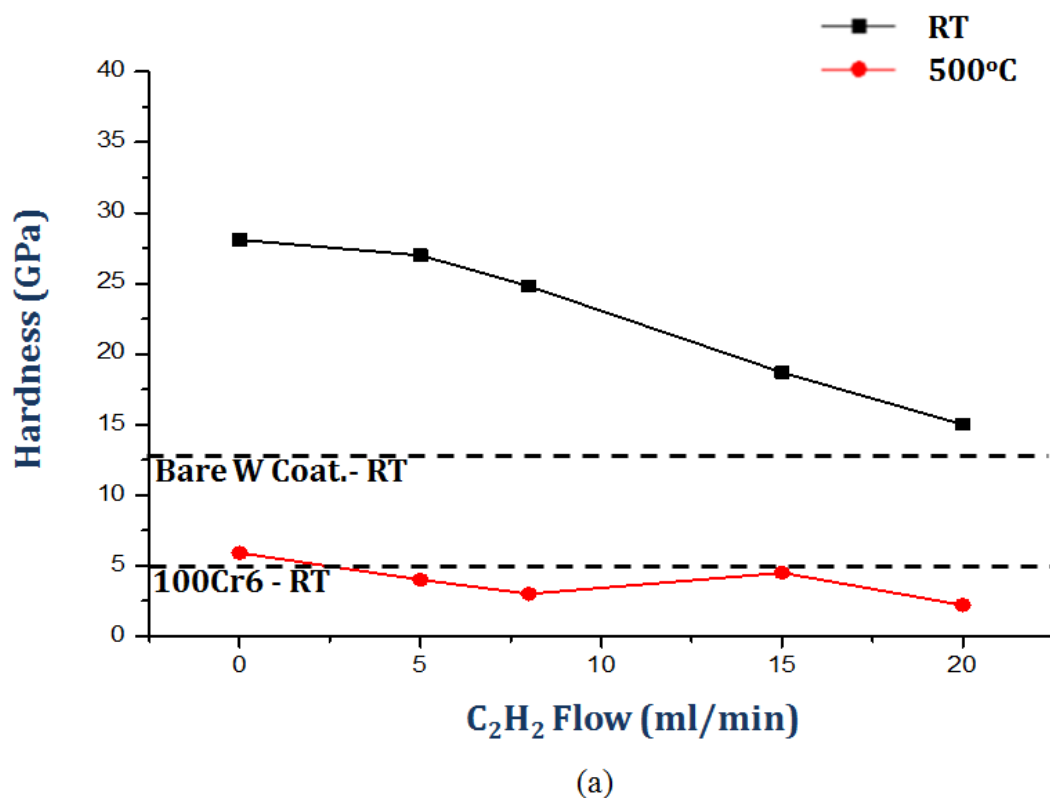


Figure 3.2.3: Detailed XPS spectra showing binding energy regions of (a) W 4f, (b) C 1s, and (c) B 1s peaks for the acetylene gas series experiments (SET 1 in Table 2.1.2). Assigned coordination ranges for each region are depicted on the corresponding peaks.

The last and the most important step is the interpretation of the hardness and wear performances of the synthesized coatings. For that matter, the hardness and wear rate plots for coatings in SET 1 are given in Figure 3.2.4a and Figure 3.2.4b, respectively. As shown in the plot, hardness of the coatings decrease with increasing C_2H_2 flow at room temperature that is most probably a result of the increase in the excess C in the films forming a softer phase. On the other hand, at 500°C hardness of these coatings suffer a serious decrease and the average hardness is even lower than pure W coating, which is represented with a dashed line on the plot. This could be due to the excess carbon in the films forming larger patches of soft amorphous regions. However, this needs to be investigated further. On the other hand, there is a slight increase in the wear rate values with increasing C_2H_2 flow at room and high temperature. Wear rates get almost ten times higher at 500°C. These results support the possibility of increasing amount of unreacted (and amorphous) C regions. Overall, flow of acetylene did not seem to provide an improvement on the properties of coatings.



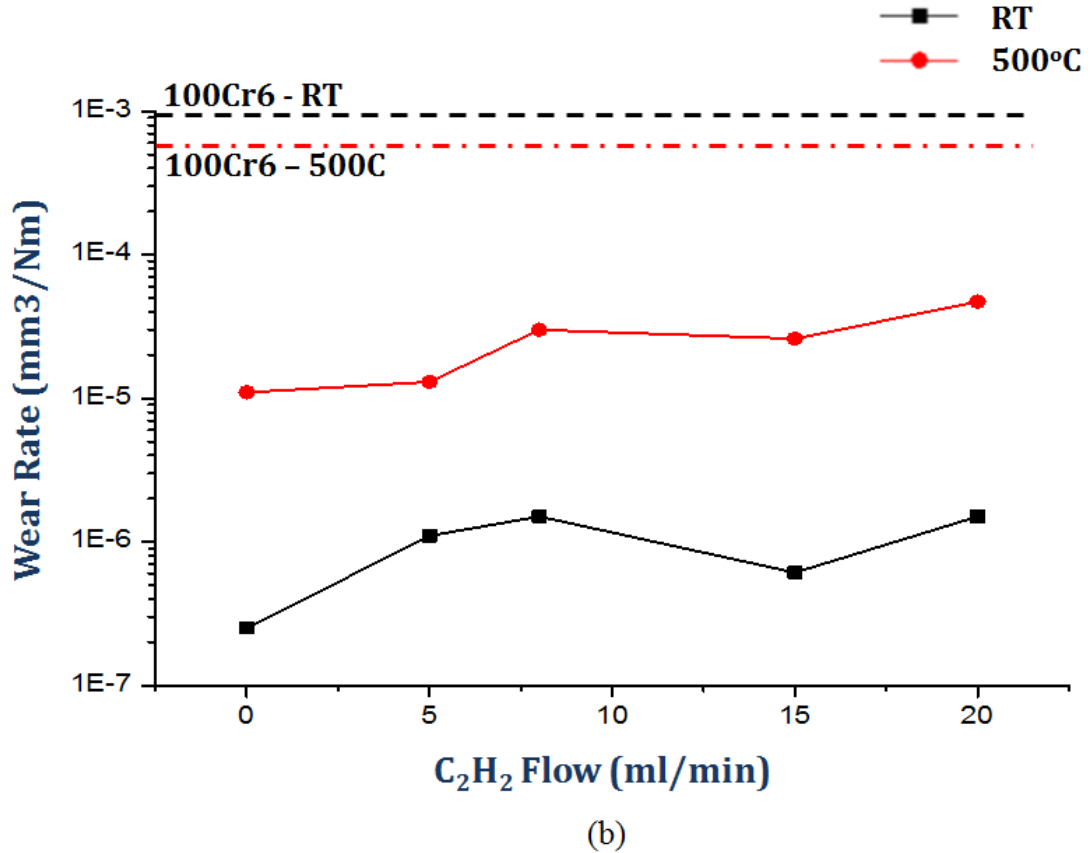
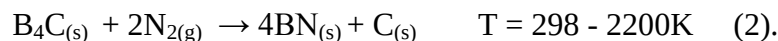


Figure 3.2.4: (a) Nano-hardness and (b) wear rate results measured at room temperature and 500°C for the acetylene gas flow experiments (SET 1).

The results of acetylene gas flow series (SET 1) indicates that during film formation it is almost inevitable to obtain large and unreacted pockets/islands of W and C. This complicates the formation of highly crystalline WC film formation due to the requirement of a) diffusion of carbon into the W-rich domains and b) the onset of WC phase formation through reaction of C with W. It can be seen from the results that the coating produced without C₂H₂ flow is superior mechanically to the coating synthesized under C₂H₂ flow. It is possible that the rate of carbon atoms reaching to the surface of the growing films is larger than the rate of WC formation. Therefore, introduction of carbon atoms to the growing film in a slower and controlled manner could be utilized for the synthesis of well crystalline and stoichiometric WC coatings. In this thesis, the use of a solid-state source for carbon is decided. For this matter, material properties of B₄C are investigated as a potential carbon source in the synthesis. B₄C consists of a

rhombohedral lattice (space group: R3m No. 166, lattice parameters: $a = 5.16 \text{ \AA}$ and $\alpha = 65.7^\circ$) where distorted $B_{11}C$ icosahedra (a geometric arrangement which contains 12 corners and 20 equilateral triangle faces) are at the corners and a 3-atom chain lies along (111) rhombohedral axis and links these icosahedra. The atoms on the chain ends bridge the neighboring icosahedra (97). Ideally, this central chain can contain at most three carbon atoms as it is seen in Figure 3.2.5, but, in general, one or two boron atoms replaces the carbons in this chain and this brings different solubility's of carbon for the boron carbide structure (98). This structural feature may lead to a significant decrease in the formation of carbon clusters on the surface of the film will be severely limited in size and carbon content during sputtering of B_4C .

On the other hand, during sputtering of B_4C even a larger amount of boron atoms will be reaching to the growing film. In order to avoid formation of the borides of tungsten, nitrogen will be used to bind excess boron from B_4C . Reaction of B_4C with N_2 gives free C atoms together with BN in a very wide range of temperatures including room temperature(77):



Furthermore, reaction of B_4C with W also results in the formation of WC as one of the products (99):



So, the appropriate combination of equations (2) and (3) may improve the possibility of depositing well-crystalline WC structures together with hexagonal BN phase (Figure 3.2.5). The possible presence of BN in the structure of the WC coatings, depending the phase of the BN may improve the hardness, wear rate and also the oxidation resistance of the coatings at room temperature as well as at high temperatures as it is mentioned in the literature (100, 101).

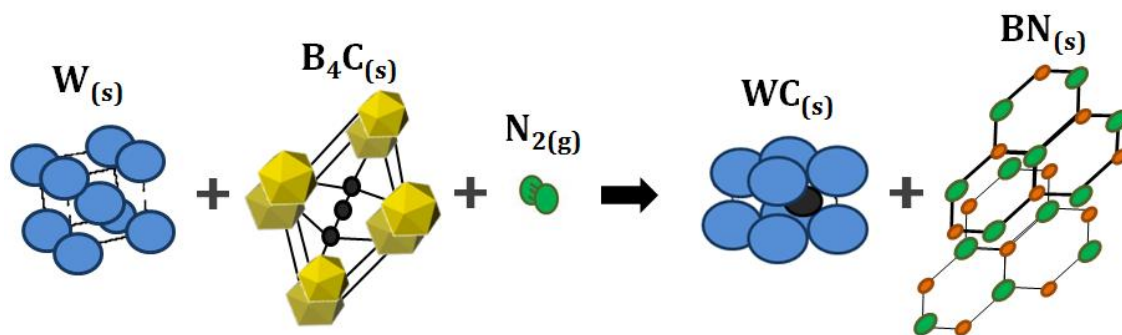


Figure 3.2.5: Schematical representation of reaction between W and B_4C where WC and BN are reaction products.

As mentioned earlier, when gaseous C sources are used, excess portion of the C atoms reaching at the substrate surface was not able to react with W atoms and form amorphous clusters as seen in Figure 3.2.6. Using higher substrate temperatures could improve the diffusion and reaction rate of C, and in literature there has been examples of post deposition annealing at excessively high temperatures such as $1000^{\circ}C$.

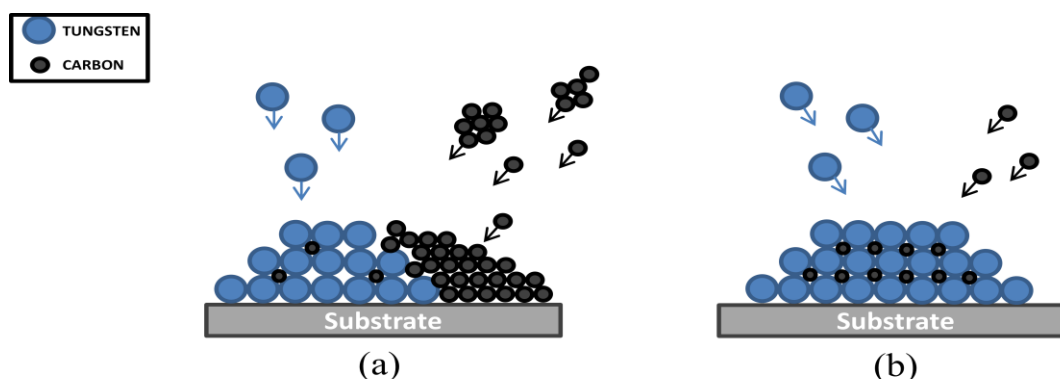


Figure 3.2.6: Schematic representation of hypothetical progress of the deposition processes in (a) where acetylene was used and, (b) with the use of B_4C as the C source.

In order to test the hypothesis of using B_4C as the carbon source, further experiments were planned and conducted for successful synthesis of WC coatings, as shown in Table 2.1.2. Finally, one more set of experiments (SET 3 in Table 2.1.2) is performed where three different coatings with various combinations of WC, WB_4C and W_2C targets were deposited.

The XRD data obtained from the coatings deposited using B₄C target was used as the carbon source (SET 2) is given in Figure 3.2.7. As it is seen on the plots, the coating on the sample just next to B₄C target contains an amorphous phase or combination of phases similar to those in the acetylene gas series. The XRD of the sample deposited in the middle of W and B₄C targets matches well with cubic WC (or β -WC_{1-x}) phase (JSPDS=07-4123) while the sample next to the W target can be identified with metallic-W (JSPDS=02-1058). For co-sputtering experiments (SET 3), XRD data of the samples sputtered with only WC targets and WC+WB₄C target combination both shows presence of cubic WC phase textured along (111) direction (Figure 3.2.7b). Here, it should be noted that WC phase in the middle sample of the SET 2 displayed a higher degree of crystallinity than the ones obtained from the WC and WC+ WB₄C co-sputtering samples (SET 3). Finally, on the last sample from WC+W₂C co-sputtering experiment in SET 3, hexagonal W₂C (α -W₂C – JSPDS=07-8653) phase appears to be the dominant crystalline phase in the structure of the coating. Another important fact is that, none of the coatings displayed any evidence for the presence of α -WC phase (most common WC phase) or any B-N related crystalline phases.

Literature on WC coatings shows that non-reactive sputtering from WC targets without substrate heating generally resulted in β -WC_{1-x} and/or α -W₂C phases. In the studies where graphite target or gaseous C sources were used, and reactive sputtering is performed, β -WC_{1-x} phase was found to be the dominant phase (77, 83, 85, 102–104). Depositions performed at low substrate temperatures also resulted in XRD plots with low intensity and broad peaks indicating nanocrystalline phases. For growing coatings with well-crystalline phases higher substrate temperatures at least in the range of 500°C were used (73, 105). In that sense, results from the coatings in SET 1 confirmed the literature. Metallic α -W phase was also observed in some studies only when the carbonaceous gas flow is low (106).

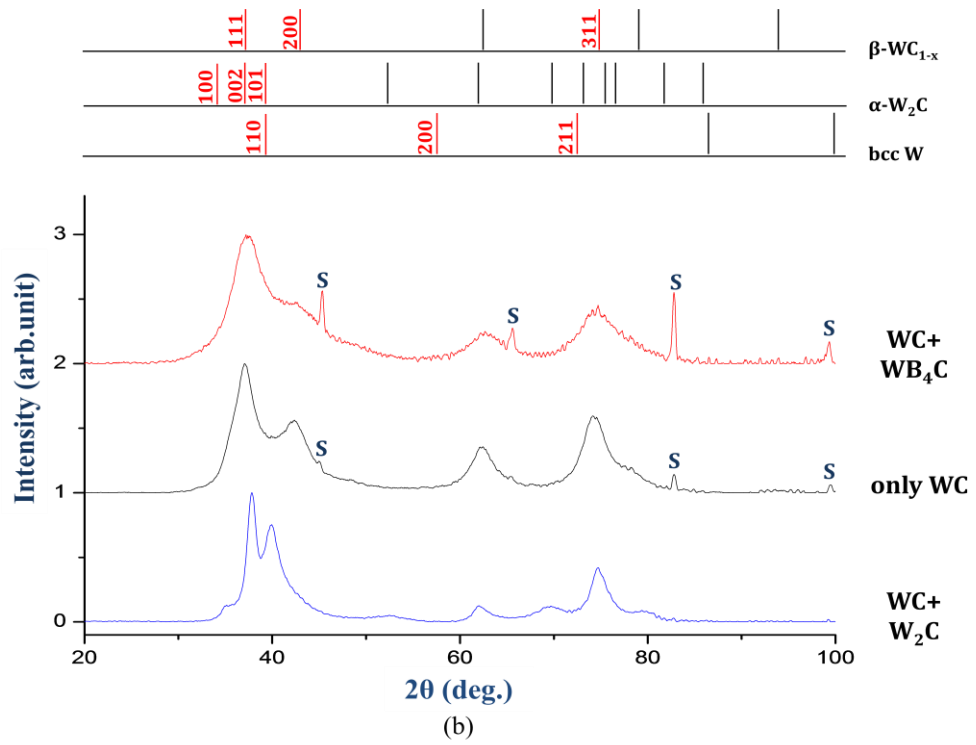
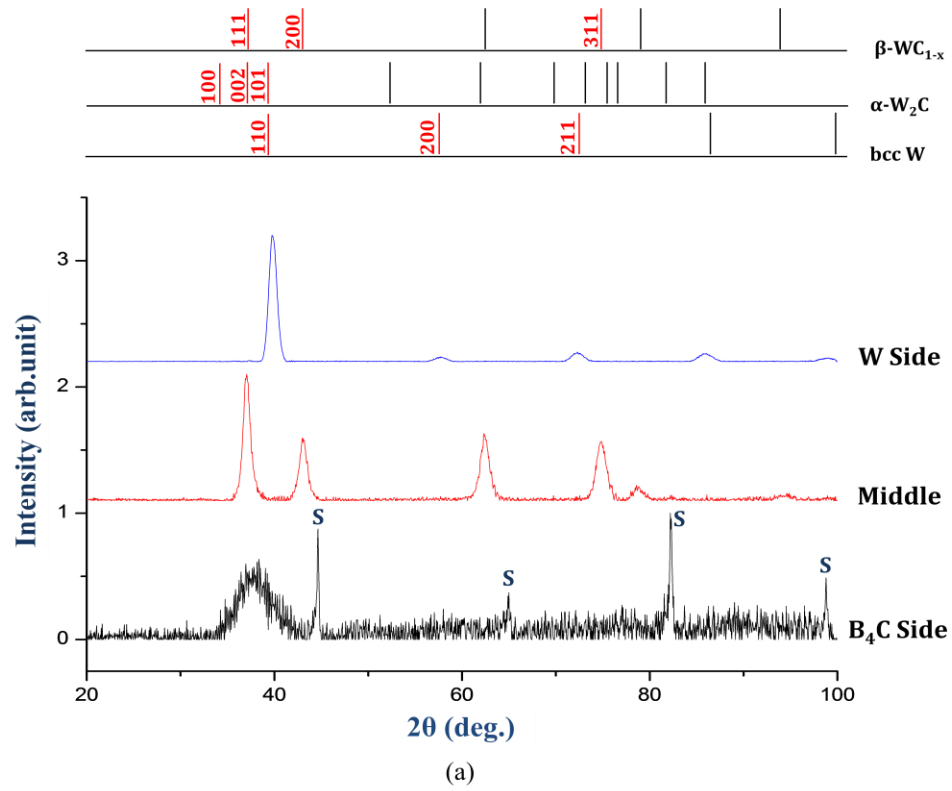


Figure 3.2.7: X-ray Diffraction Data for samples with (a) B_4C used as C source (SET 2),
(b) co-sputtering trials with different target combinations (SET 3).

Cross-sectional SEM micrographs obtained from the coatings synthesized where B_4C is used as the C source (SET 2) is given in Figure 3.2.8. The images clearly show that the coating microstructure changed from columnar to a denser structure (can be termed as nanocrystalline) when going from B_4C side to the W side in the chamber.

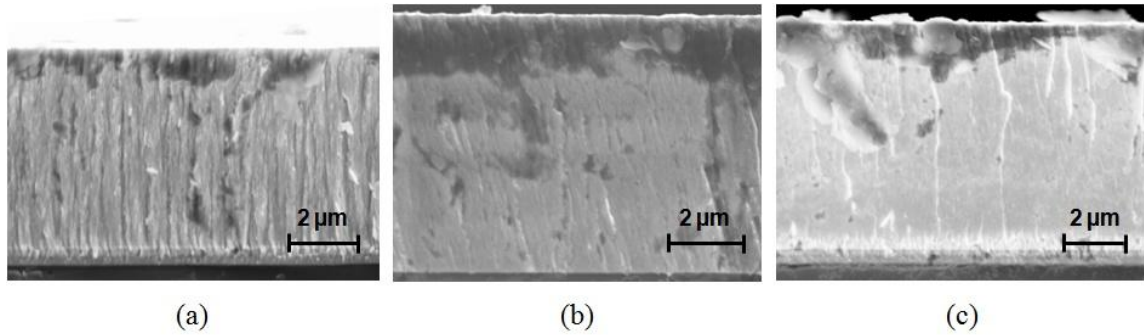


Figure 3.2.8: SEM cross-sectional images of the coatings produced in experiments that utilized B_4C as the C source (SET 2): (a) B_4C side, (b) middle, (c) W side samples.

Cross-sectional SEM images of coatings from SET 3 experiments (Figure 3.2.9) shows that all the experiments were resulted with columnar microstructures. WC+ WB_4C combination seemed to give the less dense microstructure among these experiments.

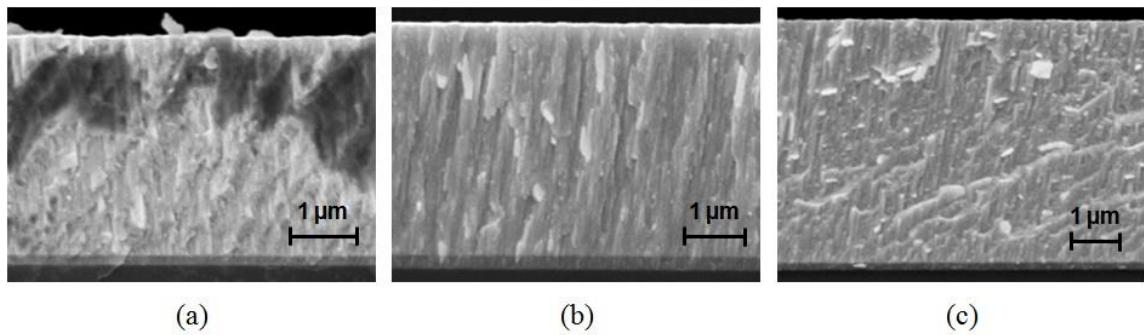
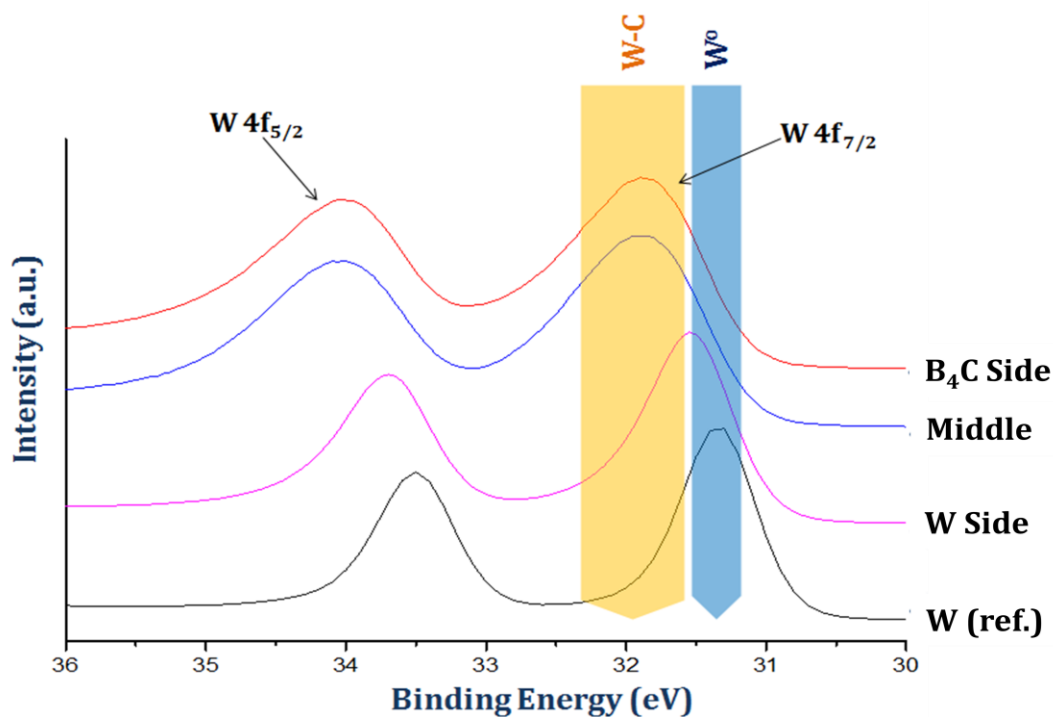


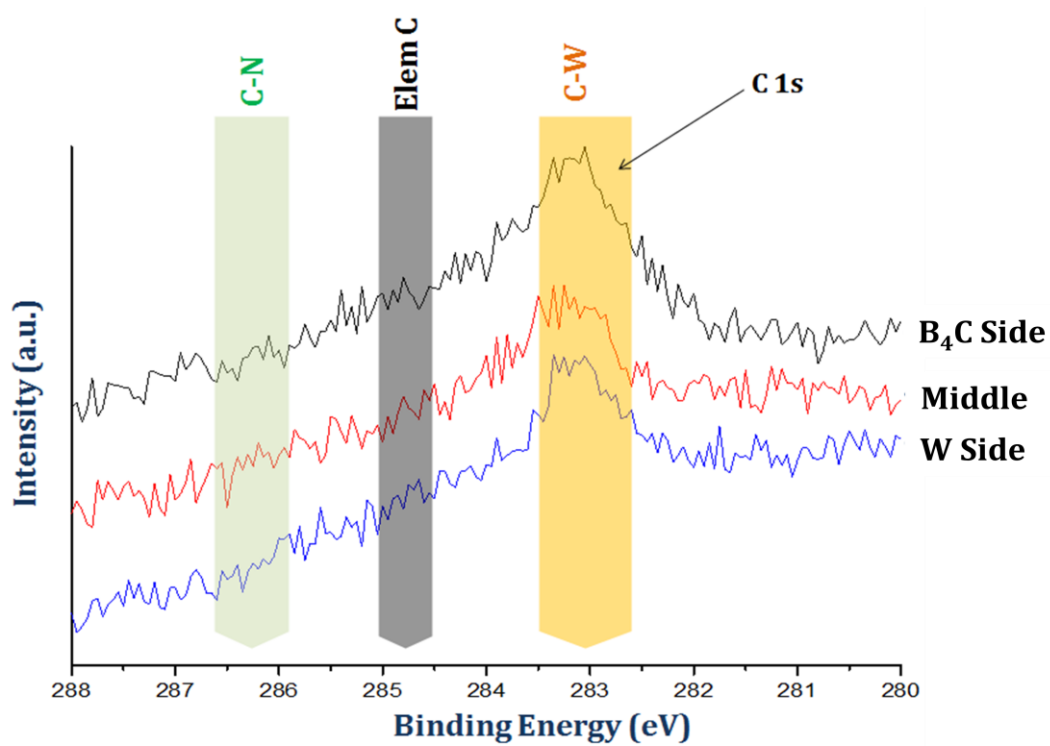
Figure 3.2.9: SEM cross-sectional images of the coatings produced during co-sputtering experiments (SET 3): sputter deposited from (a) only WC, (b) WC+ WB_4C , (c) WC+W $_2$ C targets

Further analysis of the coatings produced in SET 2 and SET 3 was done using XPS. As for the coatings in SET 2; W 4f peaks for B_4C side and middle sample suggest a strong coordination between W and C atoms, while a small low energy shoulder on the W 4f peak may suggest a small amount of W atoms are not coordinated with C and remained metallic (Figure 3.2.10a). The C 1s peak (Figure 3.2.10b) also supports the

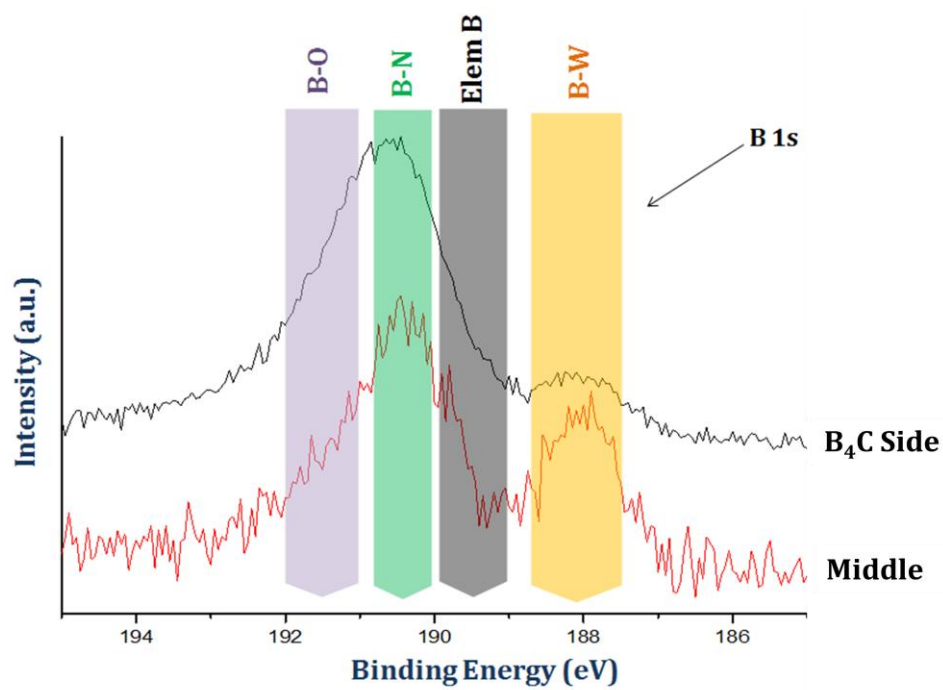
above-mentioned points by indicating that nearly all C present in these coatings to be coordinated with W atoms. Furthermore, B 1s and N 1s plots shows that B-N coordination is established as expected. Yet, still there is strong evidence that some portion of B and N atoms are interacting with W atoms in these coatings (Figure 3.2.10c and Figure 3.2.10d).



(a)



(b)



(c)

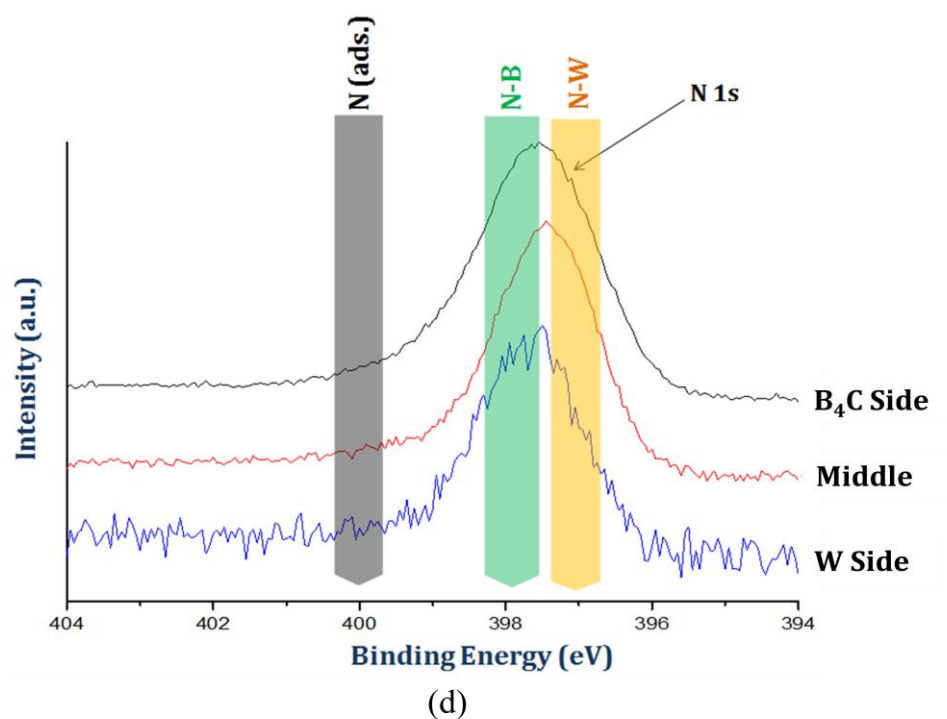
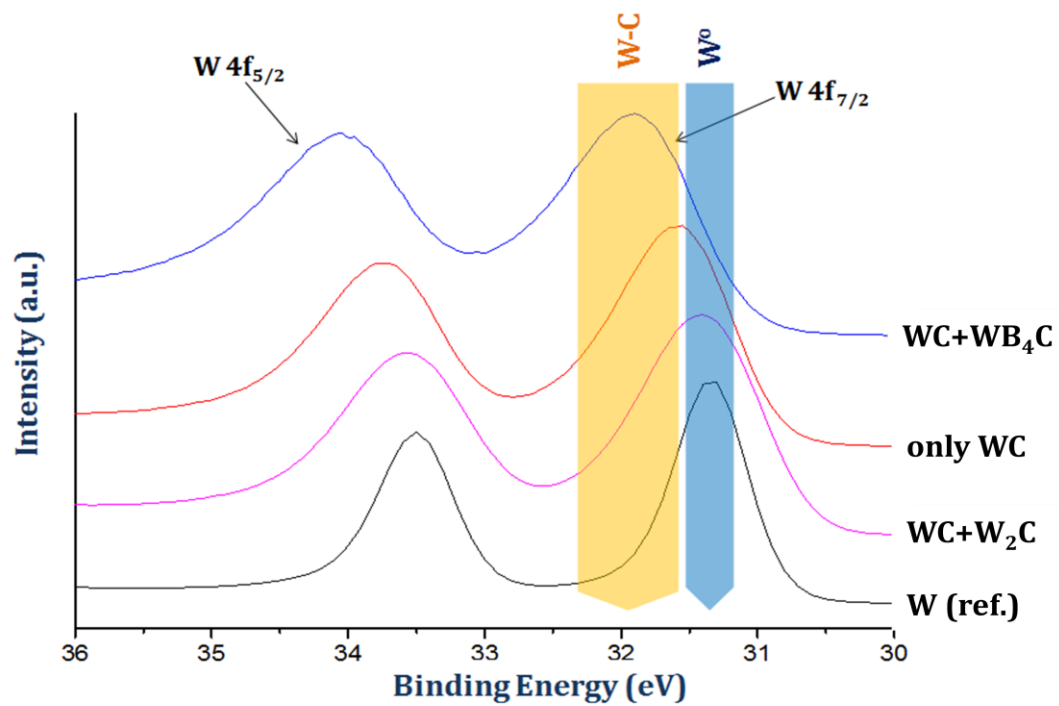


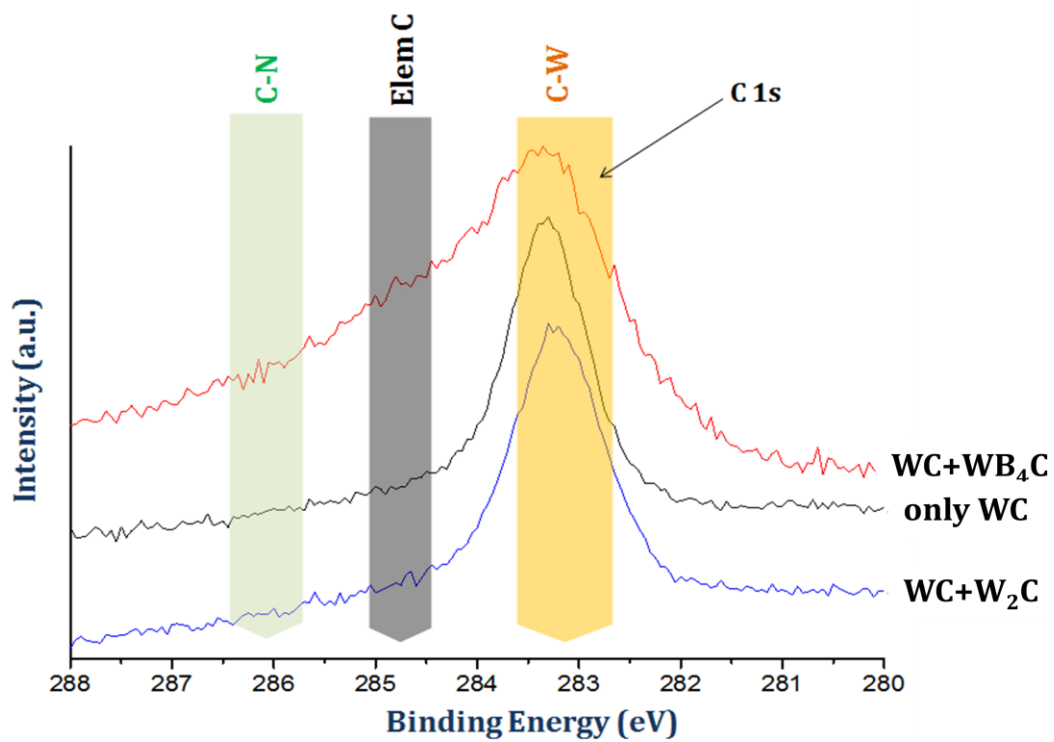
Figure 3.2.10: Detailed XPS spectra showing binding energy regions of (a) W 4f, (b) C 1s, (c) B 1s, and (d) N 1s peaks for the coatings in SET 2. Assigned coordination ranges for each region are depicted on the corresponding peaks.

The detailed analysis of the spectra from the coatings synthesized during co-sputtering experiments in SET 3 yielded unexpected results. In the binding energy spectra, W 4f binding energy data (Figure 3.2.11a) indicated that only the WC+WB₄C co-sputtered sample had fully coordinated W with C. Other coatings indicated presence of a mostly elemental W presence similar to coatings produced in SET 1. However, as mentioned earlier both samples seem to contain crystalline W-C phases according to their XRD analysis.

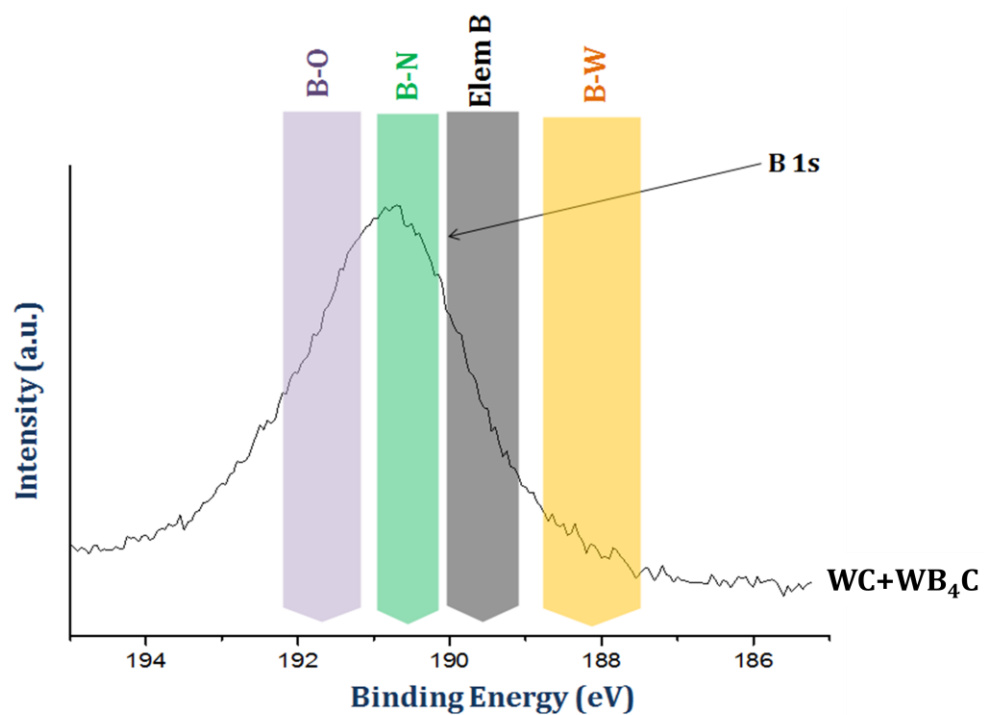
Analysis of the C 1s peaks revealed similar conclusions indicating mainly the presence of C-W coordination in the coatings except for WC+WB₄C co-sputtering sample. Here, a low energy shoulder on C 1s peak suggests that some of the C atoms in this structure remained unreacted (Figure 3.2.11b). Detailed interpretation of B 1s and N 1s peaks (Figure 3.2.11c and Figure 3.2.11d) also pointed out that B-N coordination is fairly well-established on the WC+WB₄C sample. N 1s peak of WC sputtered and WC+W₂C co-sputtered samples seems to be very small in intensity.



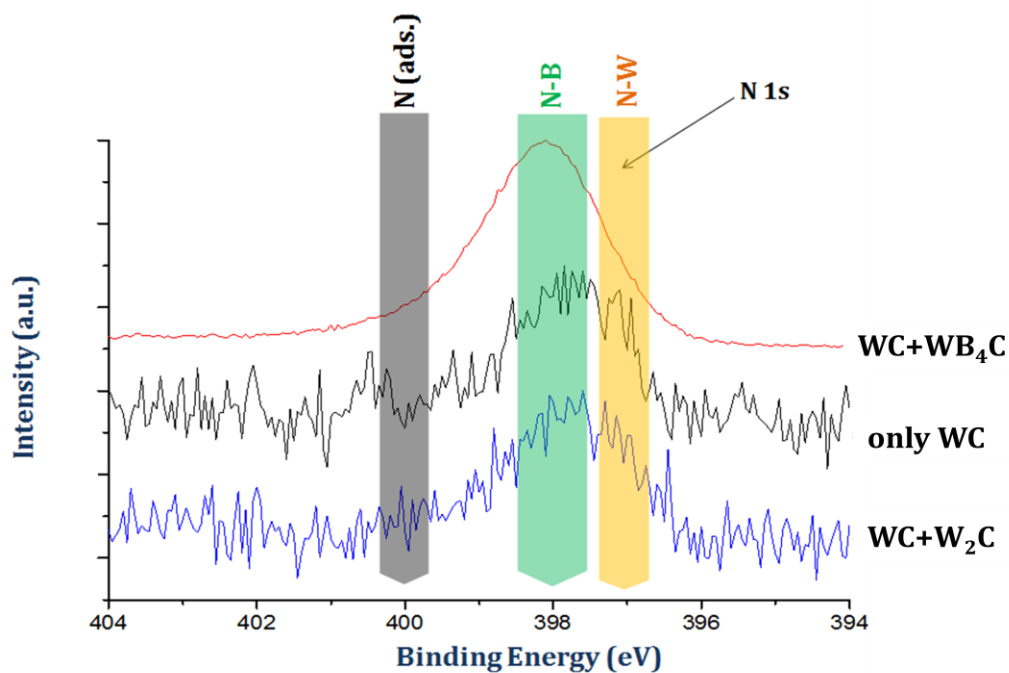
(a)



(b)



(c)



(d)

Figure 3.2.11: Detailed XPS spectra showing binding energy regions of (a) W 4f, (b) C 1s, (c) B 1s, and (d) N 1s peaks for the co-sputtering experiments in SET 3. Assigned coordination ranges for each region are depicted on the corresponding peaks.

After the analysis of the XPS results and comparison with the available literature, the coatings synthesized in SET 2 and SET 3 indicate significant common features with those in literature which are reported to be containing a dominant β -WC_{1-x} phase or lower carbon containing carbides (72, 80, 107–110). The alternative approach used in SET 2 as expected resulted in well-crystallized coatings as well.

Hardness and wear rate results for the coatings in SET 2 are given in Figure 3.2.12 (a and b). Hardness values exhibited a gradual increase for the coatings going from B₄C side to W side at room temperature. Both the middle and W-side coatings retained their hardness to a degree at 500°C. On the other hand, wear rates of the coatings were similar to each other at room temperature (at around low 10⁻⁶ mm³/Nm). However, the coating on B₄C side indicated a severe drop in wear performance at 500°C, while others retained low wear rates.

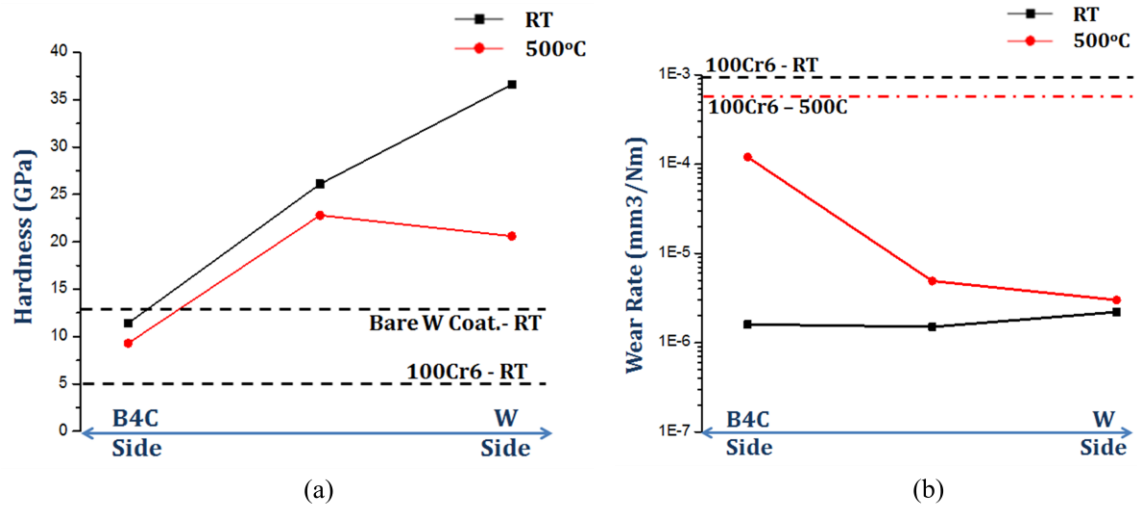


Figure 3.2.12: (a) Nano-hardness and (b) wear rate results measured at room temperature and 500°C for the coatings where B₄C is used as a C source for the synthesis of WC coatings (SET 2).

The hardness and wear rate values for the coatings in SET 3 can be seen in Figure 3.2.13 (a and b) for comparison. Hardest coating seems to be the sample sputtered from only WC targets at room temperature, but this sample could not retain its hardness at 500°C, while the WC+W₂C co-sputtered coatings does. On the other hand,

wear rates were close to each other at room temperature at around 10^{-7} levels, while all the coatings in this set suffer from wear rate degradation at 500°C.

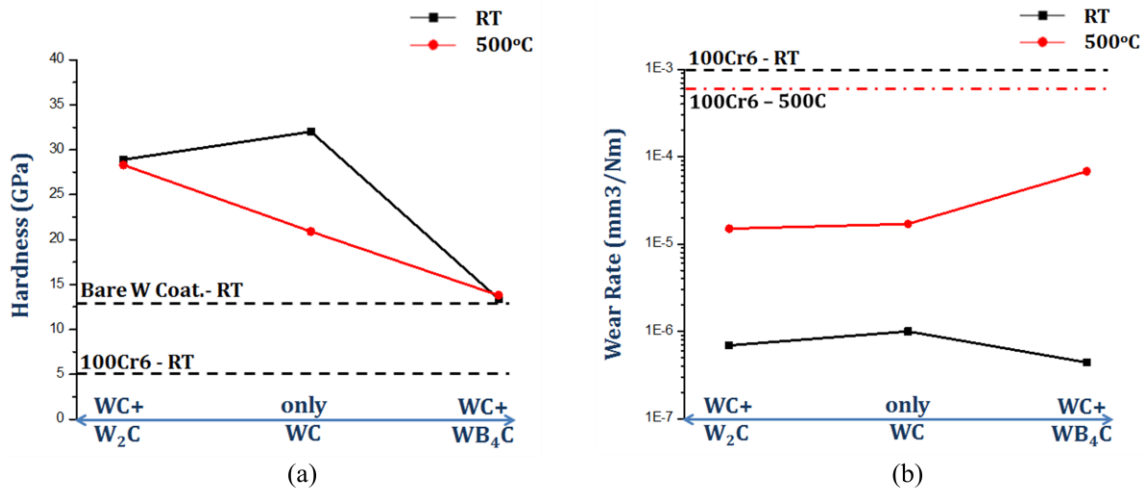


Figure 3.2.13: (a) Nano-hardness and (b) wear rate results measured at room temperature and 500°C for the co-sputtering experiments (SET 3).

Generally, in the literature, wear and related performance issues and their comparisons for WC coatings were found to be depending on the C content in the coatings. When the carbon content of the coatings were found to be increasing, hardness of the coatings were reported to be lower (76, 111, 112), friction coefficients and wear rates interestingly got better (75, 80). In the first set of coatings (SET 1) in this thesis, similar results with the literature were observed except that wear rates deteriorated with increasing acetylene flow. The reason for this could be that in the literature the main purpose for the use of acetylene was to form a DLC-like layer, while in this thesis acetylene was the only source of carbon for WC formation.

In the experiments SET 2 and SET 3, the measured hardness values (Figure 3.2.12a and Figure 3.2.13a) for the coatings at room temperature were found to be similar with those reported in the literature which were in the 26-41GPa range. As for the wear rate results reported in literature (pin-on-disc test), mostly wear rates of coatings against AISI52100 grade steel or WC balls were reported (106, 113) rather than the alumina balls as was done in this work. Hence, the comparison of the results with the literature has to be done carefully. Hence, this could be reason for lower wear rates

($\sim 10^{-7}$ or 10^{-8} mm³/Nm levels) and friction coefficients (~ 0.1 levels) reported in the literature.

4 CONCLUSION

In this thesis, several attempts were carried out to synthesize and improve the wear resistant properties of WN and WC coatings at RT as well as 500°C. Alternative and unique approaches were developed and applied for the optimization of the tribological properties of WC and WN coatings.

The results of the optimization attempts on WN coatings can be summarized as follows:

1. Nitrogen rich WN phases were found to have high RT hardness and wear rates, however both hardness and wear rates indicated a sharp drop at 500°C. Growth of the soft WO_3 phase over the WN coatings was found to be the leading cause for the deterioration of the tribological properties.
2. Nitrogen deficient WN phase synthesized with N_2 flows less than 30% displayed comparable RT hardness and hot hardness values. Also, metallic W and nitrogen deficient WN phases were found to resist oxidation better than nitrogen rich WN.
3. Multi-layer W/WN coatings where WN layers were synthesized using N_2 flow less than 30% showed almost no change in hardness and wear resistance after treatment at 500°C.
4. XPS and XRD data suggest appreciable nitrogen solubility in W despite published phase diagrams.

The results of the synthesis attempts on WC coatings can be summarized as follows:

1. XRD data did not indicate well-crystallized WC phase formation for coatings synthesized using C_2H_2 and graphite. Furthermore, upon increase in the C_2H_2 flow hardness deteriorated.
2. Use of B_4C target as a source for carbon during sputter deposition resulted in the formation of well-crystallized WC phase. Furthermore, coatings with hardness as high 37 GPa were synthesized using B_4C target. This result indicates that one of the primary barriers in synthesizing high quality WC

films could be the diffusion barrier for C in W and activation energy for required for reaction between C and W for WC formation,

3. WC films deposited using WC and W_2C targets exhibited similar hardness values to those sputter deposited using B_4C , however their high temperature wear rates were lower.

Finally, in this thesis alternative synthesis approaches were proposed and successfully applied to the deposition of WN and WC coatings. Significant improvements in hardness and wear resistance for these coatings were achieved at room and high temperature. Furthermore, data regarding both W-N and W-C systems suggest appreciable solid solubility of carbon and nitrogen in metallic W, which has been disregarded in the earlier literature.

5 FUTURE WORKS

Following the analysis described in this thesis, performing:

- Electron Energy Loss Spectroscopy (EELS) and,
- Transmission Electron Microscopy (TEM) techniques to the coatings would have helped to exactly reveal the atomic structures and chemical composition that are not being able to uncover clearly such as N₂ flow experiments for WN deposition series and acetylene (C₂H₂) flow experiments for WC deposition series.

Furthermore, several new experimental sets can be designed and operated as the ones given below:

- The thickness of W and WN layers in the W/WN multilayer experiments can be modified and tested in the same conditions.
- Heat treatments can be held for the coatings under controlled atmosphere conditions (ie. vacuum furnace) and effect of the structural changes occurred in the coatings due to these treatments can be investigated.
- The roles of B and N on the resultant performances can be clarified with the controlled experimental designs including the changes in their relative amounts in the coatings.

As an additional test opportunity, coatings can be applied on several cutting tools and drills with the same deposition parameters and the coated tools can be tested in real time conditions in machining operations. This can give an idea of the life-time of the optimized coatings and how these life-times can be increased.

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