

Performance Of CrN/TiN Coated On High Speed Steel

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Abstract: Surface modification by means of thin film deposition is an important industrial process used to protect base materials against wear, fatigue, corrosion and many other surface related damage phenomenon. Thin hard coatings such as TiN, CrN, and TiAlN have been accepted particularly in the cutting and forming tool industries. TiN and TiAlN coating widely used for dry cutting operations due to its high hardness. Especially, CrN coatings have been used to forming tool dies for its hardness and corrosion resistance. Tool steels are supplied with heat treated state, generally hardened and tempered to provide for particular application. Tool dies are precision products whose final shape and dimensions are important in micron level accuracy for production of parts. The tool steels have different machinability which varies with the chemical composition and microstructure of steels.

The objective of this project is to optimize the thickness of coat CrN on 6959 steel die components by using response surface methodology (RSM). It is very essential to substantiate the role of different sputtering conditions for achieve desired microstructural properties. The microstructural characteristics of thin film are effectively governed by sputtering parameters. The characterization of coating is to be examined by using X-rays diffraction method (XRD), scratch tester, pin on disc and microhardness tester.

I. INTRODUCTION

Surface engineering is an economic method for the production of material, tools and machine parts with required surface properties, such as wear and corrosion resistance when two surface contact, wear occur on both surface. Individuals and industry tend to focus on the wearing surface that has the greatest impact on their own economic situation, and consider the other surface to be abrasive. Plasma assisted coatings have proved themselves excellent for economical, reliable surface modification processes.

A. VAPOR DEPOSITION

There are two main groups of methods for thin film deposition, chemical vapor deposition (CVD) and physical vapor deposition (PVD). As the methods for producing the films in this work were PVD methods, the CVD is described only briefly in the beginning of this section. Chemical vapor deposition is a method where a solid film is deposited via chemical reactions at an elevated temperature.

The reactants are gaseous and any other reaction products than the film must be gases. The reaction isothermally activated, i.e. heated to a temperature often exceeding 1000 °C, what many substrates cannot endure. Note that there is possible to avoid external heating of substrates in CVD

methods assisted or induced by plasma. Advantages of CVD are the possibility for batch processing and mostly a very good film adhesion and the step coverage, i.e. the ability to cover substrates with complicated shapes.

a. PHYSICAL VAPOR DEPOSITION

Physical vapor deposition (PVD) is a concept that gathers a great number of different deposition methods where the initial material is in solid phase. And then it is turned into vapor phase during the process.

A common feature for almost all methods is that they require a low pressure (vacuum) to avoid impurities in the film. But also to avoid loss of energy of particles deliberated from the solid source due to collisions and mainly to keep enough energy of bombarding particles in sputtering (ions) or in evaporation (electrons and orions). In PVD the film is formed when the evaporated or sputtered species condensate or sublimate on the substrate and all other colder surfaces in the vacuum chamber. Unlike most of CVD techniques.

PVD processing is carried out in high vacuum at temperatures between 150 and 500°C. The high-purity, solid coating material (metals such as titanium, chromium and aluminium) is either evaporated by heat or by bombardment with ions (sputtering). At the same time, a reactive gas (e.g. nitrogen or a gas containing carbon) is forms a compound with the metal vapour and is deposited on the tools or components as a thin, highly adherent coating. In order to obtain a uniform coating thickness, the parts are rotated at uniform speed about several axes.

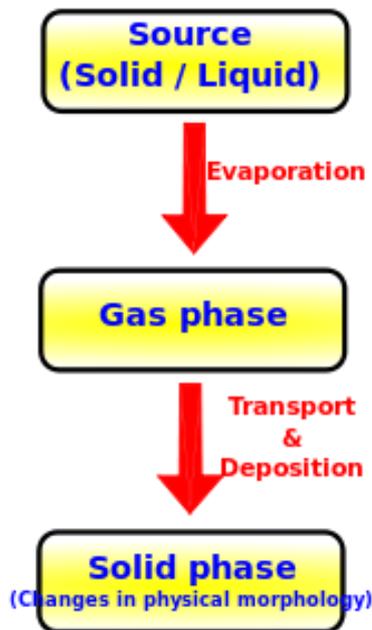


Figure 1.1: Physical Vapor Deposition

B. TYPES OF PVD PROCESSES

- ✓ Cathodic Arc Deposition
- ✓ Electron beam physical vapor deposition

- ✓ Evaporative deposition
- ✓ Pulsed laser deposition
- ✓ Sputter deposition

a. CATHODIC ARC EVAPORATION

This process, an arc with a diameter of just a few microns is run over the solid, metallic coating material, causing it to evaporate. Because of the high currents and power densities used, the evaporated material is almost totally ionised and forms a high-energy plasma. The metal ions combine with the reactive gas that is introduced into the chamber and strike the tools or components to be coated with high energy. They are deposited as a thin and highly adherent coating.

The arc evaporation process begins with the striking of a high current, low voltage arc on the surface of a cathode (known as the target) that gives rise to a small (usually a few micrometers wide), highly energetic emitting area known as a cathode spot. The localized temperature at the cathode spot is extremely high (around 15000 °C), which results in a high velocity (10 km/s) jet of vaporized cathode material, leaving a crater behind on the cathode surface.

The cathode spot is only active for a short period of time, and then it self-extinguishes and re-ignites in a new area close to the previous crater. This behavior causes the apparent motion of the arc. The arc has an extremely high power density resulting in a high level of ionization (30-100%), multiple charged ions, neutral particles, clusters and macro-particles (droplets). If a reactive gas is introduced during the evaporation process, dissociation, ionization and excitation can occur during interaction with the ion flux and a compound film will be deposited.

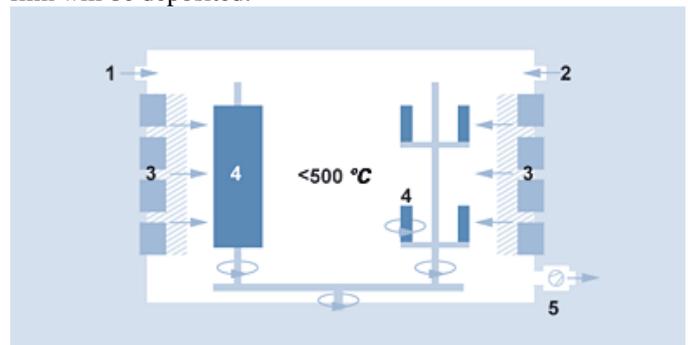


Figure 1.2: Cathodic Arc Evaporation Model

b. ELECTRON BEAM PHYSICAL VAPOR DEPOSITION

Electron Beam Physical Vapor Deposition is a form of physical vapor deposition in which a target anode is bombarded with an electron beam given off by a charged tungsten filament under high vacuum. The electron beam causes atoms from the target to transform into the gaseous phase. These atoms then precipitate into solid form, coating everything in the vacuum chamber with a thin layer of the anode material.

Upon striking the evaporation material, the electrons will lose their energy very rapidly. The kinetic energy of the electrons is converted into other forms of energy through interactions with the evaporation material. The thermal energy

that is produced heats up the evaporation material causing it to melt or sublimate. The resulting vapor can then be used to coat surfaces. Accelerating voltages can be between 3 kV – 40 kV.

When the accelerating voltage is between 20 kv-25 kV and the beam current is a few amperes, 85% of the electron's kinetic energy can be converted into thermal energy. Some of the incident electron energy is lost through the production of X-rays and secondary electron emission. There is three main EBPVD configurations, electromagnetic alignment, electromagnetic focusing and the pendant drop configuration.

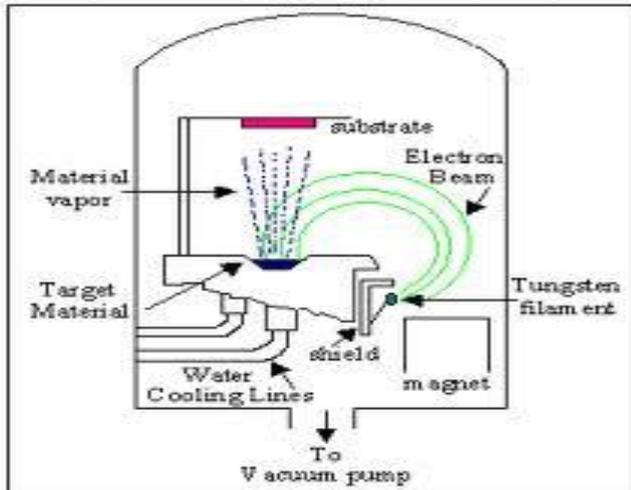


Figure 1.3: Electron Beam Physical Vapor Deposition

c. EVAPORATIVE DEPOSITION

Evaporation is a common method of thin film deposition. The source material is evaporated in a vacuum. The vacuum allows vapor particles to travel directly to the target object (substrate), where they condense back to a solid state. Evaporation is used in micro fabrication, and to make macro-scale products such as metalized plastic film. Evaporation involves two basic processes are hot source material evaporates and condenses on the substrate. It resembles the familiar process by which liquid water appears on the lid of a boiling pot. However, the gaseous environment and heat source are different.

Evaporation takes place in a vacuum, i.e. vapors other than the source material are almost entirely removed before the process begins. In high vacuum evaporated particles can travel directly to the deposition target without colliding with the background gas. Hot objects in the evaporation chamber, such as heating filaments, produce unwanted vapors that limit the quality of the vacuum. Evaporated atoms that collide with foreign particles may react with them. For instance, if aluminium is deposited in the presence of oxygen, it will form aluminium oxide. They also reduce the amount of vapor that reaches the substrate, which makes the thickness difficult to control.

d. PULSED LASER DEPOSITION

Pulsed laser deposition is a thin film deposition technique where a high power pulselaser beam is focused inside a vacuum chamber to strike a target of the material that is to be deposited.

This process can occur in ultra-high vacuum or in the presence of a background gas, such as oxygen which is commonly used when depositing oxides to fully oxygenate the deposited films. PLD are very complex including the ablation process of the target material by the laser irradiation.

The development of a plasma flame with high energetic ions, electrons as well as neutrals and the crystalline growth of the film itself on the heated substrate. The process of PLD can generally be divided into four stages

- ✓ Laser ablation of the target material and creation of a plasma
- ✓ Dynamic of the plasma
- ✓ Deposition of the ablation material on the substrate
- ✓ Nucleation and growth of the film on the substrate surface



Figure 1.4: Pulsed Laser Depositions

e. SPUTTER DEPOSITION

Sputter deposition is a physical vapor deposition of depositing thin films by sputtering. This involves ejecting material from a "target" that is a source onto a "substrate" such as a silicon wafer. Sputtered atoms ejected from the target have a wide energy distribution, typically up to tens of eV (100,000 K). The sputtered ions can ballistically fly from the target in straight lines and impact energetically on the substrates or vacuum chamber.

Alternatively, at higher gas pressures, the ions collide with the gas atoms that act as a moderator. The entire range from high-energy ballistic impact to low-energy thermalized motion is accessible by changing the background gas pressure. The sputtering gas is often an inert gas such as argon.

For efficient momentum transfer, the atomic weight of the sputtering gas should be close to the atomic weight of the target, so for sputtering light elements neon is preferable, while for heavy elements krypton or xenon are used.

Reactive gases can also be used to sputter compounds. The compound can be formed on the target surface, in-flight or on the substrate depending on the process parameters. The availability of many parameters that control sputter deposition make it a complex process, but also allow experts a large degree of control over the growth and microstructure of the film.

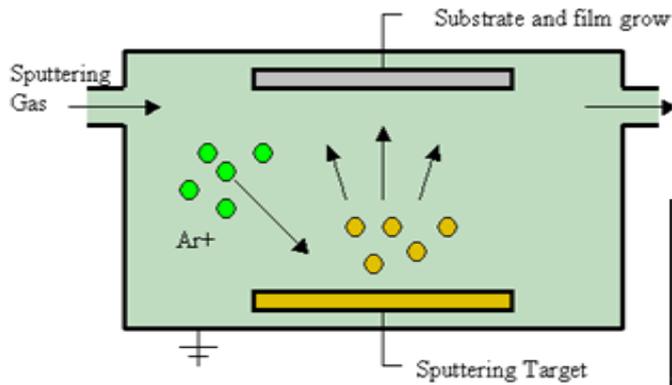


Figure 1.5: Sputtering Physical Vapour Deposition

C. TYPES OF SPUTTER DEPOSITION

Sputtering sources often employ magnetrons that utilize strong electric and magnetic fields to confine charged plasma particles close to the surface of the sputter target. In magnetic field electrons follow helical paths around magnetic field lines undergoing more ionizing collisions with gaseous neutrals near the target surface than would otherwise occur. (As the target material is depleted, a "racetrack" erosion profile may appear on the surface of the target.) The sputter gas is typically an inert gas such as argon. The extra argon ions created as a result of these collisions leads to a higher deposition rate. It also means that the plasma can be sustained at a lower pressure.

The sputtered atoms are neutrally charged and so are unaffected by the magnetic trap. Charge build-up on insulating targets can be avoided with the use of RF sputtering where the sign of the anode-cathode bias is varied at a high rate (13.56 MHz). RF sputtering works well to produce highly insulating oxide films but with the added expense of RF power supplies and impedance matching networks. Stray magnetic fields leaking from ferromagnetic targets also disturb the sputtering process. Specially designed sputter guns with unusually strong permanent magnets must often be used in compensation.

- ✓ Ion-beam sputtering
- ✓ Reactive sputtering
- ✓ Ion-assisted deposition
- ✓ High target utilization sputtering
- ✓ High power impulse magnetron sputtering
- ✓ Gas flow sputtering

a. ION-BEAM SPUTTERING

Ion-beam sputtering is a method in which the target is external to the ion source. A source can work without any magnetic field like in a hot filament ionization gauge.

Since the flux that strikes the target is composed of neutral atoms, either insulating or conducting targets can be sputtered. IBS has found application in the manufacture of thin-film heads for disk drives. A pressure gradient between the ion source and the sample chamber is generated by placing the gas inlet at the source and shooting through a tube into the sample chamber. This saves gas and reduces contamination in UHV application

b. REACTIVE SPUTTERING

In reactive sputtering, the deposited film is formed by chemical reaction between the target material and a gas which is introduced into the vacuum chamber. Oxide and nitride films are often fabricated using reactive sputtering. The composition of the film can be controlled by varying the relative pressures of the inert and reactive gases. Film stoichiometry is an important parameter for optimizing functional properties like the stress in SiN_x and the index of refraction of SiO_x .

c. ION-ASSISTED DEPOSITION

In ion-assisted deposition, the substrate is exposed to a secondary ion beam operating at a lower power than the sputter gun. Usually a Kaufman source like that used in IBS supplies the secondary beam. IAD can be used to deposit carbon in diamond-like form on a substrate. Any carbon atoms landing on the substrate which fail to bond properly in the diamond crystal lattice will be knocked off by the secondary beam. IAS is used in other important industrial applications such as hard transition metal nitride coatings on medical implants.

d. HIGH-TARGET-UTILIZATION SPUTTERING

Sputtering may also be performed by remote generation of high density plasma.

The plasma is generated in a side chamber opening into the main process chamber, containing the target and the substrate to be coated. As the plasma is generated remotely, and not from the target itself, the ion current to the target is independent of the voltage applied to the target.

e. HIGH-POWER IMPULSE MAGNETRON SPUTTERING

HIPIMS is a method for physical vapor deposition of thin films which is based on magnetron sputter deposition. HIPIMS utilizes extremely high power densities of the order of kW/cm^2 in short pulses (impulses) of tens of microseconds at low duty cycle.

f. GAS FLOW SPUTTERING

Gas flow sputtering makes use of the hollow cathode effect, the same effect by which hollow cathode lamps operate. In gas flow sputtering a working gas like argon is led through an opening in a metal subjected to a negative electrical potential. Enhanced plasma densities occur in the hollow cathode, if the pressure in the chamber p and a characteristic dimension L of the hollow cathode.

D. PLASTIC MOULDING

Plastics are synthetically produced non-metallic compounds. It can be molded into various forms and hardened for commercial use. Plastic molding products can be seen everywhere. Examples are jars, protective caps, plastic tubes,

grips, toys, bottles, cases, accessories, kitchen utensils and a lot more. The basic idea in plastic molding is inserting molten liquid plastic into a ready shaped mold. For example the mold of a bottle. It will be then allowed to cool, and then the mold will be removed to reveal the plastic bottle. Plastic molding can also custom-mold a wide variety of plastic products such as garden pots, cabinets, office trays and boxes, barriers, barricades and traffic signage etc.

E. TYPES OF PLASTIC MOULDING

a. INJECTION MOULDING

In Injection Moulding, melted plastic is forced into a mold cavity. Once cooled, the part can be removed. This plastic moulding process is commonly used in mass-production or prototyping of a product. These can be used for production of toys, kitchen utensils, and cell phone stands to name a few.

b. BLOW MOULDING

Blow moulding is like injection moulding except that hot liquid plastic pours out of a barrel vertically in a molten tube. The mold closes on it and forces it outward to conform to the inside shape of the mold. When it is cooled, the hollow part is formed.

Examples of blow moulding products are bottles, tubes and containers. Equipment needed in setting-up a blow moulding business is relatively higher than injection molding.

c. COMPRESSION MOULDING

In this type of plastic moulding, a slug of hard plastic is pressed between two heated mold halves. Compression moulding usually uses vertical presses instead of the horizontal presses used for injection and blow moulding. The parts formed are then air-cooled. Prices of equipment used for compression moulding are moderate.

d. FILM INSERT MOULDING

This plastic moulding technique imbeds an image beneath the surface of a molded part. A material like film or fabric is inserted into a mold. Plastic is then injected.

e. GAS ASSIST MOULDING

Gas injection moulding is used to create plastic parts with hollow interiors. Partial shot of plastic is then followed by high-pressure gas to fill the mold cavity with plastic.

f. ROTATIONAL MOULDING

Hollow molds packed with powdered plastic are secured to pipe-like spokes that extend from a central hub. The molds rotate on separate axes at once. The hub swings the whole mold to a closed furnace room causing the powder to melt and stick to the insides of the tools. As the molds turn slowly, the tools move into a cooling room.

Here, sprayed water causes the plastic to harden into a hollow part. In this type of plastic moulding, tooling costs are low and piece prices are high. Cycle time takes about 40-45 minutes.

g. STRUCTURAL FOAM MOULDING

Structural foam molding is a process of plastic molding usually used for parts that require thicker walls than standard injection molding. Inserting a small amount of nitrogen or chemical blow agent into the plastic material makes the walls thicker. Foaming happens as the melted plastic material enters the mold cavity. This type of plastic molding can be used with any thermoplastic that can be injection molded.

h. THERMOFORMING

In this plastic molding process, sheets of pre-extruded rigid plastics are horizontally heated and sucked down into hollow one-piece tools. When the hot plastic solidifies, its shape conforms to that of the mold.

i. CENTRAL COMPOSITE DESIGN (CCD)

CCD is the most popular second order design is a factorial or fractional factorial design with centre point and star points. The star points are added to estimate the curvature. The factorial design points in CCD contribute to the estimation of the interaction terms.

A second-order model can be constructed efficiently with central composite designs. CCD is first-order (2N) designs augmented by additional centre and axial points to allow estimation of the tuning parameters of a second-order model. Figure shows a CCD for 3 design variables.

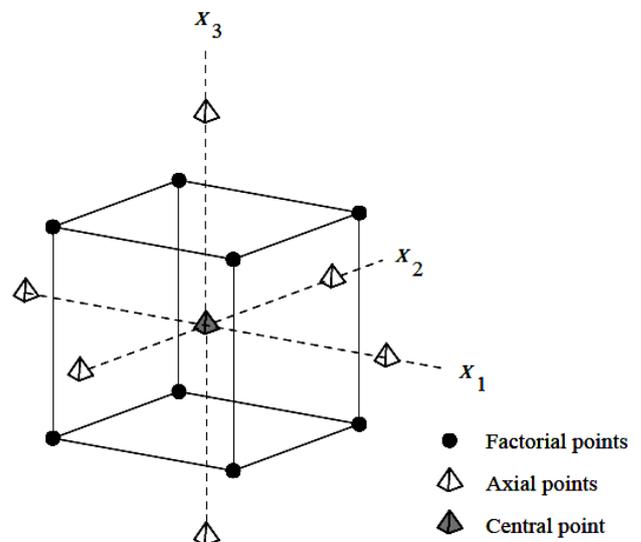


Figure 1.6: CCD

Central composite design for 3 design variables at 2 levels. In Figure, the design involves 2N factorial points, 2N axial points and 1 central point. CCD presents an alternative to 3N designs in the construction of second-order models because the number of experiments is reduced as compared to a full factorial.

II. LITERATURE REVIEW

- A. "MICROSTRUCTURAL CHARACTERIZATIONS AND HARDNESS EVALUATION OF D.C. REACTIVE MAGNETRON SPUTTERED CRN THIN FILMS ON STAINLESS STEEL SUBSTRATE" BY HETAL N SHAH ET AL., BULL IN MATER. SCI., VOL. 33, NO. 2, APRIL 2010, PP. 103–110. © INDIAN ACADEMY OF SCIENCES.

Investigate the microstructural characterization of CrN coating on stainless steels as a function of substrate temperature, working pressure and power. At low working pressure residual stress buildup on the thin film. Deposition rate is decreased with increase in working pressure due to decrease in MFP. The stress induced in the film decrease within increase in pressure.

Microhardness of thin film decreases with increase of pressure. It is because of presence of crystal imperfection in film growth. Low temperature causes residual stress which leads to poor adhesion between film and substrate. The microhardness of thin film is increased with increase in temperature due to grain refinement. The mobility of atoms leads to more perfect structure. This leads to reduction in grain size which increases the minimum stress required to activate the dislocation.

- B. "CORROSION OF STAINLESS STEEL COATED WITH TIN, (TiAl) N AND CrN IN AQUEOUS ENVIRONMENTS" BY M.A.M.IBRAHIM, S.F. KORABLOV AND M.YOSHIMURA IN CORROSION SCIENCE 44 (2002) 815-828.

The corrosion behavior of TiN and CrN coated on M2 HSS by physical vapor deposition was examined in 8 M NaCl solution. The study was performed using open circuit potential, potentiodynamic polarization and cyclic polarization techniques, complemented with XRD and laser microscopy. However they are prone to corrosive attack as consequence of the presence of microstructure defects such as pinholes and pores.

- C. "CHARACTERIZATION OF LOW TEMPERATURE CRN AND TIN (PVD) HARD COATINGS" BY B. NAVINSEK, P. PANJAN, A. CVELBAR IN ELSEVIER SURFACE AND COATINGS TECHNOLOGY 74 – 75 (1995) 155-161.

The plasma beam sputtering process was used to prepare CrN and TiN hard coatings on steel, sapphire and alumina Superstrate substrates at a temperature of 200°C. The microstructural characteristics, coating morphology, interfacial properties, microhardness and internal stresses were studied for coatings 3 μm thick. Their oxidation behaviour in an oxygen flow in a tube furnace was studied at temperatures up to 600°C for TiN and up to 800°C for CrN coatings.

The initial stage of oxidation of TiN and CrN coatings 350 nm thick was also studied by continuous electrical resistivity measurements. This measurement technique offers high reproducibility and accuracy, so can be used to study

oxidation for all types of hard coating, and especially for new multilayer and duplex coatings. Weight gain measurements and Auger electron spectroscopy depth profile analyses of oxidized stoichiometric CrN coatings showed that oxidation in an oxygen flow at 800°C for 4 h induced the growth of a stable Cr₂O₃ film.

The thickness of this oxide film was only 15% of the total (3 μm) coating thickness. The surface morphology and small roughness changes - as also observed after a long-term test at 800 °C for 200 h in oxygen - indicated that a stoichiometric CrN coating with the measured properties can be successfully.

- D. "OPTIMIZATION OF NITRIDED CASE STRUCTURE IN COMPOSITE LAYERS CREATED BY DUPLEX TREATMENT ON THE BASIS OF PVD COATING ADHESION MEASUREMENT" BY J.WALKOWICZ, J.SMOLIK, J. TACIKOWSKI IN SURFACE AND COATINGS TECHNOLOGY 116–119 (1999) 370–379.

The paper concerns the process of the composite: 'nitrided layer-PAPVD coating' creation on substrates made of hot working steel. The composite properties are determined by the appropriate selection of coating parameters and nitrided case structure. The results of research concerning the influence of a method of substrate nitriding and the created nitrided case structure on the adhesion and plastic properties of the PAPVD coatings are presented in the paper. Substrates made of hot working steel EN X₃₅CrMoV₅ (0.4% C, 0.4% Mn, 1.0% Si, 5.0% Cr, 1.3% Mo, 0.3% V) underwent different processes of thermo-chemical and finishing surface treatment in order to obtain a nitrided layer of a different structure: Fea(N), Fea(N)+'white layer'-e,c³/₄.

Research was carried out for nitrided layers created in a controlled gas nitriding process. Four different coatings of nitrides, TiN, Ti(C,N), CrN, (Ti,Cr)N, were deposited on substrates with nitrided layers using the arc-vacuum method and the MZ-383 equipment manufactured by Metaplas Ion. Thanks to an appropriately selected coating material (e.g. CrN), it is possible to create the composite nitrided layer (Fea(N)+'white layer' e and c³/₄)+PAPVD coating. This is important for composites, where the nitrided layer is created together with the 'white layer' of iron nitrides e and c³/₄ on the surface. The feasibility of in-process structuring for producing controllable thin film morphologies with features suitable for the modification of tribological properties was indicated. The coarser surface structures seem to act as lubricant reservoirs and wear debris traps, in contrast to surfaces that do not contain sufficient pores and crevices.

- E. "IN-PROCESS STRUCTURING OF CRN COATINGS, AND ITS INFLUENCE ON FRICTION IN DRY AND LUBRICATED SLIDING" BY S. ORTMANN ET AL., IN JOURNAL OF MATERIALS PROCESSING TECHNOLOGY 187–188 (2007) 566–570.

In this study, CrN coatings deposited by plasma-activated physical vapor deposition (PAPVD) on hard metal substrates were structured by variation of the deposition parameters that were varied. In this study, the bias voltage was determined to have the greatest influence on the surface structure of the

coatings. A wide variety of structures ranging from only somewhat creviced to highly creviced were fabricated, with grain sizes ranging from 5 to 500 nm.

The feasibility of in-process structuring for producing controllable thin film morphologies with features suitable for the modification of tribological properties was indicated. In ball-on-disk tests run under conditions of minimal, single-application lubrication with mineral oil, the highly textured surfaces with larger, well-defined grains and crevices showed better sliding wear endurance and lower friction coefficients than smoother, denser surfaces. The coarser surface structures seem to act as lubricant reservoirs and wear debris traps, in contrast to surfaces that do not contain sufficient pores and crevices.

F. "SUBSTRATE DEPENDENCE OF THE SCRATCH RESISTANCE OF CRN_x COATINGS ON STEEL" BY J.-D. KAMMINGA ET AL., BYK.-D. BOUZAKIS, G. SKORDARISA, E. BOUZAKISA, B. A. TSOUKNIDASA, S. MAKRIMALLAKISA, S. GERARDISA, G. KATIRTZOGLUA, IN MANUFACTURING TECHNOLOGY 60 (2011) 587–590.

In this paper, the effect of substrate hardness on the scratch test performance is explored. CrN_x hard coatings sputter deposited under various nitrogen flows on two different steel types were subjected to scratch testing. Two different failure mechanisms that occurred, i.e. coating chipping and complete coating removal, were investigated. The critical loads for chipping and complete coating removal are higher for coatings deposited on the harder steel.

Substrate independent measures for the onset of failure are obtained if critical track widths are considered instead of critical loads. The composite scratch hardness can be written as the product of the track width independent substrate scratch hardness and a track width dependent function $b(w)$ that depends on the coating properties, but that is substrate independent. The volume law of mixtures model by Burnett and Rickerby, originally intended to describe the composite Vickers hardness cannot be used for the scratch hardness. Upon loading a coated specimen in the scratch test, the hardening of the specimen due to the presence of the coating increases with increasing load until chipping of the coating occurs.

G. "CRN/ALN SUPERLATTICE COATINGS SYNTHESIZED BY PULSED CLOSED FIELD UNBALANCED MAGNETRON SPUTTERING WITH DIFFERENT CRN LAYER THICKNESSES" BY JIANLIANG LIN ET AL., IN APPLIED SURFACE SCIENCE 255 (2008) 1865–1869.

In this study the influence of coating thickness on microstructural characteristics of CrN/AlN super lattice coating was investigated. CrN/AlN super lattice coatings with different CrN layer thicknesses were synthesized in a pulsed closed field unbalanced magnetron sputtering system by varying the Cr target powers, while keeping the Al target

power and the settle periods of the substrate in front of the targets constantly.

It was found that the bilayer period (CrN layer thickness) was decreased almost linearly with a simultaneously increase in the Al/ (Cr+Al) ratios in the coatings. The decrease in the CrN layer thickness led to a decrease in the lattice parameter and the residual stress, which are possibly due to the increased Al content and the number of the interfaces in the coatings.

H. "EFFECT OF COATING THICKNESS AND DEPOSITION METHODS ON THE STRIPPING RATE OF CR–N COATINGS" BY J.C. AVELAR-BATISTA ET AL., IN MATERIAL SCIENCE (235-242).

In this work, Cr–N coatings deposited by magnetron sputtering, arc and electron beam evaporation, having different thicknesses, were wet-stripped. The stripping rate was evaluated by statistical analyses for each deposition method and thickness. Moreover, the stripping rate was not influenced by changes in the coating structure with increased thickness, which occurred in arc and electron beam Cr–N coatings.

The highest stripping rate recorded for magnetron Cr–N coatings could not be explained by changes in coating structure/morphology and surface roughness. The differences in the stripping were attributed to the amount of CrN phase present in the coatings.

I. "INFLUENCE OF NITROGEN FLOW RATES ON MATERIALS PROPERTIES OF CRN_x FILMS GROWN BY REACTIVE MAGNETRON SPUTTERING" BY B SUBRAMANIAN ET AL., IN MEASUREMENT 50 (2014) 19–28.

They Investigated influence of nitrogen flow rates on the materials properties of reactive magnetron sputtered chromium nitride (CrN_x) thin films. They finalized that grain size increases with the increase in the nitrogen flow rate. The CrN films deposited at low nitrogen flow rate showed that the electrical resistivity correspond to a metallic-like behavior and the films prepared at higher Nitrogen flow rate and above showed a semiconducting behavior.

Increase in nitrogen flow rate increases the grain size. This is due to MFP of particles are shorter and they decrease with increase in nitrogen flow rate. At low nitrogen flow pure CrN phase exist.

III. METHODOLOGY

A. SELECTION OF TOOL STEEL

The tool steels used for plastic or rubber moulds normally classified or supplied with a) Pre-hardened steels b) annealed steels c) age hardening steels

a. PRE-HARDENED STEELS

The pre-hardened steels are supplied in hardened and tempered condition. Then straightly goes to production processes with no need of immediate heat treatment processes.

ADVANTAGE

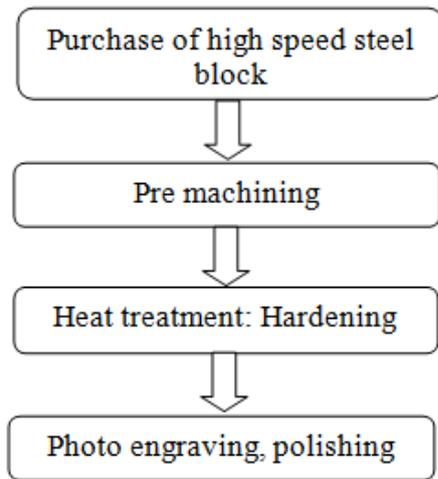
- ✓ Less time in manufacturing cycle.
- ✓ No cracking during heat treatment.

DISADVANTAGE

- ✓ The machining requires more time than annealed steel which has lower hardness.

b. ANNEALED STEELS

These steels can be put into production only after a further heat treatment since these are supplied in low hardness values. The manufacturing cycle of these steels are



ADVANTAGE

- ✓ Short machining time due to annealed condition.

DISADVANTAGE

- ✓ Occurrence of crack during heat treatment.

c. AGE HARDENING STEELS

They are supplied with solution condition with a hardness value similar to pre-hardened steels that can be further increased by heat treatment. The steels used for plastic moulds are SS420, high-speed steels, cast iron. The composition and properties of these steels are shown in table.

S.No	Material	Composition					
		C	Mn	Si	Cr	Mo	Ni
1	SS420	0.15	1	1	12-14	-	-
2	High-Speed Steel	0.35	0.75	0.3	1.5	0.65	3.5
3	Cast Iron	0.25-0.30	1.6	0.4	2.10	0.25	1.2

Table 3.1: Composition of various Tool Steels

S.No	Material	Modulus of elasticity (Gpa)	Thermal expansion (20°C) x 10 ⁻⁶ /°C	Thermal conductivity (W/m ² k)	Hardness (HRc)
1	SS420	205	12.8	29	52
2	High-Speed Steel	210	13.4	24.7	30-42

	Speed Steel				
3	CAST IRON	180	11.6	34	29-33

Table 3.2: Properties of Tool Steels

B. COATING MATERIAL

a. DEPOSITION MATERIAL [CrN]

CrN coating is conventionally used for more hardness and high corrosion resistance industrial applications. The good sliding behaviour of the coating protects against at deficient lubrication. Compared with hard chromium plating, CrN similar corrosion resistance but significantly higher hardness and better coating adhesion. For coating CrN in DC Magnetron sputtering Deposition 99.99 % of pure chromium target was selected.

b. CHARACTERISTICS OF CRN COATING

- ✓ The coated metal is hard and extremely resistant abrasion.
- ✓ It has High Corrosion resistance and surface finish.
- ✓ CrN has higher oxidation temperature (700 °C) than TiN.
- ✓ CrN has relatively higher thermal stability, low deposition temperature, superior wear and corrosion resistance than TiN.

c. APPLICATION

- ✓ Metal cutting application
- ✓ Die product
- ✓ Oil expellers, pulleys
- ✓ Conveyor, Screws
- ✓ Decorative applications

d. DEPOSITION MATERIAL [TiN]

Thin film diffusion barriers are required in semiconductor devices to prevent the migration of metalatoms from the interconnects into the adjacent dielectric and semiconductor regions. Titanium nitride (TiN)is one of the most widely used diffusion barrier materials.

TiN is a hard, refractory material and has a bulk resistivity. The shrinking of device dimensions demands thinner diffusion barrier films deposited in higher aspect ratio contact holes and vias.

Physical vapour deposition can be an ideal technique for growing conformal films on high aspect ratio structures. PVD utilizes two sequential self-limiting reactions that occur between a gaseous precursor and the solid substrate.

e. CHARACTERISTICS OF TIN COATING

- ✓ TiN has lower oxidation temperature (600 °C) than CrN.
- ✓ TiN has relatively higher thermal stability, low deposition temperature, superior wear and corrosion resistance than TiN.
- ✓ TiN is the most popular coating so far in the past year.
- ✓ Have proven their effectiveness to increase tool life.

f. APPLICATION

- ✓ Have proven their effectiveness to increase tool life
- ✓ Plastic formation
- ✓ Die product
- ✓ Metal cutting
- ✓ Decorative application

IV. DESIGN PROCEDURE

A. DESIGNS WITH DIMENSION

In this project application is to make a material with high resistance heat, wear and corrosion resistance. So that, my machining tool is having three- coordinates (x, y and z). In that I have concentrating single dimension and also specifically calling as name of specimen. The specimen dimension is 10 x 40 mm.



Figure 4.1: Sketch of Three Dimension Design

V. EXPERIMENTAL PROCEDURE

A. SPECIMEN PREPARATION

- ✓ The specimens are prepared from the M2 grade high speed steel.
- ✓ Parts are cleaned in a multi-stage cleaning process to remove soils, oils, fingerprints and produce an oxide free surface.
- ✓ The specimens are cleaned on the stage of ultrasonic effect for Removing oil and other contamination and liquid honing for surface roughness by using fine adhesive powder.
- ✓ The surface of specimens has been coated by using PVD techniques.
- ✓ The thickness of coated surface layer is existing between 3 micrometer.
- ✓ The CrN/TiN has been used for surface coating material on substrate by PVD method.
- ✓ The specimens have been prepared for dimensions of 10 x 40mm.
- ✓ The surface of specimens has been hard coated CrN/TiN by DC Magnetron sputtering deposition process.

B. COATING METHOD DEPOSITION

- ✓ Hard coating is the process in which a coating is applied to a substrate.
- ✓ The main purpose is to reduce wear or loss of material by abrasion, impact, erosion, galling, and cavitations.
- ✓ The production of a hard wear- resistant surface layer on metals by coating is known as hard coating.
- ✓ The hard face materials are usually more wear, heat & corrosion resistant.
- ✓ Here the coating technique used is PVD process- DC magnetron sputtering deposition.

a. DC MAGNETRON SPUTTERING DEPOSITION

- ✓ Argon gas is introduced in the equipment required for hard coating is used for DC Magnetron sputtering deposition process (PVD).
- ✓ The different parameters are considered, they are N2 pressure, Arc current, Substrate bias, Deposition time and other.
- ✓ The surface of hard face is throughly cleaned for the stage of ultrasonic effect for removing oil, other contamination and foreign particles and liquid honing for surface roughness by using fine adhesive powder.
- ✓ In chamber, air is pumped out, leaving a high vaccum environment.
- ✓ Substrate parts are pre-heated to process temperature.
- ✓ Substrates are ion-cleaned to remove the final atomic contaminants from the surface.
- ✓ The plasma is formed by magnetic field, argon ions in the Plasma impact on the target (Cr) and causes sputtering of atoms by momentum transfer, unlike other vapor phase techniques there is no melting of materials.
- ✓ The chamber plasma generation.
- ✓ Nitrogen gas is used as reactive gas, to form nitrides.
- ✓ Pure chromium is used as a target for CrN coatings.



Figure 5.1: DC Magnetron Sputtering Unit

C. SPUTTERING DEPOSITION PARAMETERS

From the literature review it was found that the microstructural characteristics are effectively governed by sputtering process parameters such as

- ✓ Pulsating source
- ✓ Working pressure
- ✓ Substrate Temperature

- ✓ Target to substrate distance
- ✓ Reactive gas flow rate
- ✓ Deposition time
- ✓ Target power

D. EFFECT OF PROCESS PARAMETERS

a. EFFECT OF WORKING PRESSURE

- ✓ At low working pressure residual stress buildup on the thin film.
- ✓ Deposition rate is decreased with increase in working pressure due to decrease in MFP (Mean Free Path).
- ✓ The stress induced in the film decrease within increase in pressure. Because the reduction in energies of plasma particles due to inelastic scattering.

b. EFFECT OF TEMPERATURE

- ✓ The oxidation of CrN/TiN thin films occurs around 700°C and Low temperature causes residual stress which leads to poor adhesion between film and substrate.
- ✓ The microhardness of thin film is increased with increase in temperature due to grain refinement. The mobility of atoms leads to more perfect structure.
- ✓ This leads to reduction in grain size which increases the minimum stress required to activate the dislocation.

c. EFFECT OF REACTIVE GAS (NITROGEN) FLOW RATE

- ✓ Increase in nitrogen flow rate increases the grain size and at low nitrogen flow pure CrN/TiN phase exist.
- ✓ While increasing flow rate the percentage of pure CrN/TiN phase will decrease and due to rapid solidification of highly energetic particles.
- ✓ The electrical resistivity of film is increased with increase in nitrogen flow rate because of increase in impurity defect.

d. EFFECT OF DEPOSITION RATE

- ✓ The deposition rate decreases with increasing working pressure.
- ✓ It influences the crystallinity, texture and porosity of the film.

VI. EXPERIMENTAL RESULTS

The following various tests are taken to compare the CrN and TiN coatings on high speed steel.

- ✓ Chemical composition test
- ✓ Corrosion test
- ✓ Wear test
- ✓ XRD (X-ray diffraction)
- ✓ SEM
- ✓ EDAX

A. X-RAY DIFFRACTION (XRD)

a. EXPERIMENTAL PROCEDURE

- ✓ When you have finished please remember to remove your sample and close the enclosure doors.
- ✓ Do not store your materials, samples, or sample holders in the XRD room.
- ✓ You are welcome to use the department sample holders provided you don't remove them from the lab and that you clean them when you have finished.
- ✓ Do not close XRD commander. This would prevent the machine from returning to stand-by mode and can reduce the life of the XRD tube.
- ✓ If you sign-up for time on the machine and cannot make it for any reason, please contact the SIT so your name can be removed from the scheduler.
- ✓ If you need to run a scan that will take more than 2 hours, please notify the SIT and we will arrange for an overnight scan.

b. XRD RESULT FOR CrN

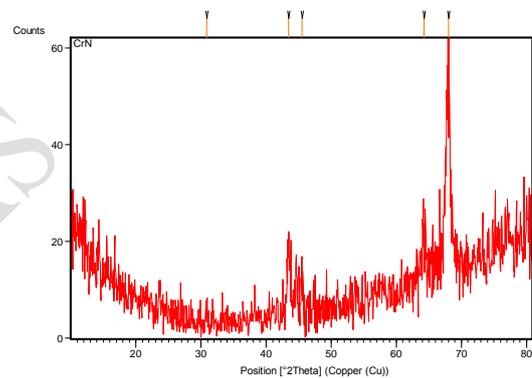


Figure 6.1: XRD Result for CrN

Peak List

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
30.8565	2.97	0.4920	2.89792	7.26
43.4453	17.41	0.4920	2.08297	42.60
45.5398	7.93	0.2952	1.99193	19.41
64.2132	10.05	0.5904	1.45050	24.59
67.9814	40.86	0.5904	1.37899	100.00

Table 6.1: XRD Result for CrN

c. XRD RESULT FOR TiN

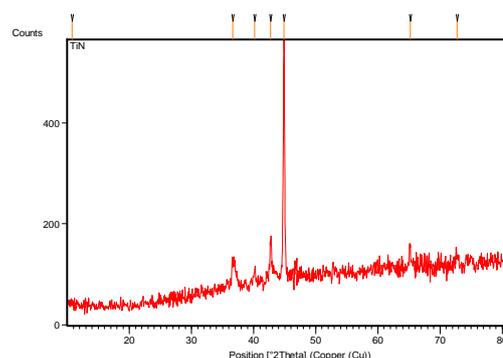


Figure 6.1: XRD Result For TiN

PEAK LIST

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
10.7793	6.23	1.1808	8.20771	1.30
36.6703	53.38	0.5904	2.45073	11.17
40.1555	29.72	0.2952	2.24570	6.22
42.7566	89.06	0.1968	2.11491	18.64
44.8753	477.68	0.1968	2.01986	100.00
65.1683	47.85	0.2952	1.43154	10.02
72.7115	19.60	0.5904	1.30051	4.10

Table 6.1: XRD Result for TiN

B. CHEMICAL COMPOSITION TEST

a. EXPERIMENTAL PROCEDURE

- Initially the optical emission spectrometer is arranged for testing the materials such as high speed steel, high speed steel with chromium nitrate coated, high speed steel with titanium nitrate coated as manner.
- The materials are holded to test the chemical composition and as well as the power supply is to it.
- When the power supply is given, the spark is produced on the testing materials such as HSS, HSS with CrN coated and HSS with TiN coated.
- Finally the tested materials are removed from the optical emission spectrometer as well as power supply is switched off.

COMPOSITION	PERCENTAGE		
	HSS	CrN	TiN
Carbon	0.771%	0.873%	0.869%
Manganese	0.278%	0.291%	0.274%
Silicon	0.384%	0.373%	0.366%
Sulphur	0.030%	0.032%	0.030%
Chromium	3.912%	4.052%	3.883%
Molybdenum	4.741%	4.958%	5.213%
Nickel	0.191%	0.192%	0.201%
Cobalt	1.323%	1.377%	1.411%
Vanadium	1.948%	2.133%	2.076%
Tungsten	6.425%	6.398%	6.850%
Iron	Remainder (79.9955%)	Remainder (79.319%)	Remainder (78.826%)

Table 6.2: Chemical Composition Test

C. CORROSION TEST

a. EXPERIMENTAL PROCEDURE

- Initially 350 ml of double distilled water is taken into the beaker. And 8gm of NaCl is added and it's fully mixed into the water.
- The corrosion measuring unit knobs are connected and picked with the testing piece, secondary electrode (graphite) and glass electrode.
- The power supply is given to the equipment.
- When the power supply is given, the graphite act as a counter electrode and testing material act as a working electrode.

- The required both the anodic and cathodic voltages are settled.
- At starting the corrosion behaviour waits till completion of ionic equalization process.
- After the equalization process, the corrosion action takes place on high speed steel.

b. CORROSION RATE ANALYSIS

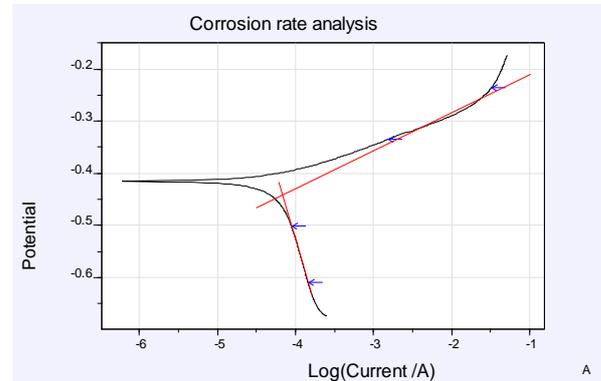


Figure 6.3: Corrosion Rate for HSS

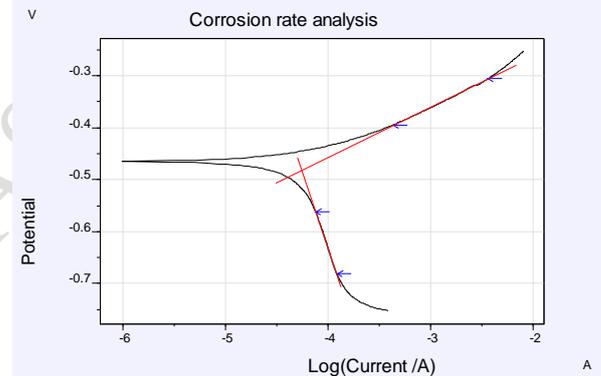


Figure 6.3: Corrosion Rate for CrN

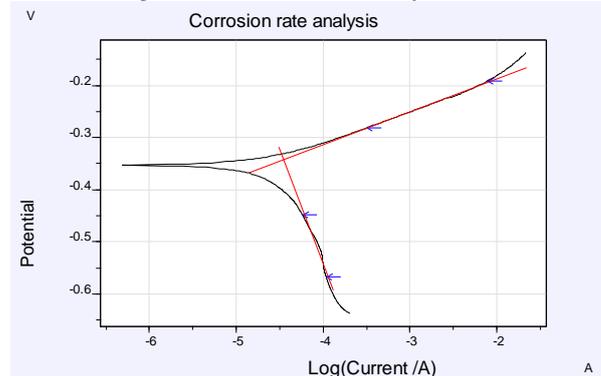


Figure 6.3: Corrosion Rate for TiN

	Tafel Data		
	HSS	CrN	TiN
E. corr V	-0.4413	-0.4816	-0.3421
i cor. A	6.888E-5	5.607E-5	3.531E-5
I cor. A/cm ²	6.888E-5	5.607E-5	3.531E-5
Rp Ohm	403.8	643.7	677.2
ba V/dec	0.073	0.097	0.063
bc V/dec	0.525	0.595	0.438
C. Rate mm/y	0.2254	0.1835	0.1155

Table 6.3: Corrosion Test

D. WEAR TEST

a. EXPERIMENTAL PROCEDURE

- ✓ Take care to remove all dirt and foreign matter from the specimens. Use nonchlorinated, non-film-forming cleaning agents and solvents
- ✓ Measure appropriate specimen dimensions to the nearest 2.5 μm or weigh the specimens to the nearest 0.0001 g.
- ✓ Insert the disk securely in the holding device so that the disk is fixed perpendicular (61°) to the axis of the resolution.
- ✓ Add the proper mass to the system lever or bale to develop the selected force pressing the pin against the disk.
- ✓ Start the motor and adjust the speed to the desired value while holding the pin specimen out of contact with the disk. Stop the motor.
- ✓ Remove the specimens and clean off any loose wear debris. Note the existence of features on or near the wear scar such as: protrusions, displaced metal, discoloration, micro cracking, or spotting.
- ✓ Remeasure the specimen dimensions to the nearest 2.5 μm or reweigh the specimens to the nearest 0.0001 g, as appropriate.

Material	Time (s)	Wear rate (μm)
HSS	511.6340	1212.08
HSS+TiN	511.6340	1138.50
HSS+CrN	511.6340	1103.09

Table 6.4: Wear Test

E. ENERGY DISPERSIVE X-RAY ANALYSIS(EDXA)TEST

a. EXPERIMENTAL PROCEDURE

- ✓ Identify the sample name and information for each adhesive lift in the specimen holder.
- ✓ Turn on the power and saturate the beam.
- ✓ Adjust the X-ray dead time on the copper standard to 10 % - 20 %.
- ✓ Perform instrumental setup of each sample loaded into the sample stage previously. Include with these samples the instrument blank and control.
- ✓ Enter sample description in Analysis, including Laboratory number and Forensic Scientist's name.
- ✓ Select Perform EDS Check and verify EDS check after each analysis.
- ✓ Set the stage point to the copper standard. Use the backscatter detector and adjust its operational threshold level.
- ✓ Start automated analysis.

b. EDXATEST FOR CrN

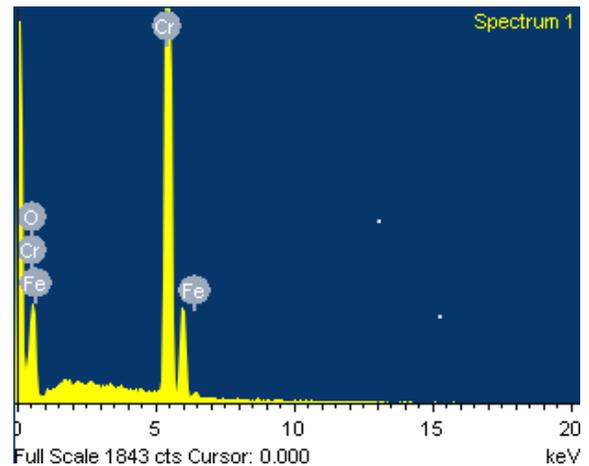


Figure 6.5: EDXA Test for CrN

Element	Weight %	Atomic weight %
Cr	94.32	86.04
Fe	1.36	1.15

Table 6.5: EDXA Test for CrN

c. EDXATEST FOR TiN

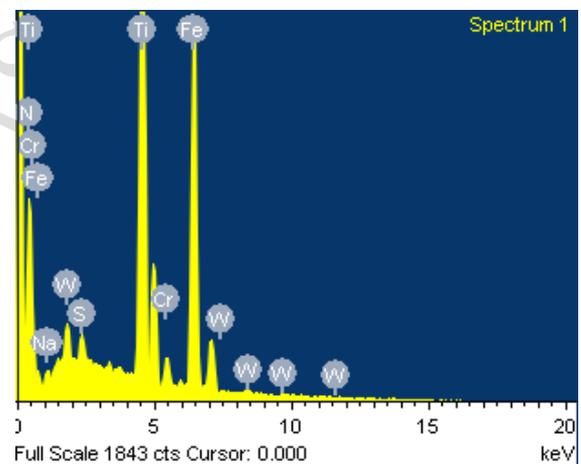


Figure 6.5: EDXA Test For TiN

Element	Weight %	Atomic weight %
N	9.06	26.78
Ti	45.23	39.11

Table 6.5: EDXA Test for TiN

F. SCANNING ELECTRON MICROSCOPE (SEM)TEST

a. EXPERIMENTAL PROCEDURE

- ✓ Identify the sample name and information for each adhesive lift in the specimen holder.
- ✓ Turn on the power and saturate the beam.
- ✓ Adjust the X-ray dead time on the copper standard to 10 % - 20 %.
- ✓ Perform instrumental setup of each sample loaded into the sample stage previously. Include with these samples the instrument blank and control.
- ✓ Enter sample description in Analysis, including Laboratory number and Forensic Scientist's name.

- ✓ Select Perform EDS Check and verify EDS check after each analysis.
- ✓ Set the stage point to the copper standard. Use the backscatter detector and adjust its operational threshold level.
- ✓ When all settings are correct, select save under Set-Up.
- ✓ Start automated analysis.

b. SEM TEST FOR CrN

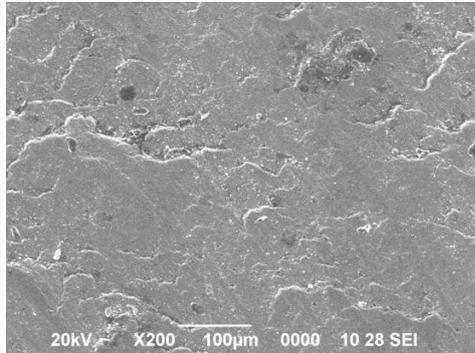


Figure A

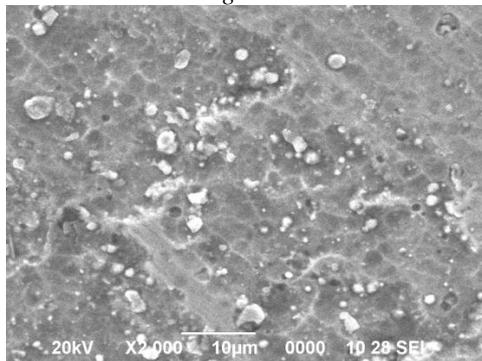


Figure B

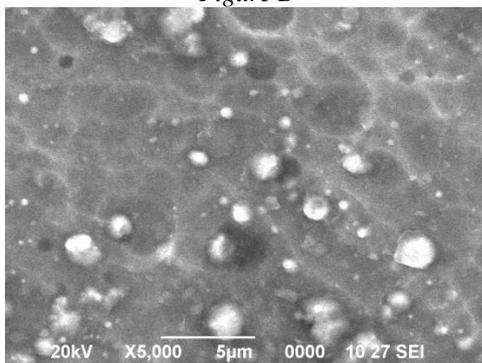


Figure C

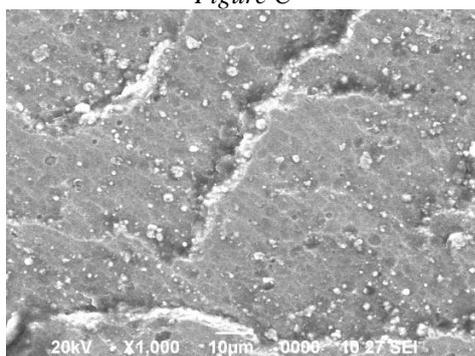


Figure D

c. SEM TEST FOR TiN

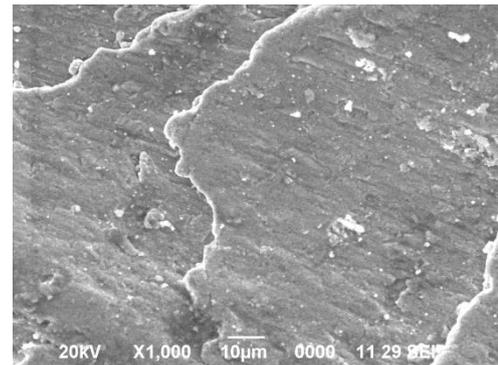


Figure A

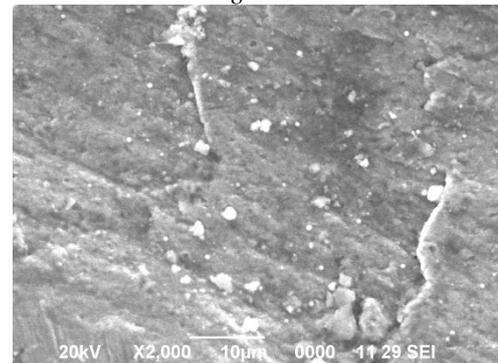


Figure B

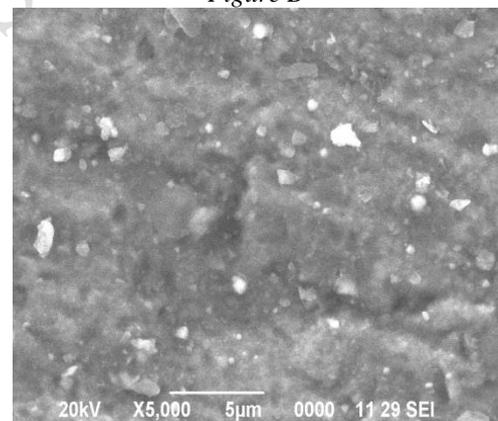


Figure c

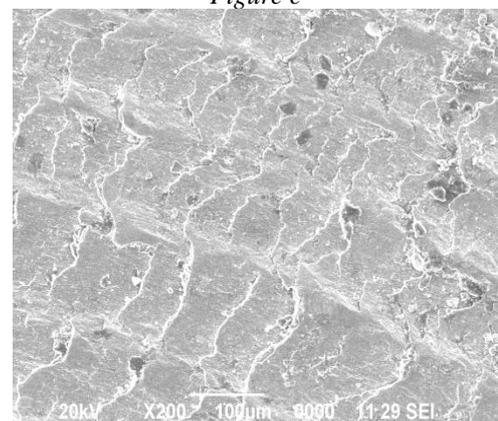


Figure D

VII. CONCLUSION

- ✓ It is concluded that M2 grade high speed steel has been selected as a substrate material because of its moderate properties of microstructure, chemical composition, deposition of materials, wear and corrosion rates when compared and analyzed with other two CrN/TiN coated high speed steels.
- ✓ Its purchasing and machining cost is low. So that selected as a substrate material.
- ✓ From the literature review it is concluded that the influencing variables of microstructural characteristics of CrN coating are substrate temperature, working pressure and reactive gas flow rate, thickness of the film and power of sputtering process.

Among the above variables the most influencing variables of microstructural, corrosion, wear and deposition of materials characteristics of CrN thin film are substrate temperature, working pressure and reactive gas flow rate are higher and more efficient than the other two types of materials such as HSS and TiN coated HSS.

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