THE MICROSTRUCTURE, MECHANICAL PROPERTIES, AND THERMAL STABILITY OF TERNARY Cr\textsubscript{1-x}Mo\textsubscript{x}N\textsubscript{y} THIN-FILMS

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THE MICROSTRUCTURE, MECHANICAL PROPERTIES, AND THERMAL STABILITY OF TERNARY Cr\(_1\)-xMoxNy THIN-FILMS

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PHYSICS

ABSTRACT

The microstructure, thermal stability and mechanical properties of ternary chromium molybdenum nitride (Cr-Mo-N) films were studied. In this work, a series of Cr-Mo-N films with different Cr/Mo ratios were deposited on CoCrMo and silicon substrates at various deposition temperatures by using a dual rf-magnetron sputtering system with Cr and Mo targets and nitrogen as reactive gas. Thermal processing at temperatures up to 700 °C in air and up to 800°C in microwave plasma with H\(_2\)/N\(_2\) gas mixture were employed to evaluate the thermal stability of films. The films’ microstructure was investigated by scanning electron microscope (SEM) and X-ray Diffraction (XRD). The surface morphology was studied by atomic force microscopy (AFM), and the chemical composition was analyzed by X-ray photoelectrons spectroscopy (XPS) and Energy-Dispersive X-ray Spectrometer (EDS). The mechanical properties were studied by Nanoindentation and Tribometry. The coatings exhibited mainly face centered cubic (fcc) structure with some secondary phase precipitates. All as prepared films showed mean grain size 13 – 21 nm and the lattice parameters varying between those of CrN and γ-Mo2N depending on the composition. The surface roughness of the films varied from the pure CrN and pure γ-Mo2N in the nanoscale range. The hardness and Young’s modulus were found in the range of 9.0 - 22 GPa and 175- 330
GPa, respectively, with larger values observed for Mo-rich layers. The coefficient of dry friction with Ti counterpart varied from 0.41 to 0.67. Thermal stabilities of Cr-Mo-N coatings during the annealing up to 700°C in air have been studied. It has been found that Cr$_{1-x}$Mo$_x$N$_y$ films with Cr-rich content are more stable than those with Mo-rich content. All properties were improved by increasing the deposition temperature.

**Key words:** Magnetron sputtering, Thermal stability, Mechanical property, Chromium molybdenum nitride
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CHAPTER 1
STATE-OF-THE-ART IN HARD COATINGS

1.1 Introduction to hard coatings

Hard coatings are thin layered coatings, which are deposited on the bulk substrates in order to achieve the desired properties of the surface, such as high hardness, low friction, high wear resistance and corrosion resistance while leaving the properties of the bulk materials unchanged. The term “hard coatings,” technically speaking, covers a broad spectrum of materials. Hard materials for coatings can be divided in three groups depending on the chemical bonding character. It includes metallic hard materials (borides, carbides, and nitrides of the transition metals), covalent hard materials (borides, carbides and nitrides of Al, Si, and B, as well as diamond), and ionic (ceramic) hard materials (oxides of Al, Zr, Ti, and Be).[1]

Some applications such as industrial machine parts, drillings, and bearings require the tribological coatings with low coefficient of friction. The term, “tribology”, comes from the Greek word, tribēin, meaning to rub, is the study of the friction and wear of materials.[2] The tribology plays an important role in tool service life. In manufacturing, friction increases tool wear and the power required to work a piece, which results in increased costs due to more cutting fluid consumed, the loss of tolerance as tool dimensions shift, and greater forces required to shape a piece. In biomedical implant applications, the wear of devices increases the frequency of replacement, then brought more suffer and pain for patients.
The high hardness in combination with a low coefficient of friction decreases the rate of abrasive wear of the coated component.

![Diagram showing growth of production in German machine industry](image)

**Fig.1.1** Growth of production in German machine industry

Fig.1.1 is provided by the VDMA (Verband Deutscher Maschinen- und Anlagenbau - German Engineering Federation); one of the key association service providers in Europe, and it shows the growth of production in German machine industry. Compared to the statistical of base year 2000, the growth of production is 21% for machine manufacturers and 17% for tool manufacturers, respectively. The surface treatment industry has shown an increase of 110% with the majority realised by thin film coating technologies, 72% in Europe and 54% in the USA\textsuperscript{[3,4]}.

Coating provides tools high performance to save costs on modern manufacturing. Testing has demonstrated as much as a 100~300% increase in tool life and up to a 20~40% increase in cutting speed in comparison with uncoated tools. The coatings can
increase speeds of machining, reduce cycle times and increase productivity, prolong the tool durability and life; reduce down time and tool-changing cost\textsuperscript{[5]}. 

The first tribological coating for controlling friction and wear was titanium carbide (TiC), introduced in 1969 on cemented carbide cutting tool inserts using chemical vapor deposition (CVD)\textsuperscript{[6]}. The problem with the CVD process was that the substrate temperature during deposition was about 1000\degree C so that CVD could not be used to coat high speed steel tooling, which is softened at those temperatures. To overcome this obstacle, industry began using physical vapor deposition (PVD) techniques that provide ion bombardment of the growing film, resulting in good film adhesion and densification.

Since the first PVD coating material, TiN, was introduced for cutting tools in the early 1980s, PVD coating on cutting tools have saved companies billions in expenses\textsuperscript{[3]}.

![Standard coatings developed in the last three decades](image-url)

Fig.1.2 Standard coatings developed in the last three decades
Fig 1.2 is provided by LMT(Leading Metalworking Technologies) in Germany. The Fig 1.2 shows the development of coating technology on the cutting tool industry. Coating technology for cutting tools has developed rapidly. In 1980, only the TiN coating and until 1988 only TiCN and CrN were used. In 2000, 14 standard coatings became available. Considering the different stoichiometries and structures, it can be seen that several hundred different coatings are now available. In the case of coatings with different chemical compositions, there are 70 or so different coatings on the market.

1.2 Review of binary nitride coatings

Intensive development of the superhard coatings such as single element diamond (diamond-like-carbon DLC) and cubic boron nitride (CBN) peaked in the 90’s. It seems that an insurmountable technical barrier – extremely high residual stress during deposition – has not been overcome and still prevents successful commercialization [3].

The first commercially successful PVD hard coating was titanium nitride (TiN). TiN coatings provide wear resistance, reduce friction, maintain sharp edges, and improve surface hardness. Some companies have achieved the TiN coatings successfully. For example, Balzers deposited it with their low voltage electron beam process, Ulvac with their hot hollow cathode process, and Multi-Arc with their cathodic arc process. Since the cost of the arc coating equipment was less than that of competing deposition processes, the cost of the arc coatings was lower, and the use of cathodic arc deposited hard coatings became widespread.

Initially, sputtering was not used for the commercial deposition of the tribological films because the quality of the films did not equal that of films produced by low voltage
electron beam or cathodic arc methods. This situation was significantly improved with the introduction of closed-field unbalanced magnetron sputtering that provided for a higher degree of substrate ion bombardment during deposition.

One of the early themes in PVD tribological coatings was their high hardness. It is true that a coating used for a machining application must be hard, but it is now understood that a coating should be both hard and ductile if it is going to perform well in a tribological application, and it has been shown by Leyland and Matthews\textsuperscript{[7,8]}. The commercial acceptance of hard coatings for cutting tools is driven by demands on machining productivity, environmental mandates, and increased usage of new difficult-to-cut materials (e.g., Ti-6Al-4V and Inconel 718). Improved cutting performance is derived from synergies of machine tool system and cutting tool development. The latter strives for an optimized combination of tool material, hard coating and cutting edge geometry.

In industry, the tools are always exposed to increased temperature, high oxidation and other severe environments, so besides the high hardness and ductility, the coatings need high thermal stability, oxidation resistance, and corrosion resistance. The hard nitride coatings are suitable, and now commonly used in a wide range of tribological applications to improve performance and to extend the life of metal cutting, drilling, and forming tools, as well as bearings and various machine parts.

Table 1.1 show selected properties of important representative of the metallic hard materials. All the compounds stand out for their high hardness and high melting points.
Table 1.1 Selected properties of metallic hard materials\[9\]

<table>
<thead>
<tr>
<th>Phase</th>
<th>Density (g/cm(^3))</th>
<th>Melting point (°C)</th>
<th>Hardness (HV)</th>
<th>E modulus (kN/m(^2))</th>
<th>Spec. el. resistivity (µΩ cm)</th>
<th>Thermal exp. coeff. (x 10(^{-5}) K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiB(_2)</td>
<td>4.50</td>
<td>3225</td>
<td>2800</td>
<td>560</td>
<td>7</td>
<td>7.8</td>
</tr>
<tr>
<td>TiC</td>
<td>4.93</td>
<td>3067</td>
<td>2800</td>
<td>470</td>
<td>52</td>
<td>8.0-8.6</td>
</tr>
<tr>
<td>TiN</td>
<td>5.40</td>
<td>2950</td>
<td>2100</td>
<td>590</td>
<td>25</td>
<td>9.4</td>
</tr>
<tr>
<td>ZrB(_2)</td>
<td>6.11</td>
<td>3245</td>
<td>2300</td>
<td>540</td>
<td>6</td>
<td>5.9</td>
</tr>
<tr>
<td>ZrC</td>
<td>6.63</td>
<td>3445</td>
<td>2560</td>
<td>400</td>
<td>42</td>
<td>7.0-7.4</td>
</tr>
<tr>
<td>ZrN</td>
<td>7.32</td>
<td>2982</td>
<td>1600</td>
<td>510</td>
<td>21</td>
<td>7.2</td>
</tr>
<tr>
<td>VB(_2)</td>
<td>5.05</td>
<td>2747</td>
<td>2150</td>
<td>510</td>
<td>13</td>
<td>7.6</td>
</tr>
<tr>
<td>VC</td>
<td>5.41</td>
<td>2648</td>
<td>2900</td>
<td>430</td>
<td>59</td>
<td>7.3</td>
</tr>
<tr>
<td>VN</td>
<td>6.11</td>
<td>2177</td>
<td>1560</td>
<td>460</td>
<td>85</td>
<td>9.2</td>
</tr>
<tr>
<td>NbB(_2)</td>
<td>6.98</td>
<td>3036</td>
<td>2600</td>
<td>630</td>
<td>12</td>
<td>8.0</td>
</tr>
<tr>
<td>NbC</td>
<td>7.78</td>
<td>3613</td>
<td>1800</td>
<td>580</td>
<td>19</td>
<td>7.2</td>
</tr>
<tr>
<td>NbN</td>
<td>8.43</td>
<td>2204(e.)</td>
<td>1400</td>
<td>480</td>
<td>58</td>
<td>10.1</td>
</tr>
<tr>
<td>TaB(_2)</td>
<td>12.58</td>
<td>3037</td>
<td>2100</td>
<td>680</td>
<td>14</td>
<td>8.2</td>
</tr>
<tr>
<td>TaC</td>
<td>14.48</td>
<td>3985</td>
<td>1550</td>
<td>560</td>
<td>15</td>
<td>7.1</td>
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<tr>
<td>CrB(_2)</td>
<td>5.58</td>
<td>2188</td>
<td>2220</td>
<td>540</td>
<td>18</td>
<td>10.5</td>
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<td>CrC(_2)</td>
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<td>2150</td>
<td>400</td>
<td>75</td>
<td>11.7</td>
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<tr>
<td>CrN</td>
<td>6.12</td>
<td>1050</td>
<td>1100</td>
<td>400</td>
<td>660</td>
<td>13.7</td>
</tr>
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<td>MoB(_3)</td>
<td>7.45</td>
<td>2140</td>
<td>2350</td>
<td>670</td>
<td>18</td>
<td>8.6</td>
</tr>
<tr>
<td>MoC</td>
<td>9.18</td>
<td>2517</td>
<td>1660</td>
<td>540</td>
<td>57</td>
<td>7.8-9.3</td>
</tr>
<tr>
<td>W(_2)B(_3)</td>
<td>13.03</td>
<td>2365</td>
<td>2700</td>
<td>770</td>
<td>19</td>
<td>7.8</td>
</tr>
<tr>
<td>WC</td>
<td>15.72</td>
<td>2776</td>
<td>2550</td>
<td>720</td>
<td>17</td>
<td>3.8-3.9</td>
</tr>
<tr>
<td>LaB(_6)</td>
<td>4.73</td>
<td>2790</td>
<td>2530</td>
<td>(400)</td>
<td>15</td>
<td>6.4</td>
</tr>
</tbody>
</table>

The most commonly used nitride coatings which include TiN, CrN, MoN, ZrN, WN, AlN, BN, etc, have been well studied\[10,11,12,13,14,15\]. For example, CrN has excellent corrosion resistance, oxidation resistance, and good wear resistance, for the oxidation behaviour, linear increase in the surface roughness and surface grain size with the oxide layer thickness was found\[16\], however, the better mechanical properties are still desirable. Cr\(_2\)O\(_3\) is the hardest material among all oxides. It has a high hardness of 29 GPa as compared to 12 GPa for silicon dioxide and 22 GPa for alumina.\[17\]

1.3 Review of ternary nitride coatings

Ternary nitride films can, under appropriate conditions, form coating systems with a combination of useful properties similar to or better than those of binary nitrides. It has been reported that TiAlN and TiZrN films have superior wear resistance compared to binary TiN films\[18,19,20\]. Reactive cathodic sputtered TiCrN exhibited improved
corrosion behavior when compared with TiN\textsuperscript{21}. Ternary Cr-X-N(X=Ti, Al, Si, C, B, Ta, Nb, Ni)\textsuperscript{22,23,24,25,26,27,28,29,30,31,32,33} coatings have been explored as an evolutionary step from CrN coatings. The TiAlN PVD coating is currently the most widely deposited PVD coating for cutting tools, however, for certain particular applications, TiCN and CrN offer better solutions when the coefficient of friction is critical. Nanocrystalline CrCN coating has been found with higher hardness than CrN and good coefficient friction values depending on C content added.\textsuperscript{34}

1.4 Deposition Methods

Vapor deposition processes can principally be divided into two types, (1) physical vapor deposition (PVD) and chemical vapor deposition (CVD). PVD processes involve the creation of materials vapors by evaporation, sputtering, or laser ablation, and their subsequent condensation onto a substrate to form the film. CVD processes are generally defined as the deposition of a solid material from the vapor phase onto a heated substrate as a result of chemical reactions\textsuperscript{35,36}. No matter PVD or CVD techniques were used, the film deposition can be modeled in terms of three steps\textsuperscript{37}.

![Film vapor deposition process flow diagram](image-url)
Fig 1.3 shows the three steps of the film deposition process.

Step 1: Creation of Vapor Phase Species 
Source can be converted into the vapor phase by evaporation, sputtering, laser ablation, vapors, or delivered as precursor gases, etc.

Step 2: Transport from source to substrate - The vapor species are transported from the source to the substrate. During transport, some of the vapor species can be ionized by creating plasma in this space.

Step 3: Film growth on the substrate - This process involves the condensation of the vapor species onto the substrate and subsequent formation of the film by nucleation and growth processes. The nucleation and growth processes can be strongly influenced by bombardment of the growing film by ionic species resulting in a change in microstructure, composition impurities, and residual stress.

The degree of independent control of these three steps determines the versatility or flexibility of the deposition process. For example, these three steps can be independently controlled in PVD process, and, therefore, give greater degree of flexibility in controlling the structure, properties, and deposition rate, whereas all of the three steps take place simultaneously at the substrate, and cannot be independently controlled in the CVD processes.

Physical Vapor Deposition (PVD) coating technology for cutting tools has multiple successful commercial applications over the last 30 years. Most cutting tools are PVD coated. The basic PVD processes fall into two general categories: (1) sputtering and (2) evaporation.
Sputtering is the phenomena of momentum transfer from an incident energetic projectile to a solid or liquid target resulting in the ejection of surface atoms or molecules. In the sputter deposition process, the target, (a source of coating material) and the substrate are placed in the vacuum chamber, and evacuated to a pressure typically in the rage of $10^{-4}$ to $10^{-7}$ torr. The target (also called a cathode) is connected to a negative voltage supply, and the substrate generally faces the target. An electric discharge is initiated after an inert gas (usually argon gas) is introduced into evacuated chamber. Typical working pressure is in the range of 20-150 mtorr.

In evaporation process, vapors are produced from a source material which is heated by various methods. It consists of an evaporation source to vaporize the desired material, and the substrates which are located at an appropriate distance facing the evaporation source. Resistance, induction, arc electron beam, or lasers are the possible heat sources for evaporation.

Here we only discuss the two most common PVD deposition methods, the magnetron sputtering and cathodic arcs.

1.4.1 Magnetron sputtering

Magnetron sputtering is an extremely flexible coating technique that can be used to coat virtually any solid substrate. Sputtering is basically the removal of atomized material from a solid by energetic bombardment of its surface layers by ions or neutral particles.

Prior to the sputtering coating process a vacuum of less than one ten millionth of an atmosphere must be achieved. Once the appropriate pressure has been reached a
controlled flow of an inert gas such as argon is introduced. This raises the pressure to the minimum needed to operate the magnetrons, although it is still only a few ten thousandth of atmospheric pressure.

When power is supplied to a magnetron, a negative voltage of typically -300V or more is applied to the target. This negative voltage attracts positive ions to the target surface. Generally when a positive ion collides with atoms at the surface of a solid an energy transfer occurs. If the energy transferred to a lattice site is greater than the binding energy, primary recoil atoms can be created which can collide with other atoms and distribute their energy via collision cascades. A surface atom becomes sputtered if the energy transferred to it normal to the surface is larger than about 3 times the surface binding energy (approximately equal to the heat of sublimation). Sputtering of a target atom is just one of the possible results of ion bombardment of a surface. Aside from sputtering the second important process is the emission of secondary electrons from the target surface. These secondary electrons enable the electronic discharge to be sustained.

The sputter process has almost no restrictions in the target materials, ranging from pure metals where a d.c. power supply can be used, to semiconductors and isolators which require a r.f. power supply or pulsed dc. Deposition can be carried out in either non reactive (inert gas only) or reactive (inert & reactive gas) discharges with single or multi-elemental targets.

During the sputter process a magnetic field can be used to trap secondary electrons close to the target. The electrons follow helical paths around the magnetic field lines undergoing more ionizing collisions with neutral gases near the target than would
otherwise occur. This enhances the ionization of the plasma near the target leading to a higher sputter 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.

Fig 1.4 gives a schematic diagram of a typical magnetron sputtering system. During sputtering, energized plasma ions strike a ‘target’, which is composed of the desired coating material. Atoms from that target are dislodged by the impact of the ion and ejected from the surface with enough energy to travel to and bond with the substrate. Magnetron sputtering cathodes use powerful magnets to confine the plasma to the region closest to the ‘target’. This condenses the ion-space ratio, increases the collision rate, and thus improves deposition rate.

![Schematic diagram of a typical magnetron sputtering system](image)

Fig.1.4 Schematic diagram of a typical magnetron sputtering system
Magnetron sputtering is commonly used in industry because of its relatively less cost and the primary advantages of magnetron sputtering are

1) High deposition rates,
2) Ease of sputtering any metal, alloy or compound,
3) High-purity films,
4) Extremely high adhesion of films,
5) Excellent coverage of steps and small features,
6) Ability to coat heat-sensitive substrates,
7) Ease of automation,
8) Excellent uniformity on large-area substrates.

In the simplest of applications the magnetron is used to deposit metallic materials by DC sputtering. The DC magnetron is the cheapest of magnetron processes. RF sputtering equipment is more expensive to purchase than a DC magnetron. DC magnetrons will not work if an insulating target is used, because no current can flow through it. The solution to this problem is to use an alternating current at high frequency. RF sputtering was developed to enable the sputtering of dielectric materials and has the double advantage that it will sputter metals as well.

The utilization of this technique is impeded by the limitations in choice of target materials, and the difficulties in fabrication of the target. For example, if ferromagnetic materials are used as the sputtering target, their thickness should be thin enough so as to be saturated by the magnetic field. Since high power is localized in a selected area in magnetron sputtering process, targets should be prepared without voids or bubbles to avoid local melting and spitting[^38].
1.4.2 Cathodic Arcs

Fig. 1.5 shows the schematic diagram of a typical cathodic arc source\textsuperscript{[39]}. 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, then it self-extinguishes and re-ignites in a new area close to the previous crater.

Cathodic arc plasma deposition has become the technology of choice for hard, wear and corrosion resistant coatings for a variety of applications. Cathodic arc plasmas stand out due to their high degree of ionization, with important consequences for film nucleation, growth, and efficient utilization of substrate bias. Industrial processes often use cathodic arc plasma in reactive mode.

Cathodic arc source (Sablev type)

Fig.1.5 Schematic diagram of a typical cathodic arc source
The most frequent application of cathodic arc plasma deposition is the reactive deposition of compound films such as CrN, ZrN, TiN, TiAlN, and multilayers thereof. When the compound layer is formed, the metal reacts preferentially with those gases whose energy of compound formation is large, i.e. with the thermodynamically preferred gas species. The plasma may contain contamination such as water vapor, which is typical for high vacuum systems. This issue is especially important for pulsed plasma systems where the water layer on the arc cathode and chamber wall is periodically “scrubbed” by the plasma pulse, and where water vapor is partially ionized. Hydrogen can be incorporated in a film that is supposed to be an oxide or nitride\textsuperscript{[40]}. The incorporation of hydrogen can greatly affect the desired coatings properties such as hardness and elastic modulus\textsuperscript{[41]}.

Reactive deposition is commercially done at elevated temperature. One reason is that the deposition process itself heats the substrate. Heating is often utilized to obtain the desired coating texture. A side effect of elevated temperature is the reduction of hydrogen incorporation.

Macroparticles are liquid or solid debris particles that are produced at cathode spots. Macroparticles are a major issue in cathodic arc coatings. For instance, the corrosion resistance is compromised when a macroparticle is incorporated in the coating, disrupting the dense, continuous film. Macroparticle filters is a possible direction, but reduces deposition rate and increases equipment complexity and cost.

1.5 Influence of deposition parameters on film’s microstructure
Film growth conditions and resulting structure are often summarized schematically in so-called structure zones, which predict the morphology and microstructure of a film independently of its materials, as a function of the adatom mobility. Movchan and Demchishin\textsuperscript{[42]} were the first to observe that the morphological structure of evaporated coatings of Ti, Ni, W, ZrO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} could be related to a normalized, or reduced temperature $T^*$ ($T_s/T_m$, where $T_s$ is the actual film temperature during deposition, and $T_m$ is its melting temperature, both in K). These diagrams have been developed for thermal evaporation and sputtering\textsuperscript{[43,44]}, but recently also adapted for plasma based deposition\textsuperscript{[45]}. The temperature, $T^*$, is generalized by including a shift caused by potential energy of arriving particles; the normalized energy, $E^*$, includes pressure and kinetic energy of bombarding particles and the $t^*$ is the net thickness of the coating.

Fig 1.6 shows the structure zone diagram for plasma based thin film deposition. The diagram is schematically divided in four zones for different conditions.

In Zone 1 ($T^*<0.3$) a fine-grained structure consisting of textured and fibrous grains with domed tops and a high density of lattice imperfections and porous grain boundaries is formed. The structure is produced by a process of continued nucleation of grains during deposition due to the low adatom mobility (incident atoms stick at the point of impact) in combination with shadowing effects\textsuperscript{[46,47]}.

Zone 2 structure ($0.3<T^*<0.5$) is characterized by unconstrained surface diffusion leading to uniform columnar grains.

Zone 3 ($T^*>0.5$), at high temperature and energy, allows also bulk diffusion with resulting recrystallization and densification of large grains. Thornton\textsuperscript{[48,49]} extended this
zone classification to include the bombardment-induced mobility process in sputtering through the use of sputtering gas pressure parameter. The normalized energy, $E^*$, includes pressure and kinetic energy of bombarding particles.

Zone T is a transition zone with improved surface diffusion, however limited over grain boundaries, which results in competitive growth of V-shaped grains. Zone T films are denser and have a much smoother surface morphology than the two surrounding zones.

Fig. 1.6 Structure Zone Diagram for plasma based thin film deposition

1.6 Stress in the films
Films grown by PVD techniques quite often are very highly stressed. The stresses can be either tensile or compressive, but tensile stresses are in general most damaging. The thermal stresses in the coating after cooling from the deposition temperature are tensile when the thermal expansion coefficient of the coating materials is larger than the one of the substrate and compressive if the reverse is true.

A plate system composed of a stress bearing thin film, of uniform thickness $h_f$, deposited on a relatively thick substrate, of uniform thickness $h_s$, a simple relation between the curvature, $\kappa$, of the system and the stress, $\sigma^{(f)}$, of the film as follows:

$$\sigma^{(f)} = \frac{E_s h_s^2 \kappa}{6 h_f (1 - v_s)}$$

$f$ and $s$ denote the thin film and substrate, respectively, and $E$ and $v$ are the Young’s modulus and Poisson’s ratio, respectively.

1.7 Structure/property relationship for hard coatings

The macroscopic properties of a material are strongly dependent on its structure. Studies of structure/properties relationships are among the most important issues in material science. Most commonly the structure studies involve the phase, grain and defect structure. For thin films, the structure/property relationship is particularly important to study since thin films usually are deposited far from equilibrium conditions. In most cases, thin films contain a much higher content of lattice defects such as vacancies, dislocations, and grain boundaries than conventionally prepared bulk materials. Furthermore, since the material flux during growth of a thin film often is directional, the microstructure, and thus also most of the physical properties of thin films are often highly anisotropic. However, due to the complex nature of the deposition process, and the large
number of parameters imposing kinetic limitations to the growth process, it is difficult to predict the microstructure and physical properties of the deposited film from knowledge of the used deposition conditions.

The most generic feature observed in thin film microstructures is the small grain size $d$. The small grain size cause a hardening of the material in agreement with the Hall-Petch relation $^{[52]}

$$H=H_0+kd^{1/2}$$

where $H$ is the film hardness, $H_0$ the intrinsic hardness, and $k$ a material dependent constant. For hardness, the Hall-Petch relation has been found to be valid for $d$ values as low as 20nm for single-phase metal films.$^{[53,54,55]}$ As the decrease in crystal size, the hardness of materials increases, especially for crystal size down to tens of nanometer. However, a new deformation mechanism called grain boundary sliding replaces the dislocation activity that dominates deformation process in conventional materials.$^{[56]}$

1.8 Case of ternary CrMoN coatings

As mentioned above, the nitrides of group VIB elements stand out from the hard nitride coatings. CrN has excellent corrosion resistance under severe environment conditions, superior oxidation resistance, and good wear resistance, however, it has low toughness $^{[57,58,59]}$. MoN has been found to exhibit many attractive physical properties such as high hardness, low solubility in non-ferrous alloys and low friction, etc $^{[60]}$. Mo$_x$N coatings showed good tribological performance due to the formation of MoO$_3$ as a solid lubricant $^{[61,62,63,64,65,66,67,68]}$.

Several reports have indicated that ternary Cr-Mo-N coatings could have properties superior to Mo$_x$N and CrN tailored through the appropriate combinations of Cr
and Mo ratio $^{69,70,71}$. However, the CrMoN coating is not well explored and only limited findings have been reported.

1.9 Goals of the research

The CoCrMo alloy system is still a material of choice for many articulating biomedical implants, and the improvement of their performance is important. The methods to increase the hardness and corrosion resistance of metallic implants include nitrogen ion implantation, thermal diffusion, and deposition of hard coatings. Many of these innovations have not been proven to be successful in clinical applications. For example, nitrogen ion implantation increases the surface hardness and wettability. However, the ion-implanted surface layer is less than a micrometer in thickness, which may quickly get worn through. Thermal diffusion hardening of the metallic surface can produce a thicker surface layer than ion implantation, but scratching and oxidative wear are still possible. Among the surface modification methods used, a significant improvement of CoCrMo implant performance has been obtained with TiN, CrN, CrCN coatings in various combinations, and with nanocrystalline structure $^{72,73}$. Such a ternary system is compositionally close to the substrate and may have the potential for improving the performance of CoCr alloy-based articulating implants when compared to binary CrN or MoN coating systems.

In the areas of machining and tooling, PVD coatings are widely used to increase the life and productivity of cutting tools, saving companies billions of dollars worldwide. PVD coated cutting tools can be run faster, reducing cycle times and enabling the production of more components in less time. In metal cutting, wear processes exist on the
work-piece material. Cutting fluids are commonly used to reduce the wear, which cost companies today up to 15% of their total production costs. PVD coatings can reduce the wear resistance, and increase the life of cutting tools reducing tool-changing and cutting fluids costs. High speed cutting and dry machining involve extremely high temperatures at the cutting edge. PVD coatings such as TiAlN have incredible thermal stability, hot hardness and oxidation resistance. PVD coatings can therefore be run dry or with very limited amount of cutting fluid.

CrMoN coatings are the potential coatings used in a wide range of applications such as high speed cutting tools, drilling, bearing, and biomedical implants ,etc, their properties are important to be studied.

The purposes of this research is to (1) prepare CrMoN coatings by magnetron sputtering system and investigate the microstructure, phase and chemical composition in dependence on the deposition conditions; (2) investigate the mechanical properties of the CrMoN coatings; (3) estimate the microstructure/property relationship of the coatings; (4) study the thermal stability of the Cr_{1-x}Mo_xN_y coatings depending on their composition.
CHAPTER 2
EXPERIMENTAL APPROACHES

2.1 Equipment and procedures

Fig 2.1 shows the commercial Nordiko 3500 RF Magnetron Sputtering System. It equipped with generator modules, a vacuum chamber, and pumps, etc.

Fig 2.1 The Nordiko 3500 RF magnetron sputtering system

Fig. 2.2 is the vacuum diagram for the Nordiko 3500 RF magnetron sputtering system. Rough vacuum is provided with an Alcatel 2063C rotary vane pump. This pump has a peak pumping speed of 18 L/s and an ultimate base pressure of 0.02 Pa. From atmosphere down to about 0.1 Pa, the pressure is monitored by a thermocouple gauge,
marked TC-1 (DV-23 gauge tube) on Fig 2.2. Once cross-over is reached (set at ~ 7 Pa), the high vacuum valve (marked HV in Fig. 2.2) is opened and the cryogenic pump, a CTI CryoTorr-8 with a Model 8200 air-cooled compressor, takes over the main pumping of the chamber. The Cryo-Torr 8 has a peak pumping speed of 1500 L/s for air. A cold cathode Penning gauge (Alcatel CF2P; marked PG on Fig. 2.2), with an Alcatel FN121 controller, is used to measure pressure below 1 Pa. The ultimate pressure of the system is approximately $5 \times 10^{-4}$ Pa.

![Vacuum Chamber Diagram]

**Fig 2.2** The vacuum diagram of the magnetron sputtering system

In magnetron sputtering, there are primarily two methods: direct current (DC) and radio frequency (RF). In DC sputtering, the targets are energized with a DC voltage. This simple approach is great for conducting targets. However, insulating targets suffer from charge buildup. Eventually, this will kill the plasma, and the deposition. To counter this, there is RF sputtering.
RF applies a modulating potential to the target. This eliminates the problem of charge buildup, and can produce steady plasmas. In addition to insulating targets, RF can be used for conducting targets, with only a slight degradation in the deposition rate.

Originally, the Nordiko 3500 system was outfitted with only one 100 mm magnetron sputtering source, with the associated electronics for RF sputtering (Nordiko SG-1250, 1.25 kW RF generator operating at 13.56 MHz). However, the vacuum chamber has been modified, and a second 100 mm magnetron sputtering source has been added, with the associated electronics for RF sputtering at 13.56 MHz. Fig 2.3 shows the guns arrangement of the sputtering system. The two guns come into the vacuum chamber from the side, and are in a confocal arrangement for deposition onto the substrate.

Fig 2.3 Guns arrangement of the sputtering system
With respect to the normal of the substrate holder (i.e. the vertical axis), the guns are at angles of +45º and -45º, respectively, and are approximately 8 cm from the center of the holder. In addition, each gun’s shutter is operated by a Simatic C7-621 control unit.

Total deposition time is directly influenced by the shutter action. When a shutter is open, and there is plasma, there is deposition. As a result, the shutter controller is the main interface for controlling the deposition time, and the resulting film thickness. Fig. 2.4 shows the substrate holder in the chamber. The substrate holder is a disc (18 cm in diameter, 1 cm in thickness).

Fig 2.4 Substrate holder in the chamber of the sputtering system
It is mounted vertically, and the samples are typically attached via conductive carbon tape. The holder is mounted on an alcohol-cooled electrode, which is shown in Fig. 2.5. This electrode provides the necessary conductive path for both sample cleaning (prior to deposition) and sample biasing (during deposition).

![The electrode beneath the substrate holder](image)

**Fig. 2.5** The electrode beneath the substrate holder

The electrode is accomplished with a pulsed DC power supply (12 kV Physique & Industrie supply, with digital control). During the sputtering process, the pumping speed on the chamber is significantly reduced by “closing” the valve marked ISOLATION on Fig. 2.2. This “valve” does not seal, and the pumps act on this “leak” to maintain the chamber at the desired pressure during sputtering (typically ~ 0.4 Pa). Gas is introduced into the chamber via the inlets marked GAS on Fig. 2.2. Primarily, the
sputtering gas is ultra high purity (UHP) Argon. However, both UHP nitrogen and UHP oxygen can be mixed with the argon for reactive sputtering processes. Each gas is individually controlled via a HoribaSTEC SEC-E40 mass flow controller (MFC), and a L’Air Liquide Alphagaz 4-channel digital mass flow regulator. Chamber pressure is measured with a BOC Edwards Baricell 655AB capacitance gauge, marked CM on Fig. 2. This is an excellent gauge choice. The Baricell series has high accuracy (error ~ 0.5 % of reading), good long-term stability (typically less than 10 Pa), and the readings from a capacitance manometer are indifferent to the gas species.

In summary, the modified Nordiko 3500 RF magnetron sputtering system is a highly capable unit. The simplicity of the roughing pump and cryo-pump combination infers long life in an academic setting. The two RF magnetrons are capable of depositing a vast array of conducting and insulating targets. With the shutter control, the deposition time can be precisely controlled, and multilayer structures are possible. In addition, the ability to use multiple gases for both reactive and non-reactive sputtering dramatically increases the possible film combinations.

2.2 Characterization techniques

2.2.1 Characterization of film's structure

2.2.1.1 Scanning Electron Microscopy (SEM)

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure
and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm). The SEM is also capable of performing analyses of selected point locations on the sample; this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions (using EDS), crystalline structure, and crystal orientations (using EBSD). The design and function of the SEM is very similar to the Electron Probe Micro-Analyzer (EPMA) and considerable overlap in capabilities exists between the two instruments\textsuperscript{[74,75]}. 

Fig.2.6 Schematic diagram of a typical Scanning Electron Microscopy
Fig. 2.6 shows the diagram of a typical SEM. A beam of electrons is produced at the top of the microscope by an electron gun. The electron beam follows a vertical path through the microscope, which is held within a vacuum. The beam travels through electromagnetic fields and lenses, which focus the beam down toward the sample. Fig. 2.7 gives the mechanism of the beam hitting the sample in a SEM. Once the beam hits the sample, electrons and X-rays are ejected from the sample. Detectors collect these X-rays, backscattered electrons, and secondary electrons and convert them into a signal that is sent to a screen similar to a television screen\textsuperscript{[76,77]}. This produces the final image.

![Mechanism of the beam hitting sample in a SEM](image)

**Fig. 2.7** Mechanism of the beam hitting sample in a SEM

There are some limitations for SEM. Samples must be solid and they must fit into the microscope chamber. Maximum size in horizontal dimensions is usually on the order of 10 cm; vertical dimensions are generally much more limited and rarely exceed 40 mm. For most instruments samples must be stable in a vacuum on the order of $10^{-5}$ - $10^{-6}$ torr. Samples likely to outgas at low pressures (rocks saturated with hydrocarbons, "wet" samples such as coal, organic materials or swelling clays, and samples likely to decrepitate at low pressure) are unsuitable for examination in conventional SEM's.
However, "low vacuum" and "environmental" SEMs also exist, and many of these types of samples can be successfully examined in these specialized instruments. EDS detectors on SEM's cannot detect very light elements (H, He, and Li), and many instruments cannot detect elements with atomic numbers less than 11 (Na). Most SEMs use a solid state x-ray detector (EDS), and while these detectors are very fast and easy to utilize, they have relatively poor energy resolution and sensitivity to elements present in low abundances when compared to wavelength dispersive x-ray detectors (WDS) on most electron probe microanalyzers (EPMA). An electrically conductive coating must be applied to electrically insulating samples for study in conventional SEM's, unless the instrument is capable of operation in a low vacuum mode.

In this experiment, the samples are the Cr-Mo-N films coated on silicon wafers. They are solid, and with small volume and dimension. For Cr, Mo elements, they are relatively heavy, and stable under vacuum conditions. It collects X-rays, backscattered electrons and secondary electrons, which are good tools to get topography and composition of the specimen, but not the most efficient tool for the structure. A SEM (JEOL JSM 5900 LV) machine was equipped with EDS-WDS analysis tool which was used for compositional analysis.

2.2.1.2 Transmission Electron Microscopy (TEM)

The transmission electron microscope (TEM) operates on the same basic principles as the light microscope but uses electrons instead of light. What you can see with a light microscope is limited by the wavelength of light. TEMs use electrons as
"light source" and their much lower wavelength makes it possible to get a resolution a thousand times better than with a light microscope\[^{78,79}\].

The objects can be seen to the order of a few angstroms (10\(^{-10}\) m). For example, small details can be studied in the cell or different materials down to near atomic levels. The possibility for high magnifications has made the TEM a valuable tool in materials research. Fig. 2.8 shows the schematic diagram of a typical TEM. A "light source" at the top of the microscope emits the electrons that travel through vacuum in the column of the microscope. Instead of glass lenses focusing the light in the light microscope, the TEM uses electromagnetic lenses to focus the electrons into a very thin beam. The electron beam then travels through the specimen to be studied. Depending on the density of the material present, some of the electrons are scattered and disappear from the beam. At the bottom of the microscope the unscattered electrons interacted and transmitted through the specimen hit a fluorescent screen, which gives rise to a "shadow image" of the specimen with its different parts displayed in varied darkness according to their density. The image can be studied directly by the operator or photographed with a camera\[^{80,81}\].

Fig. 2.8 Schematic diagram of a typical Transmission Electron Microscopy
2.2.1.3 X-Ray Diffraction (XRD)

English physicists Sir W.H. Bragg and his son Sir W.L. Bragg developed a relationship in 1913 to explain why the cleavage faces of crystals appear to reflect X-ray beams at certain angles of incidence (θ). The variable \( d \) is the distance between atomic layers in a crystal, and the variable \( \lambda \) is the wavelength of the incident X-ray beam; \( n \) is an integer. This observation is an example of X-ray wave interference, commonly known as X-ray diffraction (XRD), and was direct evidence for the periodic atomic structure of crystals postulated for several centuries\(^{[82]}\).

Bragg’s Law: \( n\lambda = 2d \sin \theta \)

Fig. 2.9 Diagram of Bragg's Law

Fig 2.9 shows the diagram of the Bragg's Law, and Fig. 2.10 shows the schematic diagram of the x-ray beam detection in XRD. During x-ray diffraction analysis, x-ray beams are reflected off the parallel atomic layers within a mineral over a range of diffraction angles. Because the x-ray beam has a specific wavelength, for any given 'd-spacing' (distance between adjacent atomic planes) there are only specific angles at which the exiting rays will be 'in phase' and therefore, will be picked up by the detector.
producing a peak on the 'diffractogram'. Just like a 'fingerprint', every mineral has its own distinct set of diffraction peaks that can be used to identify it.

XRD is perhaps the most commonly used tool for structure analysis of as-deposited coatings. Important to note is that XRD gives integrated information from the full coating thickness, and also often from the substrate for coatings <5-10µm thick[83,84]. However, the observed diffraction peaks are often quite broad since the films usually have small grain sizes, and high defect concentrations. However, the accuracy in XRD analysis is normally sufficient for general phase identification, texture (preferred grain orientation), and lattice parameter determination. The peak broadening itself can be employed to deduct grain size and defects that are causing non-uniformly distributed strains often observed in PVD deposited coatings.

A Philips X’pert thin film X-ray diffractometer with Cu Kα radiation was used to measure the prepared sample. The X-ray diffractometer is operated at 45 kV and 40 mA, the wavelength is 0.15406 nm. The measurement range of 2θ is between 20° and 50°, and the tilt angle is 5°.

![Schematic diagram of the x-ray beam detection in XRD](image-url)

Fig.2.10 Schematic diagram of the x-ray beam detection in XRD
To calculate the particle size, the Scherrer Formula is used regardless of the strain in the film. When the phase a cubic structure,

\[ d = \frac{\lambda}{\sqrt{\Delta_M^2 - \Delta_{Si}^2 \cos \theta}} \]

Where \( d \) is the particle size, \( \lambda \) is the wavelength of the X-ray, which is 0.15406nm for this specific machine, \( \Delta_M \) is the measured full width at half maximum for the sample diffraction peak, and \( \Delta_{Si} \) is the full width at half maximum for the silicon standard, which is 0.31° (0.00541 in radians). The \( \Delta \) must be in radians when doing calculation. For a simple cubic lattice, the lattice parameters \( a=b=c=a_0 \), the d-spacing can be expressed in

\[ d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}} \]

2.2.1.4 Atomic Force Microscopy (AFM)

The Atomic Force Microscopy (AFM) is an instrument that can analyze and characterize samples on the surface morphology by measuring forces between a sharp probe (<10 nm) and surface at very short distance (0.2-10 nm probe-sample separation). It belongs to a family of techniques referred to as Scanning Probe Microscopes (SPM). The probe is supported on a flexible cantilever. The AFM tip “gently” touches the surface and records the small force between the probe and the surface\(^{[86]}\).

The AFM consists of a cantilever with a sharp tip (probe) at its end that is used to scan the specimen surface. Fig 2.11 shows the spring depiction of the cantilever and the SEM image of the cantilever. The cantilever is typically silicon or silicon nitride with a tip radius of curvature on the order of nanometers. When the tip is brought into proximity of a sample surface, forces between the tip and the sample lead to a deflection of the
cantilever according to Hooke's law. Fig.2.12 shows the schematic diagram of a AFM instrument of detection using a laser and position sensitive photodiode detector. Typically, the deflection is measured using a laser spot reflected from the top surface of the cantilever into an array of photodiodes. Traditionally, the sample is mounted on a piezoelectric tube that can move the sample in the z direction for maintaining a constant force, and the x and y directions for scanning the sample.

The probe is placed on the end of a cantilever (which one can think of as a spring). The amount of force between the probe and sample is dependent on the spring constant (stiffness of the cantilever and the distance between the probe and the sample surface. This force can be described using Hooke’s Law:

\[ F = -kx \]

where \( F \) is the force, \( k \) is the spring constant, and \( x \) is the cantilever deflection.

![Diagram showing a cantilever and a SEM image of a triangular SPM cantilever with a probe (tip).]

Fig. 2.11 a) Spring depiction of cantilever b) SEM image of triangular SPM cantilever with probe (tip)
If the spring constant of cantilever (typically ~0.1-1 N/m) is less than surface, the cantilever bends and the deflection is monitored. This typically results in forces ranging from nN (10^-9) to μN (10^-6) in the open air. Different cantilever lengths, materials, and shapes allow for varied spring constants and resonant frequencies.

![Diagram of AFM instrument showing "beam bounce" method of detection using a laser and position sensitive photodiode detector](image)

**Fig.2.12** Schematic diagram of an AFM instrument showing "beam bounce" method of detection using a laser and position sensitive photodiode detector

The AFM can be operated in a number of modes, depending on the application. In general, possible imaging modes are divided into static (also called contact) modes and a variety of dynamic (or non-contact) modes where the cantilever is vibrated\textsuperscript{[87,88]}. In the static mode operation, the static tip deflection is used as a feedback signal. Because the measurement of a static signal is prone to noise and drift, low stiffness cantilevers are used to boost the deflection signal. However, close to the surface of the
sample, attractive forces can be quite strong, causing the tip to "snap-in" to the surface. Thus static mode AFM is almost always done in contact where the overall force is repulsive. Consequently, this technique is typically called "contact mode". In contact mode, the force between the tip and the surface is kept constant during scanning by maintaining a constant deflection. The following Fig. 2.13 shows the contact and non-contact mode regime and the mechanism of AFM.

![Fig. 2.13 Plot of force as a function of probe-sample separation](image)

In this research, an Atomic Force Microscopy (AFM, Veeco Topometrix Explorer) was employed in contact mode at normal laboratory conditions to obtain the surface morphology images of the coatings. V-shaped high resonance frequency silicon nitride cantilevers with a pyramidal tip of 50 nm radius and force constant of 0.032 N/m were used. The original P, I, D number are -1, 0.1 and 0, respectively. Changing the set point effects the force that is the tip senses between it and the sample. If the Set Pont is too low then the scan will not scan because the force is not strong enough between the sample and the tip to cause deflections of the cantilever. If the Set Point is too high then the tip can
actually deform the sample or itself. Usually we keep the D number, change the P, I number to get the good quality image.

First 20x20 μm scans were run to get good alignment, then run 10x10μm and 5x5μm scans. Different surface areas were selected and the set point, P, I number, tilt angle were adjusted to repeat the measurement.

The AFM can be used to study a wide variety of samples (i.e. plastic, metals, glasses, semiconductors, and biological samples such as the walls of cells and bacteria). Unlike STM or scanning electron microscopy it does not require a conductive sample. However, there are limitations in achieving atomic resolution. As shown in Fig 2.14, the physical probe used in AFM imaging is not ideally sharp. As a consequence, an AFM image does not reflect the true sample topography, but rather represents the interaction of the probe with the sample surface. This is called tip convolution.

![Diagram](image)

Fig. 2.14 Ideally a probe (tip) with a high aspect ratio will give the best resolution. The radius of curvature of the probe leads to tip convolution. This does not often influence the height of a feature but the lateral resolution

2.2.2 Characterization of film's composition

2.2.2.1 X-ray Photoelectron Spectroscopy (XPS)
X-ray Photoelectron Spectroscopy (XPS) is an electron spectroscopic method that uses X-rays to eject electrons from inner-shell orbital. Fig 2.15 shows the mechanism of the X-rays eject electrons from inner-shell orbital. The sample is irradiated with mono-energetic x-rays causing photoelectrons to be emitted from the sample surface.

The kinetic energy, $E_k$, of these photoelectrons is determined by the energy of the X-ray radiation, $h\nu$, and the electron binding energy, $E_b$, as given by:

$$E_k = h\nu - E_b$$

The experimentally measured energies of the photoelectrons are given by:

$$E_k = h\nu - E_b - E_w$$

where $E_w$ is the work function of the spectrometer.

![Fig. 2.15 The mechanisms of X-ray ejecting electrons in XPS](image)

An electron energy analyzer determines the binding energy of the photoelectrons. From the binding energy and intensity of a photoelectron peak, the elemental identity, chemical state, and quantity of an element are determined\cite{89}.
A PHI Versaprobe imaging x-ray photoelectron spectrometer (XPS), operating a monochromatic, focused Al K-α x-ray source (E = 1486.6 eV) at 25 W with a 100 µm spot size, was used to determine the chemical bonding of the samples. All samples were grounded. Charge neutralization was provided by a cold cathode electron flood source and low-energy Ar-ions. All measurements were taken at room temperature and at a pressure of 2x10⁻⁶ Pa and the system base pressure is 5x10⁻⁸ Pa. Survey scans were taken at a pass energy of 117.4 eV, with a 1 eV step; high-resolution scans were taken at a pass energy of 23.5 eV, with a 0.2 eV step. To eliminate surface contamination, the CrMoN samples were sputtered with 4 keV Ar ion beams. This removed approximately 10 nm of material from the films. To limit cratering effects, the ion beam was rastered across a 2 x 2 mm² area. Multipak v9.0 software was used to analyze the resulting spectra.

2.2.2.2 Energy Dispersive X-ray Spectroscopy (EDS)

This instrument is one of the detectors on our scanning electron microscope (SEM). The sample is placed under vacuum and excited to a higher energy state with an electron beam. As each element falls back down to its original energy state it emits X-ray energy at different wavelengths for each element. Identification of the elements is done by matching the peak locations (on the x-axis) with known wavelengths for each element. EDS analysis is very good at determining what elements are present in samples which are as small as one micrometer (40 micro-inches). Results are plotted with X-ray wavelength on the X-axis and intensity on the Y-axis with each peak labeled with its corresponding element\textsuperscript{[90,91]}.

There are some limitations of the EDS. Analysis is normally not quantitative, but
semi-quantitative results can be provided for some materials. Detection limits are typically 1% or higher so trace elements will not be detected. Identifies which elements are present but not how they are connected so it cannot tell the difference between minerals of similar composition but different crystal structure. EDS analysis is unable to detect elements with molecular weights below that of carbon$^{[92]}$.

2.2.3 Characterization of film's mechanical properties

2.2.3.1 Nanoindentation

There has been considerable recent interest in the mechanical characterization of thin film systems and small volumes of material using depth-sensing indentation tests with indenters. Usually, the principle goal of such testing is to extract elastic modulus and hardness of the specimen material from experimental readings of indenter load and depth of penetration.

Conventional indentation hardness tests involve the measurement of the size of a residual plastic impression in the specimen as a function of the indenter load. In a nanoindentation test, the size of the residual impression is often only a few microns and this makes it very difficult to obtain a direct measure using optical techniques. In nanoindentation testing, the depth of penetration beneath the specimen surface is measured as the load is applied to the indenter. The known geometry of the indenter then allows the size of the area of contact to be determined. The procedure also allows for the modulus of the specimen material to be obtained from a measurement of the “stiffness” of the contact, that is, the rate of change of load and depth. Fig. 2.16 shows a typical load-displacement curve of fused silica. A record of these values can be plotted on a
graph to create a load-displacement curve. These curves can be used to extract mechanical properties of the material\textsuperscript{[93,94]}.

Hardness is calculated by dividing the loading force by the projected residual area of the indentation. Besides hardness, the Young’s modulus of elasticity can be obtained from the slope of the unloading curve. The hysteresis indicates that the deformation is not fully elastic and partially inelastic. For compliant materials the loading and unloading curves would be closely identical since the deformation is mainly elastic.

![Fused Silica Load-Displacement Curve](image)

Fig. 2.16 A typical load-displacement curve of fused silica

The most commonly used analysis method for obtaining hardness and modulus was developed by Oliver and Pharr\textsuperscript{[95]}. Fig. 2.17 gives the load-displacement curve showing the unloading($S_u$) and loading ($S_l$) slopes used in calculation of hardness and Young's
modulus. In this approach the total penetration depth is given by the sum of the plastic depth (contact depth), \( \delta_c \), and the elastic depth, \( \delta_e \), which represents the elastic flexure of the surface during loading. Thus the total penetration depth, \( \delta \), is given by
\[
\delta = \delta_c + \delta_e
\]
and
\[
\delta_e = \varepsilon \frac{p}{S_u}
\]
where \( S_u \) is the slope of the unloading curve at maximum load (see Fig. 2.17) and \( \varepsilon \) is a constant which depends on indenter geometry (\( \varepsilon = 0.75 \) for Berkovich indenters). \( A_c \) can be calculated from equations above and the contact area can be calculated from this if the relationship between contact depth and \( A_c \) is known. For an ideal Berkovich indenter \( A_c = 24.5\delta_c^2 \), but most indenters are blunted at their end and a more complex tip area function is then required.

The hardness, \( H \), is then given by equation:
\[
H = \frac{p}{A_c}
\]

Young’s modulus can be determined from the slope of the unloading curve using a modified form of Sneddon’s flat punch equation where
\[
S_u = \gamma \beta \frac{2}{\sqrt{\pi}} E_r \sqrt{A_c}
\]
where \( E_r \) is the contact modulus which can be derived from Young’s modulus and Poisson’s ratio of the indenter and the test material via
\[
\frac{1}{E_r} = \frac{1-v_m^2}{E_m} + \frac{1-v_i^2}{E_i}
\]
where the subscripts \( m \) and \( i \) refer to the test material and indenter, respectively. The constant \( \gamma \) was introduced by Joslin and Oliver\(^\text{[96]}\) to account for deviations from the ideal
Sneddon behaviour predicted by finite element investigations. The constant $\beta$ was introduced to correct for the fact that the Berkovich indenters generally used for this sort of experiment are not axially symmetric; in this study $\beta = 1.034^{[97]}$. It is possible to determine Young’s modulus of the test material if the properties of the indenter are known. For accurate determination a method for measuring Poisson’s ratio of the test material is required but for most metals and ceramics an estimated value of $\nu_m = 0.25$ will give only a small error that $E_r$ is not a sensitive function of $\nu_m$.

![Load-displacement curve](image)

Fig.2.17 Load-displacement curve showing the unloading(Su) and loading (Sl) slopes used in calculation of hardness and Young's modulus. Also indicated is the plastic work of indentation $W_p$ which is the area bounded by the loading and unloading curves and the displacement axis.

A Nanoindenter XP (MTS Systems Corporation, Oak Ridge TN) system is used in measuring the hardness and modulus of prepared samples. The system was calibrated by using fused silica samples for a range of operating conditions before the experiments with the samples. A Berkovich diamond indenter with total included angle of 142.3° was used for all the measurements. The maximum indentation depth was up to 10% of the
thickness of the coating to avoid the substrate effects. The data set was processed using the proprietary software (TestWorks 4, MTS Systems Corporation) to produce load-displacement curves, and the mechanical properties were calculated using the Oliver and Pharr method.

2.2.3.2 Tribometry

Tribometers determine the magnitude of friction and wear as two surfaces rub together. Fig 2.18 shows the mechanism of the tribometer works. In one measurement method a flat or a spherical probe is placed on the test sample and loaded with a precisely known weight. The sample is either rotating or reciprocating in a linear track. The resulting frictional forces acting between the probe and the sample are measured. Additionally, the wear for both the sample and probe is calculated from the volume of the material lost during the term of the test.

Fig 2.19 gives an image of a typical CSM nanotribometer. The CSM Nano-Tribometer is a unique instrument because of its low load range down to 50µN. It can perform both the linear reciprocating and rotating mode. One important feature of all the CSM Tribometers is that the experiment stops automatically when the coefficient of friction reaches a threshold value or when a specified number of turns are reached. Also, the Tribometer is supplied with an enclosure so that a controlled atmosphere of varying humidity or composition can be used.
This simple method facilitates the determination, study of friction and wears behavior of almost every solid material combination, with varying time, contact pressure, velocity, temperature, humidity, lubricants, etc. Furthermore, control of the test
parameters such as speed, frequency, contact pressure, time and the environmental parameters (temperature, humidity and lubricant) allows us to closely reproduce the real world conditions of a practical wear situation.

The linear tribometer reproduces the reciprocating motion typical of many real world mechanisms. The instrument produces a friction coefficient for both the forward and backward displacement of the stroke. The reciprocating technique is also very useful for studying the variation over time of the static coefficient of friction - as opposed to the kinetic coefficient measured with the pin-on-disk geometry. Most contact geometries can be reproduced including pin-on-plate, ball-on-plate and flat-on-plate.

Tribological behaviors of all films were evaluated using a ball-on-disk nanotribometer under dry sliding conditions at room temperature. Ti balls were used as the counterface materials. The normal loads were 100mN, 300mN and 500mN. All the test were run in laboratory air (25°C) and relatively humidity of 65% with a sliding distance of 300m and a sliding speed of 0.2m/s. Coefficient of friction was recorded during each test.

2.2.3.3 Stress measurements

Optical profilometry is a rapid, nondestructive, and noncontact surface metrology technique. An optical profiler is a type of microscope in which light from a lamp is split into two paths by a beam splitter. One path directs the light onto the surface under test; the other path directs the light to a reference mirror. Reflections from the two surfaces are recombined and projected onto an array detector. When the path difference between the recombined beams is on the order of a few wavelengths of light or less interference can
occur. This interference contains information about the surface contours of the test surface. Vertical resolution can be on the order of several angstroms while lateral resolution depends upon the objective and is typically in the range of 0.5-5 microns.

![Image of a Wyko NT1100 Profilometer](image.png)

**Fig. 2.20 Image of a Wyko NT1100 Profilometer**

The measurements were taken in vertical scanning interferometer (VSI) mode by a Wyko NT1100 profilometer which is shown in Fig. 2.20. The lens system consists of a field of view (1.0X) and objective lens (5.0X), resulting in a magnification of 5.1X. This yields a 920 µm x 1200 µm measurement area. Using the Vision software, multiple measurements are stitched together to cover the entire surface of the sample. For example, the average number of frames (i.e. individual measurements which are stitched together) is ~ 110.
CHAPTER 3
Cr-Mo-N COATINGS ON CoCrMo SUBSTRATES

3.1 Samples preparation

3.1.1 Film deposition

Cr-Mo-N coatings were prepared by using a RF dual magnetron sputtering system (NORDIKO 3500-13.56 MHz) with two 4-in targets of Cr and Mo. The nitrogen flow was adjusted in these deposition experiments to a saturation limit. The target voltages were varied to change the sputtering rate and to modify the composition of the CrMoN layers. Chromium and Molybdenum targets were co-sputtered at an optimized sputtering rate to yield uniform 1.8 μm thick films of desired \( \text{Cr}_{25}\text{Mo}_{25}\text{N}_{50} \) composition on polished CoCrMo biomedical alloy substrates. The substrate temperature during the deposition was up to 200°C.

3.1.2 Thermal processing of films

Once the films were deposited, several samples underwent various \textit{ex-situ} thermal treatments. These treatments included furnace annealing in air, argon, and microwave plasma processing in \( \text{H}_2/\text{N}_2 \) gas mixture. The latter treatment is used as an initial step in preparing the substrate for nanocrystalline diamond (NCD) deposition in a CVD process, and it was important to understand the behavior of CrMoN film as a potential interlayer for NCD.
The furnace annealing of the samples in air and Ar was conducted at temperatures up to 800°C for 1 hour. Microwave plasma annealing in a H₂/N₂ gas mixture was performed at 600 W power; this leads to a substrate temperature of 800°C. The gas pressure and flow rates were set at 30 mTorr, 10 sccm for H₂, and 36 sccm for N₂, respectively.

In addition, two combinatorial thermal treatments were conducted: (i) the sample was annealed in air at 600°C, with subsequent annealing in the H₂/N₂ microwave plasma at 800°C; and (ii) the sample was annealed in the H₂/N₂ microwave plasma at 800°C, with subsequent annealing in air at 800°C. All the samples are listed in the Table 3.1.

Table 3.1 Overview of CrMoN coatings with different thermal processes

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Coatings</th>
<th>Thermal treatments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>Cr₂₅Mo₂₅N₅₀</td>
<td>As deposited</td>
</tr>
<tr>
<td>(2)</td>
<td>Cr₂₅Mo₂₅N₅₀</td>
<td>Annealed in air at 800°C</td>
</tr>
<tr>
<td>(3)</td>
<td>Cr₂₅Mo₂₅N₅₀</td>
<td>Annealed in mw plasma at 800°C</td>
</tr>
<tr>
<td>(4)</td>
<td>Cr₂₅Mo₂₅N₅₀</td>
<td>Annealed in air at 600°C+mw plasma at 800°C</td>
</tr>
<tr>
<td>(5)</td>
<td>Cr₂₅Mo₂₅N₅₀</td>
<td>Annealed in mw plasma at 800°C+air at 800°C</td>
</tr>
</tbody>
</table>

3.2 Experimental results of microstructure and morphology
The Cr$_{25}$Mo$_{25}$N$_{50}$ films are stable with no visible changes in the microstructure and properties during furnace thermal treatments up to 600°C in both Ar and air. However, when the temperature is increased to 800°C, significant changes are observed.

3.2.1 Scanning Electron Microscopy (SEM)

The cross section of the sample was imaged by Scanning Electron Microscopy (SEM). The film is uniform, smooth, and with a thickness of 1.8µm. A representative SEM image of the resulting Cr$_{25}$Mo$_{25}$N$_{50}$ is shown in Fig. 3.1.

![SEM Image of Cr$_{25}$Mo$_{25}$N$_{50}$ coating](image)

**Fig. 3.1** A cross-sectional scanning electron micrograph of the as-prepared Cr$_{25}$Mo$_{25}$N$_{50}$ coating

3.2.2 X-Ray Diffraction (XRD)

In the XRD patterns shown in Fig. 3.2, we can clearly see the changes in the crystalline structure and phase composition of the samples with different thermal treatments. The black line in Fig.3.2 represents the original as-deposited sample; the red line in Fig.3.2 is the sample annealed in air at 800°C; and the green line in Fig.3.2 is the sample annealed in microwave plasma at 800°C.
Based on the XRD peak positions, it was suggested that in the original untreated sample, the structure can be described as a nanocrystalline Mo-rich ternary nitride phase with about 15 nm grain size dispersed in a predominantly amorphous Cr-rich nitride matrix. In the air annealed sample (Fig.3.2 red line), we see the development of Cr$_2$O$_3$ crystallites as the dominant phase, while the proposed nanocrystalline ternary phase is still mainly preserved.

Fig.3.2 X-ray diffraction patterns of (1) as-deposited CrMoN ternary film, (2) annealed in air at 800°C, and (3) annealed in H$_2$/N$_2$ microwave plasma at 800°C.

When the thermal treatment was performed in microwave plasma, a secondary nanocrystalline phase was formed in addition to the existing ternary phase as shown (Fig.3.2 green line). This new phase could not be identified through the JCPDS database.
Interestingly, the calculated grain size for both co-existing phases in plasma-treated sample is about the same, about 10 nm. The analysis of the XPS spectra recorded for the different depths across the film, coupled with the XRD results, suggest that this new phase is a metal-rich quaternary Cr-Mo-C-N where the amount of nitrogen is small when compared with the as-deposited sample. Indeed, the H$_2$/N$_2$ plasma treatment resulted in substantial depletion of nitrogen in the original ternary film and contamination of the sample with carbon. It has been also proposed that the new phase can form, at least partially, at the expense of the original nanocrystalline ternary phase in the coating. This could lead to a reduction in the grain size and/or partial decomposition of the original nanocrystalline ternary phase.

3.2.3 X-ray Photoelectron Spectroscopy (XPS)

Fig.3.3-Fig.3.7 show the XPS spectra recorded after 30 min sputter etching of the as-deposited and thermal treated Cr$_{25}$Mo$_{25}$N$_{50}$ sample. The composition of the sample was found to be uniform throughout the film thickness.
Fig. 3.3 XPS results of (1) as deposited CrMoN coating

Fig. 3.3 shows the bonding stage of the as-deposited CrMoN coating. The Cr$2p$ peaks were deconvoluted into two distinct states, which were located at 574.5 eV and 583.9 eV; the Mo$3d$ peaks were deconvoluted into two states, with two peaks located at 228.8 eV and 232 eV. The Mo$3p^{3/2}$ and N$1s$ peaks overlap with two peaks located at 394 eV and 397.5 eV, respectively. Some carbon and oxygen impurities were found; the carbon was partially present in a carbide form. Fig. 3.4 shows the XPS results of the CrMoN coating annealed in air at 800°C. The bonding characters behave in a similar way as the as-deposited CrMoN coatings.
Fig. 3.4 XPS results of (2) CrMoN coating annealed in air at 800°C

After the H$_2$/N$_2$ plasma treatment, oxygen content was below the detection limit, and nitrogen content was significantly reduced. However, the amount of metal-carbon bonding increased which was shown in the C1s states in Fig. 3.5. The new secondary nanocrystalline phase was formed in this process as discussed above.
On the other hand, when plasma treatment was performed with an initially oxidized sample (air oxidation at 600°C which neither forms chromium oxide nor induces phase changes), as Fig. 3.6 shows, the loss of nitrogen was reduced and a very small amount of the secondary phase was observed. When the coating was initially under plasma treatment and with subsequent annealing in air at 800°C, as shown in Fig. 3.7, the carbon existed in the carbide form and the coating was oxidized with increased amount of oxygen detected.

Based on all of the XPS data above, it was suggested that the thermal treatments didn’t change the metallic bonding due to the high bonding energy; the plasma treatment cause the depletion of nitrogen and contamination of carbon which change the amorphous carbon into a carbide form.

Fig.3.5 XPS results of (3) CrMoN coating annealed in mw plasma at 800°C
Fig. 3.6 XPS results of (4) annealed in air at 600°C+in mw plasma at 800°C

Fig. 3.7 XPS results of (5) annealed in mw plasma at 800°C+in air at 800°C
3.2.4 Atomic Force Microscopy (AFM)

The surface roughness of the fabricated films was found to be in the nanoscale range. However, the thermal treatment changes the surface topography as the result of stress, grain growth, and phase transformations. The representative AFM 5x5µm² images of the surface topography for the Cr$_{25}$Mo$_{25}$N$_{50}$ samples exposed to different treatments are shown in Figure 3.8. The surface roughness increases significantly due to the growth of a chromium oxide crystalline phase when the sample is annealed in air. The plasma annealing does not change the surface roughness, but cracks are often observed in the film (e.g., in Fig. 3.8(3)) as the result of thermal stress.

![AFM images](image)

**Fig.3.8 Atomic Force Microscopy (AFM) results of Cr$_{25}$Mo$_{25}$N$_{50}$ coatings under different treatments** (1) as deposited Cr$_{25}$Mo$_{25}$N$_{50}$ coating (2) annealed in air at 800°C (3) annealed in mw plasma at 800°C

As shown in Fig.3.9, sample annealed in air followed with mw plasma treatment, there is a slight decrease in surface roughness; and the sample with reverse order treatments, there is a significant reduction in the grain size with the surface roughness increased.
3.3 Mechanical properties

3.3.1 Nanoindentation

The results of nanoindentation tests are shown in Fig.3.10. The measurements were conducted by 10 times and taken the average value. It shows that the hardness of the original sample is relatively low, about 9 GPa. However, thermal processing resulted in significant changes in both the hardness and the Young’s modulus of the samples. The sample annealed in the air at 800°C showed an increase in the hardness by 50%. Unfortunately, this sample also shows an increase in surface roughness. For the microwave plasma annealed sample, the surface roughness was comparable to the untreated sample. However, the hardness only showed a modest increase of about 20%.
In Table 3.2, we can see representative mechanical results of the two thermal treatments in comparison with the untreated sample. From this, we can see the modulus of the air annealed sample increased about 33% with respect to the untreated sample. The modulus of the plasma annealed sample shows no significant change with respect to the untreated sample. Following the discussion above, a combinatorial post-deposition processing was proposed as the pathway for further modification of the microstructure and properties of the ternary CrMoN films; in addition, this approach may lead to a better understanding of the observed phenomena.
Table 3.2 Mechanical properties and surface roughness overview of the CrMoN coatings under various thermal processes

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Hardness (GPa)</th>
<th>Modulus (GPa)</th>
<th>Roughness (Ra)nm</th>
<th>Cracking</th>
</tr>
</thead>
<tbody>
<tr>
<td>As deposited</td>
<td>9</td>
<td>200</td>
<td>11.1</td>
<td>No</td>
</tr>
<tr>
<td>air at 800°C</td>
<td>15</td>
<td>280</td>
<td>20.3</td>
<td>No</td>
</tr>
<tr>
<td>mw plasma at 800°C</td>
<td>11</td>
<td>190</td>
<td>12.0</td>
<td>Yes</td>
</tr>
<tr>
<td>air 600°C+plasma 800°C</td>
<td>10</td>
<td>225</td>
<td>10.7</td>
<td>No</td>
</tr>
<tr>
<td>Plasma 800°C+air 800°C</td>
<td>7</td>
<td>175</td>
<td>30.0</td>
<td>No</td>
</tr>
</tbody>
</table>

Conclusion:

Cr$_{25}$Mo$_{25}$N$_{50}$ coatings were successfully deposited on CoCrMo-alloy substrates, using RF reactive magnetron sputtering. These films were subjected to various thermal treatments. There are no significant changes observed in the film properties for thermal treatments in the air or argon up to 600 ºC. Films annealed in the air at 800 ºC, show the oxidation, as confirmed with both XRD and XPS. The dominant phase is Cr$_2$O$_3$. The thermal treated films show an increase in both hardness and Young’s modulus, but there is a corresponding increase in grain size and surface roughness. Films treated in Argon at 800 ºC, show a smaller increase in hardness, with an increase in grain size and surface roughness. However, films annealed in microwave plasma at 800ºC, in an H$_2$/N$_2$ gas mixture, show a slight increase in the mechanical properties, but with a decrease in surface roughness, and grain size. The drawback is the possibility of crack formation in
the film, due to increased thermal stress. In addition, this process leads to the formation of a new, presumably ternary or quaternary, nanocrystalline phase. Furthermore, we treated samples with a combinatorial thermal process to further understand the observed trends. For films annealed in the air at 600ºC, with subsequent annealing in H₂/N₂ microwave plasma at 800ºC, there is a slight increase in the mechanical parameters of the film, with a slight decrease in surface roughness. By reversing the order of thermal treatments, we observe a significant reduction in the grain size. However, the resultant mechanical properties are substantially declined, and the surface roughness increased.

The use of thermal treatments has been successfully demonstrated to control grain size, surface morphology, and mechanical properties in Cr₂₅Mo₂₅N₅₀ coatings on CoCrMo substrates. These simple processing techniques may be used for further improvement of the surface characteristics of nanocomposite coatings on biomedical implants. However, further research is necessary to understand the underlying physical processes involved. As a result, we plan to continue this research with various compositions of Cr-Mo-N coatings, and a wider range of thermal treatments.
CHAPTER 4

Cr$_{1-x}$Mo$_x$N$_y$ COATINGS ON Si SUBSTRATES

4.1 Samples preparation

4.1.1 Film deposition

CrMoN coatings are the potential coatings used in a wide range of applications such as high speed cutting tools, drilling, bearing, and biomedical implants. Their properties dependent on the composition are important to be studied. To avoid the substrate effect on the coatings, standard and uniform Si wafers (100) were used as the substrate.

Ternary Cr$_{1-x}$Mo$_x$N$_y$ coatings were deposited on Si wafers (100) by using a dual rf-magnetron sputtering system (Nordiko 3500-13.56MHz) with Cr and Mo targets and a 60/40 argon/nitrogen gas mixture at 6µbar working pressure. The distance between the substrate and the centers of 100-mm diameter targets was fixed around 150 mm. Purities of Cr and Mo targets were 99.9%, respectively. The N$_2$ gas was injected near the substrate holder. The sputtering target bias voltages were varied from -500 V to -900 V which allowed to preparing the ternary layers with Cr/Mo ratios in the range from 1/3 to 3/1. Binary CrN and MoN coatings were also prepared under similar conditions for comparison. The binary films are deposited in about 6µbar with Ar$_2$/N$_2$ ratio of 80/20. The residual pressure was in the range of $10^{-5}$ Pa before the introduction of the sputtering gases argon and nitrogen. All films have a Cr under-layer (deposited for 10 min, at -900 V/ 500 W, in ~6 µbar of Ar). The deposition processes were approximately 3-hour long,
to achieve about the same thickness of up to 2 μm of the deposited films.

For the first set of the coatings, which named as (a1),(b1),(c1),(d1),(e1), the substrate temperature during the process did not exceed 200 °C. For the second set of coatings, (a2),(b2),(c2),(d2),(e2), the heater was set at 5 A, 22 V, and the deposition temperature is around 400°C. Table 4.1 below shows the list of all the as-deposited coatings.

Table 4.1 Deposition parameters of the as-deposited Cr_{1-x}Mo\textsubscript{x}N\textsubscript{y} coatings on Si substrates

<table>
<thead>
<tr>
<th>Films with target composition</th>
<th>Deposition Temp(°C)</th>
<th>%(\text{N}_2/\text{Ar}) in plasma</th>
<th>Cr target voltage(V)</th>
<th>Mo target voltage(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)CrN</td>
<td>(a1) 200</td>
<td>(20/80)</td>
<td>-900</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>(a2) 400</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b)Cr\textsubscript{32}Mo\textsubscript{18}N\textsubscript{50}</td>
<td>(b1) 200</td>
<td>(40/60)</td>
<td>-900</td>
<td>-500</td>
</tr>
<tr>
<td></td>
<td>(b2) 400</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(c)Cr\textsubscript{25}Mo\textsubscript{25}N\textsubscript{50}</td>
<td>(c1) 200</td>
<td>(40/60)</td>
<td>-720</td>
<td>-780</td>
</tr>
<tr>
<td></td>
<td>(c2) 400</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(d)Cr\textsubscript{18}Mo\textsubscript{32}N\textsubscript{50}</td>
<td>(d1) 200</td>
<td>(40/60)</td>
<td>-500</td>
<td>-900</td>
</tr>
<tr>
<td></td>
<td>(d2) 400</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(e)MoN</td>
<td>(e1) 200</td>
<td>(20/80)</td>
<td>0</td>
<td>-900</td>
</tr>
<tr>
<td></td>
<td>(e2) 400</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.1.2 Thermal processing of films
The samples were annealed in air atmosphere at temperatures up to 700°C for 1 hour in a conventional laboratory furnace at a heating rate of 10°C/min. The samples were cooled down naturally in the furnace, and the total time of the annealing procedure was about 4 hours.

4.2 Experimental results of structure and morphology

4.2.1 Scanning Electron Microscopy (SEM)

The Fig4.1 shows the cross-sectional picture of the as deposited sample (c1) Cr\textsubscript{25}Mo\textsubscript{25}N\textsubscript{50} and (b1) Cr\textsubscript{32}Mo\textsubscript{18}N\textsubscript{50} which were deposited at 200°C. The film thickness is about 1.5µm with columnar structure.

![SEM cross-section image](image-url)

Fig. 4.1 SEM cross-section image of (c1)Cr\textsubscript{25}Mo\textsubscript{25}N\textsubscript{50} and (b1) Cr\textsubscript{32}Mo\textsubscript{18}N\textsubscript{50} films deposited at room temperature

Fig 4.2 shows the surface morphology SEM images of the as-deposited (a1)CrN (b1) Cr\textsubscript{32}Mo\textsubscript{18}N\textsubscript{50} (c1) Cr\textsubscript{25}Mo\textsubscript{25}N\textsubscript{50} (d1) Cr\textsubscript{18}Mo\textsubscript{32}N\textsubscript{50} (e1)MoN coatings deposited at room temperature. It was shown from these images that binary CrN has some level of porosity, while MoN has smoother surface and slightly larger grain size. With different composition of Cr/Mo, the Cr\textsubscript{1-x}Mo\textsubscript{x}N\textsubscript{y} films have the porosity between the CrN and MoN coatings.
Fig 4.2 The surface morphology SEM images of the as-deposited (a1)CrN (b1) Cr$_{32}$Mo$_{18}$N$_{50}$ (c1) Cr$_{25}$Mo$_{25}$N$_{50}$ (d1) Cr$_{18}$Mo$_{32}$N$_{50}$ (e1)MoN coatings deposited at room temperature.

The Fig4.3 shows both the surface and cross-sectional morphology of as deposited Cr$_{1-x}$Mo$_x$N$_y$ coatings which were deposited at 400°C. From the cross-sectional images, the ternary films (b2) (c2) (d2) show preferred oriented growth direction with clear columnar structure, which can also be told from the surface morphology. There is no great difference between the surface morphology of ternary films. However, the binary films (a2) (e2) show much denser structure.

Fig. 4.3 Cross sectional and surface SEM pictures of (a2)CrN (b2)Cr$_{32}$Mo$_{18}$N$_{50}$ (c2)Cr$_{25}$Mo$_{25}$N$_{50}$ (d2)Cr$_{18}$Mo$_{32}$N$_{50}$ (e2)MoN coatings deposited at 400°C

Fig. 4.4 shows the surface morphology of the coatings which deposited at 400°C after annealing in air at 600°C. For the films deposited at 400°C, the surface morphology of films (a2) (b2) (c2) (d2) didn't change after being annealed at air at 600°C for one hour.
However, the film (e2) MoN, is fully oxidized with the growth of oxidation, which can be observed as a plate-like structure (oxidation) on the surface.

Fig. 4.5 shows the surface morphology of the 400°C deposited coatings after annealing in air at 700°C. Only (a2)CrN (b2)Cr$_{32}$Mo$_{18}$N$_{50}$ (c2)Cr$_{25}$Mo$_{25}$N$_{50}$ coatings survived without delamination after annealing in air at 700°C. It was suggested that there was a growth of oxidation on the surface of (b2)Cr$_{32}$Mo$_{18}$N$_{50}$ coating, and the (a2)CrN and (c2) Cr$_{25}$Mo$_{25}$N$_{50}$ were still with smooth surface.

![SEM picture of (a2)CrN (b2)Cr$_{32}$Mo$_{18}$N$_{50}$ (c2)Cr$_{25}$Mo$_{25}$N$_{50}$ (d2)Cr$_{18}$Mo$_{32}$N$_{50}$ (e2)MoN coatings deposited at 400°C after annealed in air at 600°C](image_url)
4.2.2 X-Ray Diffraction (XRD)

Fig.4.6 shows X-ray diffraction patterns of Cr$_{1-x}$Mo$_x$N$_y$ coatings at various Cr/Mo ratios which were deposited at 200°C. We can see clearly in Fig.4.6 from the patterns that for pure CrN(a1) and MoN(e1) coating, the patterns show preferred orientations of (111) and (200) crystal planes of face-centered-cubic (fcc) CrN, Mo$_2$N crystal structure, respectively. As the Mo content in the Cr$_{1-x}$Mo$_x$N$_y$ coatings increased, the diffraction peaks were gradually shifted from those of pure CrN coating to those lower angle diffraction of pure MoN coating, reveals larger lattice parameters which will be shown later. From Scherrer equation, we can calculate that the mean grain size of the coatings is 13-21 nm.
Fig. 4.6 XRD patterns of as deposited (a) CrN (b) Cr$_{32}$Mo$_{18}$N$_{50}$ (c) Cr$_{25}$Mo$_{25}$N$_{50}$ (d) Cr$_{18}$Mo$_{32}$N$_{50}$ (e) MoN deposited at room temperature

Fig. 4.7 and Fig. 4.8 show the XRD patterns of these Cr$_{1-x}$Mo$_x$N$_y$ (deposition temperature 200°C) annealed at 600 °C and 700 °C, respectively. The MoN coating was completely oxidized after annealing in air at 600 °C for one hour, and ternary Cr$_{18}$Mo$_{32}$N$_{50}$ coating (d), which had a higher Mo content, also oxidized and delaminated after annealing in air at 700°C, whereas the ternary Cr$_{32}$Mo$_{18}$N$_{50}$ coating (b1), with Cr/Mo ratio more than 1.7, survived at 700 °C without cracking or delamination. Based on the XRD peaks positions in Fig.4.6 and Fig.4.7, it is indicated that Cr$_2$O$_3$ is the main crystalline phase after annealing process.
Fig. 4.7 XRD patterns of (a1) CrN (b1) Cr$_{32}$Mo$_{18}$N$_{50}$ (c1) Cr$_{25}$Mo$_{25}$N$_{50}$ (d1) Cr$_{18}$Mo$_{32}$N$_{50}$ (e1) MoN deposited at room temperature after annealed at air at 600°C

Fig. 4.8 XRD patterns of (a1) CrN (b1) Cr$_{32}$Mo$_{18}$N$_{50}$ (c1) Cr$_{25}$Mo$_{25}$N$_{50}$ deposited at room temperature after annealed at air at 700°C
For the films deposited at 400°C, the XRD patterns illustrated the difference on the phase transformation.

![XRD patterns](image)

**Fig.4.9** XRD patterns of (a2)CrN as deposited at 400°C and under thermal processes

For the pure (a2)CrN (Fig.4.9), the effect of deposition temperature on phase formation was found that with higher deposition temperature, the films consist of primarily fcc CrN phase and with hexagonal h-Cr$_2$N phase. With low deposition temperature, the deposition results in films of nearly stoichiometric CrN and the films
show strong (111) type texture. It is reasonable that the formation the hexagonal Cr$_2$N phase has a much narrower window than the formation of fcc CrN phase. During oxidation of Cr$_2$N a transformation into CrN was observed as shown in Fig.4.8 that as the increase of the annealing temperature, the hexagonal Cr$_2$N phase disappeared, and with the enhancement of the fcc CrN (111) peak. (a2)CrN had no oxidation when annealed at 600°C, and started to have small oxidation at 700°C.

For the (a2)MoN (Fig.4.10), face-centered cubic phases (γ-Mo$_2$N) were formed with pronounced (111) direction growth. However, a secondary phase precipitate was observed at the left side of the (111) peak. This secondary phase didn't change after thermal treatments. The resistance of Mo–N coatings to oxidation is poor because of their non-protective nature and the volatility of the oxides at moderately high temperatures. At annealing temperature 400°C, the (a2)MoN films were oxidized with the main oxidation product of MoO$_3$, which were also responded to the SEM results.
Fig.4.10 XRD patterns of (e)MoN as deposited at 400°C and under thermal processes

For the ternary Cr₁₈Mo₃₂N₅₀ coating (d2) which contains more Mo (Fig.4.10), survived at 600°C annealing temperature, but oxidized and delaminated after annealing in air at 700°C.
Fig. 4.11 XRD patterns of (d2)Cr$_{18}$Mo$_{32}$N$_{50}$ as deposited at 400°C and under thermal processes.

Whereas the ternary Cr$_{32}$Mo$_{18}$N$_{50}$ coating (b2) (Fig. 4.12) and (c2)Cr$_{25}$Mo$_{25}$N$_{50}$ (Fig. 4.13), with higher Cr/Mo ratio, survived at 700 °C without cracking or delamination. This behavior followed the same trend as we got from the films deposited at 200°C. It should be mentioned that, secondary phase precipitates were observed both in (c2) and (d2). This was not observed at the first set of samples which were deposited at lower temperature. It relies on changes in solid solubility with temperature to produce fine...
particles of an impurity phase, which impede the movement of dislocations, or defects in a crystal's lattice. This may lead to better thermal stability and mechanical properties.

Fig.4.12 XRD patterns of (b2)Cr_{32}Mo_{18}N_{50} as deposited at 400°C and under thermal processes

Compare the XRD patterns of (c1) and (c2) which were with the same composition of Cr/Mo, but with different deposition temperature, both of the films survived at annealing temperature 700°C, the (c1) coating which deposited at room
temperature, had some amount of oxidation, however, the (c2) coatings which deposited at 400°C, had no oxidation.

Fig. 4.13 XRD patterns of (c2)Cr$_{25}$Mo$_{25}$N$_{50}$ as deposited at 400°C and under thermal processes

Fig. 4.14 shows the lattice parameter of CrN F.C.C phase as a function of Mo content. The lattice parameter were measured by (111) (200) peaks and taken the average value. The lattice parameter of CrN coating (a$_0$=0.414 nm for the CrN powder from JCPDS No. 11-0065$^{[98]}$) increased with Mo content, due to the larger atomic size of Mo.
The peak shift phenomenon due to Mo addition toward lower angle reflects that the Cr-Mo-N coatings were substitutional solid solutions of (Cr,Mo)N. This will be discussed in the discussion chapter 5. The difference in lattice parameters of the coatings deposited at different temperature resulted from the selection of (111) or (200) peak, for the reason that for the coatings deposited at 400°C, there are combination of fcc and hexagonal phase, and the fcc (111) peak are not pronounced.

![Graph showing lattice parameters of Cr,N and Mo,N](image)

**Fig. 4.14** Lattice parameters Cr,N and Mo,N selected (111) or (200) crystal plane as a function of Mo content

The thermal stability of the coatings was found to increase with a larger amount of Cr in the ternary system.

**4.2.3 Transmission Electron Microscopy (TEM)**

Due to the facility limitation, only the (c1) Cr₂₅Mo₂₅N₅₀ was taken with TEM high magnification picture. As showed in Fig.4.15, the clear columnar structure was observed.
Also on the surface, a typical area was shown in here, with clear interplannar distances correspond to those measured by XRD.

Fig.4.15 TEM high magnification cross-sectional and surface morphology of (c1) Cr$_{25}$Mo$_{25}$N$_{50}$ coatings deposited at room temperature

4.2.4 X-ray Photoelectron Spectroscopy (XPS)

The XPS data characterize a very thin layer (2-4 nm). According to the XPS data of the first set of samples as shown in Fig.4.16 (deposition temperature 200°C), the surface layer of (a1)CrN sample after 4 keV Ar$^+$ ion-beam sputtering consists of 74 at. % Cr, 17 at. % N, 5 at % C, and 4 at % O. The Cr2p peaks are deconvoluted into two
distinct states; the Cr2p$^{3/2}$ peaks are located at 571.4 eV and 575.9 eV. The N1s peak is also in two states at 396.5 eV and 397.5 eV. While not shown, the C1s is in two states, with a weak peak centered at 282.3 eV and much stronger peak at 284.7 eV. The O1s has a strong peak at 530.7 eV, with a much weaker peak at 532.2 eV. This information implies that the sample is mainly composed of two Cr-N bonds (probably, in Cr$_2$N and CrN phase), with small, but detectable amounts of Cr-O, Cr-C, and C-C bonds. Similarly, the Mo$_x$N sample deconvoluted into several Mo-N bond states, with some portion assigned to Mo-O, Mo-C, and C-C bonding. Fig. 4.16 only shows representative XPS data for (a)CrN, (c)Cr$_{25}$Mo$_{25}$N$_{50}$, and (e)MoN coatings.

For the (d)Cr$_{18}$Mo$_{32}$N$_{50}$ sample, there were only 7 at.% Cr, 63 at.% Mo, 27 at.% N, 1 at.% C, and 2 at.% O, according to XPS measurements. Looking more closely at the high resolution spectra, the Cr2p peaks deconvoluted into two distinct states, with 2p$^{3/2}$ peaks at 574.9 eV and 575.8 eV. Unfortunately, the Mo3p$^{3/2}$ and N1s peaks overlap with two peaks located at 394 eV and 397 eV, respectively. Using standard references [PHI, NIST], the peak at 397 eV is most likely due to a Mo-N bonding state of N1s level, and the 394 eV peak is tied to Mo-N state in Mo3p$^{3/2}$ energy level. In addition, the Mo3d spectra deconvolute into three peaks at 228.3 eV, 230 eV, and 232.7 eV. Finally, the O1s state has two peaks at 529.6 eV and 531.6 eV, and C1s is in one state at 284.7 eV. From this complex picture, the bonding structure of Cr$_{18}$Mo$_{32}$N$_{50}$ sample emerges as mostly Mo-N with Cr-N inclusions, and small amounts of metal oxides and C-C bonds.
Fig. 4.16 XPS results of (a1)CrN (c1) Cr_{25}Mo_{25}N_{50} (e1)MoN coatings deposited at room temperature

Interestingly, the shapes and positions of Mo3d and Cr2p peaks (see Fig.4.16 for the examples) were almost the same through the entire range of the ternary Cr_{1-x}Mo_{x}N_{y} compositions. The major differences were observed in the positions of N1s and Mo3p^{3/2} levels. First, the intensity of N1s peak at 397.4 increases with the increase of Cr content.
However, the position of this peak does not change in all ternary compositions. The N1s peak is located at 396.5 eV in binary CrN film. The Mo3p$^{3/2}$ level in Cr$_{1-x}$Mo$_x$N$_y$ shifts from 393.8 for binary MoN to 394.3 with the increase of Cr content.

For the Cr-rich (b1)Cr$_{32}$Mo$_{18}$N$_{50}$ sample, there were 34 at. % Cr, 27 at. % Mo, 33 at. % N, 3 at. % C, and 3 at. % O according to XPS. The Cr2p peaks deconvolute into two states, with the 2p$^{3/2}$ peaks at 574.2 eV and 574.6 eV. The spectra containing the Mo3p$^{3/2}$ and N1s states have two peaks at 394.3 eV and 397.4 eV. Following the same arguments from the prior sample, these states are most likely a nitride and Mo-N bonds. The Mo3d consists of two states at 228.3 eV and 231.6 eV. O1s has two peaks at 530.2 eV and 531.1 eV; C1s shows two peaks at 284.7 eV and 288.94 eV. The most likely bonding structure is similar to the Cr$_{18}$Mo$_{32}$N$_{50}$ sample. There is mainly Mo-N with Cr-N inclusions, and detectable amounts of metal oxides, carbonate, and C-C bonds.

The last sample, Cr$_{25}$Mo$_{25}$N$_{50}$(c1), consists of 24 at. % Cr, 35 at. % Mo, 38 at. % N, 2 at. % C, and 2 at. % O as XPS shows. Once again, the Cr2p deconvolutes into two states, with 2p$^{3/2}$ peaks at 574.2 eV and 574.4 eV. The Mo3p$^{3/2}$ spectra break down into two peaks at 394.1 eV and 397.4 eV. Peaks located at 228.2 eV and 231.4 eV make up the Mo3d spectra. O1s consists of 529.7 eV and 530.4 eV peaks. For C1s, there are peaks at 283 eV, 285.1 eV, 289.8 eV, and 291.5 eV. Again, there is a very similar bonding structure; the sample appears to be Cr-N inclusions within a matrix of Mo-N. There are some small amount of metal oxide, carbonate, and C-C bonds.

Fig. 4.17 shows the bonding stage of the CrMoN coatings deposited at 400°C. The samples deposited at higher temperature, generally the evolution of the chemical bonding is very similar to those of with lower deposition temperature. For example, in
(a2)CrN, the Cr2p peaks are deconvoluted into two distinct states which suggested there were two Cr-N bonds (probably, in Cr2N and CrN phase), this is correspond to the XRD results. For the films contained Mo, the N1s peak overlapped with the Mo3p peaks at 394eV. All films are with small, but detectable amounts of Cr-O, Cr-C, and C-C bonds.

![XPS spectra](image)

**Fig.4.17** XPS results of as deposited (a)CrN (b)Cr32Mo18N50 (c)Cr25Mo25N50 (d)Cr18Mo32N50 (e)MoN coatings deposited at 400°C

Overall, based on the XRD and XPS data, it is possible that the ternary Cr$_1$xMo$_n$N$_y$ material in these experiments is a true solid solution, and no phase segregation, needed for the nanocomposite formation, is observed. A relatively low substrate temperature during the deposition may be a factor. Indeed, the decomposition of such Cr$_{25}$Mo$_{25}$N$_{50}$ ternary phase into two nanocrystalline phases (CrN-rich and MoN-rich) was observed at above 800 °C in non-oxidizing atmosphere.
4.2.5 Energy Dispersive X-ray Spectrometry (EDS)

EDS analysis provides the compositional data practically through the whole volume of the films, Table 4.2 shows the real chemical composition of the $\text{Cr}_{1-x}\text{Mo}_x\text{N}_y$ coatings which were deposited at 400°C.

Table 4.2 Chemical compositions of the $\text{Cr}_{1-x}\text{Mo}_x\text{N}_y$ coatings deposited at 400°C

<table>
<thead>
<tr>
<th>Targeted Composition</th>
<th>Actual Composition</th>
<th>Cr(%)</th>
<th>Mo(%)</th>
<th>N(%)</th>
<th>O(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a2) $\text{Cr}<em>{50}\text{N}</em>{50}$</td>
<td>(a2) $\text{Cr}<em>{57.4}\text{N}</em>{40.6}$</td>
<td>57.4</td>
<td>0</td>
<td>40.6</td>
<td>2</td>
</tr>
<tr>
<td>(b2) $\text{Cr}<em>{32}\text{Mo}</em>{18}\text{N}_{50}$</td>
<td>(b2) $\text{Cr}<em>{39.1}\text{Mo}</em>{10}\text{N}_{40.5}$</td>
<td>39.1</td>
<td>10</td>
<td>49.5</td>
<td>1.3</td>
</tr>
<tr>
<td>(c2) $\text{Cr}<em>{25}\text{Mo}</em>{25}\text{N}_{50}$</td>
<td>(c2) $\text{Cr}<em>{16.1}\text{Mo}</em>{34.9}\text{N}_{47.1}$</td>
<td>16.1</td>
<td>34.9</td>
<td>47.1</td>
<td>1.9</td>
</tr>
<tr>
<td>(d2) $\text{Cr}<em>{18}\text{Mo}</em>{32}\text{N}_{50}$</td>
<td>(d2) $\text{Cr}<em>{8.1}\text{Mo}</em>{44.7}\text{N}_{46.1}$</td>
<td>8.1</td>
<td>44.7</td>
<td>46.1</td>
<td>1.2</td>
</tr>
<tr>
<td>(e2) $\text{Mo}<em>{50}\text{N}</em>{50}$</td>
<td>(e2) $\text{Mo}<em>{51.5}\text{N}</em>{46.9}$</td>
<td>0</td>
<td>51.5</td>
<td>46.9</td>
<td>1.9</td>
</tr>
</tbody>
</table>

All the results are normalized and the values are in the atomic%. All the films has an amount of O below 2%. For the (a2)CrN, it consists of 57.4% Cr and 40.6% N, and for (e2)MoN, it contains 51.5% Mo and 46.9% N, which almost meet the Cr/N, Mo/N 1/1 ratio. Also, (b2) $\text{Cr}_{32}\text{Mo}_{18}\text{N}_{50}$ is with actual Cr/Mo ratio of 3.91/1. However, the (c2) and (d2) ternary films, the actual Cr/Mo ratio are about 0.46/1, 0.18/1, respectively. This shows dramatic departure from the deposition parameters. One possible reason for the phenomenon is that the surface diffusion is typically a thermally promoted process with rates increasing with increasing temperature. The temperature affects the Cr adatom mobility more than Mo which leading to a Cr deficit; the other possible reason is that the
confocal arrangement of the Cr and Mo guns cross-talked during the deposition, led to the non-uniformed composition.

4.2.6 Stress

The elliptical curvature was observed with the profilometer, and after applied to the Stoney formula, the stress in the films which were deposited at 400°C, was listed in the Table.4.3. All these films show low stress. The binary (a2)CrN shows tensile stress of 1.23 GPa and (e2)MoN shows the compressive stress of -1.01 GPa, this due to the thermal expansion coefficient difference among the Cr, Mo and the Si substrate. As the simple combination principle, the lower stresses in the ternary films were obtained. The stress of targeted compositional (b2) Cr$_{32}$Mo$_{18}$N$_{50}$ (c2) Cr$_{50}$Mo$_{50}$N$_{50}$ (d2) Cr$_{18}$Mo$_{32}$N$_{50}$ are 0.41GPa, 0.64 GPa, and 0.48 GPa, respectively. The initial stress in the films could improve the mechanical properties of the film at some level.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stress (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a2) Cr$<em>{57.4}$N$</em>{40.6}$</td>
<td>1.23</td>
</tr>
<tr>
<td>(b2)Cr$<em>{39.1}$Mo$</em>{10}$N$_{49.5}$</td>
<td>0.41</td>
</tr>
<tr>
<td>(c2)Cr$<em>{16.1}$Mo$</em>{34.9}$N$_{47.1}$</td>
<td>0.64</td>
</tr>
<tr>
<td>(d2)Cr$<em>{8.1}$Mo$</em>{44.7}$N$_{46.1}$</td>
<td>0.48</td>
</tr>
<tr>
<td>(e2) Mo$<em>{51.3}$N$</em>{46.9}$</td>
<td>-1.01</td>
</tr>
</tbody>
</table>
4.2.7 Atomic Force Microscopy (AFM)

All the deposited films were well adherent to Si substrate and exhibited smooth surface with the roughness in a sub-10 nm range. Fig.4.18 shows the AFM 2.5μm x 2.5μm images of Cr$_{1-x}$Mo$_x$N$_y$ films deposited at room temperature.

![AFM Images](image)

Fig.4.18 AFM images of (a1)CrN (b1)Cr$_{32}$Mo$_{18}$N$_{50}$ (c1)Cr$_{25}$Mo$_{25}$N$_{50}$ (d1)Cr$_{18}$Mo$_{32}$N$_{50}$ (e1)MoN coatings deposited at room temperature.

From these images and compare with the SEM images shown before, it was suggested that binary CrN has some level of porosity which results in its higher roughness and lower hardness in nanoindentation tests, while MoN has smoother surface and slightly larger grain size. With different composition of Cr/Mo, the Cr$_{1-x}$Mo$_x$N$_y$ films have the properties between the CrN and MoN coatings. We believe that Cr$_{32}$Mo$_{18}$N$_{50}$ coating (b1), which contains more Cr, still has many pores which results in a relatively higher roughness. As the Mo content increased from (c1) Cr$_{25}$Mo$_{25}$N$_{50}$ to (d1) Cr$_{18}$Mo$_{32}$N$_{50}$, the surface becomes smoother.

The thermal processing has been found to reduce roughness of the films that survived the corresponding temperatures (Fig.4.19). This could be the result of the reduction of porosity in Cr-rich films due to the oxide growth. The surface grain growth seems to occur as seen in AFM images, which can be related to the partially amorphous oxide layer formation. While not shown, several initial tests at higher temperatures inevitably led to the increased roughness.
Fig.4.19 Surface roughness changes of (a) CrN (b) Cr$_{32}$Mo$_{18}$N$_{50}$ (c) Cr$_{25}$Mo$_{25}$N$_{50}$ deposited at room temperature after annealing processes

For the coatings deposited at 400°C, while not shown here, the AFM pictures presented low porosity films. As simply shown in Fig.4.20 the surface roughness changes of the CrMoN coatings deposited at 400°C after annealing processes. All the as-deposited films were smooth with the roughness in a sub-3 nm range, which is a dramatic improvement from the low temperature deposited samples (in a sub-10nm range). It was suggested that binary (a2)CrN is dense and with very low porosity which results in its low surface roughness about 2nm and kept it at the same level after annealing process, while as-deposited (e2)MoN had smooth surface (3nm) and became rougher (over 10nm) after annealing process with oxidation growth. With different composition of Cr/Mo, the Cr$_{16.1}$Mo$_{34.9}$N$_{47.1}$ films have the surface roughness between the CrN and MoN coatings. Especially for (c2) with real composition of Cr$_{16.1}$Mo$_{34.9}$N$_{47.1}$, it survived under 700°C
annealing and still with surface roughness in the sub-4nm.

Fig. 4.20 Surface roughness changes of (a)CrN (b)Cr$_{32}$Mo$_{18}$N$_{50}$ (c)Cr$_{25}$Mo$_{25}$N$_{50}$ (d)Cr$_{18}$Mo$_{32}$N$_{50}$ (e)MoN coatings deposited at 400°C after annealing processes.

4.3 Mechanical properties

4.3.1 Nanoindentation

Fig. 4.21 shows the nanoindentation hardness and modulus value of Cr$_{1-x}$Mo$_x$N$_y$ films at low deposited temperature. The binary (a1)CrN coating has a hardness of 9 GPa, whereas the binary (e1)MoN coating has a higher hardness at 15 GPa. The CrMoN coatings have the hardness value between CrN and MoN coatings. The elastic modulus qualitatively follows the evolution of the hardness. All the samples show an increase in the hardness and modulus after the annealing below the delamination or severe oxidation.
(i.e., MoN) thresholds. The hardness of (a1)CrN coating increased by about 40% and its modulus increased about 50% after annealing at 600 °C, and the \( \text{Cr}_{1-x}\text{Mo}_x\text{N}_y \) coatings with higher Cr content also showed a noticeable increase both in hardness and modulus. The hardness of (b1)\( \text{Cr}_{32}\text{Mo}_{18}\text{N}_{50} \) film increased by about 20% and for (c1)\( \text{Cr}_{25}\text{Mo}_{25}\text{N}_{50} \) it increased by about 30%. The increase of hardness after thermal treatment may due to the reduction of porosity by the oxidation (rule of mixtures) of the coating. However, the partial phase segregation cannot also be ruled out.

![Graph showing hardness and Young’s Modulus changes](image)

**Fig.4.21** Hardness and Young’s Modulus changes of (a1)CrN (b1)\( \text{Cr}_{32}\text{Mo}_{18}\text{N}_{50} \) (c1)\( \text{Cr}_{25}\text{Mo}_{25}\text{N}_{50} \) (d1)\( \text{Cr}_{18}\text{Mo}_{32}\text{N}_{50} \) (e1)MoN coatings after annealing processes

For the coatings deposited at higher temperature (400°C), the mechanical properties have been dramatically improved. The elastic modulus qualitatively follows the evolution of the hardness. As shown in **Fig.4.22**, The binary (a2)CrN coating has a hardness of 18 GPa, compared to the (a1)CrN, the hardness doubled with the increase of the deposition temperature. The binary (e2)MoN coating has a higher hardness at 22GPa compared to (e1) MoN at15 GPa. The (b2)(c2)(d2) CrMoN coatings have the hardness value between (a2)CrN and (e2)MoN coatings, however, only have a slightly increase in the hardness in comparison with the first set which were deposited at room temperature,
are still not desired. These results were indicated by the SEM cross-section pictures that the binary films are much denser than the ternary films (columnar structure).

Fig. 4.22 Hardness and Young’s Modulus of (a2)CrN (b2)Cr_{32}Mo_{18}N_{50} (c2)Cr_{25}Mo_{25}N_{50} (d2)Cr_{18}Mo_{32}N_{50} (e2)MoN coatings deposited at 400°C

Fig.4.23 shows the hardness changes of the CrMoN coatings deposited at 400°C after annealing processes. For the samples after the annealing process at 600°C, (a2)CrN, (b2) Cr_{32}Mo_{18}N_{50} and (c2)Cr_{25}Mo_{25}N_{50} show an increase in the hardness and modulus. As the growth of the oxidation when the annealing temperature increased to 700°C, the hardness of (a2)CrN and (b2)Cr_{32}Mo_{18}N_{50} film decreased by about 30%. It is very promising that for (c2) Cr_{25}Mo_{25}N_{50}, the hardness increased nearly by linearly under the thermal processes (Fig.4.22).
Fig. 4.23 Hardness and Young’s Modulus changes of (a)CrN (b)Cr$_{12}$Mo$_{18}$N$_{50}$ (c)Cr$_{25}$Mo$_{25}$N$_{50}$ coatings deposited at 400°C after thermal processes.

As discussed above, the mechanical properties of the ternary Cr$_{1-x}$Mo$_x$N$_y$ coatings are the critical issue for achieving the desired coatings, in order to overcome the defects such as boundary defects and dislocation, two multilayer samples were prepared at similar conditions with a layer periodicity of 10nm and 25nm, respectively. Table 4.4 shows the deposition parameters of the multilayer CrN/MoN coatings and comparison with the Cr$_{25}$Mo$_{25}$N$_{50}$ coatings which were deposited at room temperature and 400°C.
Table 4.4 Deposition parameters of multilayer coatings CrN/MoN (m1),(m2) and single layer Cr$_{25}$Mo$_{25}$N$_{50}$ coatings deposited at room temperature (c1) and high temperature (c2)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Deposition temperature</th>
<th>Layer periodicity (nm)</th>
<th>Layers</th>
<th>Film thickness(µm)</th>
<th>Cr Bias (V)</th>
<th>Mo Bias (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(m1)CrN/MoN</td>
<td>400°C</td>
<td>10</td>
<td>100</td>
<td>2</td>
<td>-900</td>
<td>-900</td>
</tr>
<tr>
<td>(m2)CrN/MoN</td>
<td>400°C</td>
<td>25</td>
<td>40</td>
<td>2</td>
<td>-600</td>
<td>-600</td>
</tr>
<tr>
<td>(c1)Cr$<em>{25}$Mo$</em>{25}$N$_{50}$</td>
<td>200°C</td>
<td></td>
<td>1.5</td>
<td></td>
<td>-720</td>
<td>-780</td>
</tr>
<tr>
<td>(c2)Cr$<em>{25}$Mo$</em>{25}$N$_{50}$</td>
<td>400°C</td>
<td></td>
<td>2.5</td>
<td></td>
<td>-720</td>
<td>-780</td>
</tr>
</tbody>
</table>

Fig. 4.24 Cross-sectional SEM images of multilayer CrN/MoN (m1) and (m2) coatings

Fig. 4.24 shows the cross-sectional image of the multilayer CrN/MoN coatings. The layer structure is composed of two materials CrN, which is darker layer in the cross-sectional image, and MoN, which is lighter layer presented. The Mo layers are thicker than as expected, this corresponds to the EDS result of the chemical composition of the single layer Cr$_{25}$Mo$_{25}$N$_{50}$ coatings, which also presented higher Mo content.
Fig. 4.25 gives the surface morphology SEM images and AFM images. The multilayer (m1) with thinner layer shows smoother surface with surface roughness of 3.6nm, whereas the multilayer (m2) with thicker layer shows a surface roughness of 7.4nm. Compared with the single layer (c2) Cr$_{25}$Mo$_{25}$N$_{50}$ coating, the multilayer (m1) Cr/MoN had the competitive surface roughness ((c2) Cr$_{25}$Mo$_{25}$N$_{50}$ with surface roughness of 3.3nm).

![SEM and AFM images of multilayer CrN/MoN coatings](image)

Fig. 4.25 Surface morphology SEM and AFM images showing the surface roughness of multilayer CrN/MoN coatings

The nanoindentation test found the mechanical properties has been greatly improved by multilayer (m1) CrN/MoN which contained thinner layers of 10nm, with hardness of 21 GPa and Modulus of 310 GPa which is shown in Fig. 4.26.
Fig. 4.26 Mechanical properties of multilayer CrN/MoN coatings compared with the Cr$_{25}$Mo$_{25}$N$_{50}$ coatings

The multilayer CrN/MoN coating with thinner layer periodicity gives better mechanical properties than that with thicker layer periodicity and those of the single layers CrMoN coatings, which is due to the superlattice structure in the multilayer coatings greatly improved the lattice deficit, dislocations, grain boundaries, etc.

4.3.2 Tribology

Fig. 4.27 shows the average friction coefficient of Cr$_{1-x}$Mo$_x$N$_y$ coatings with various Mo contents (x value) which were deposited at 200°C against Ti ball. The average coefficient of friction of CrN was at a value of 0.55, while the lower value of 0.41 was obtained in MoN film. This results is explained by the tribo-chemical reaction, where the coating layer reacts with ambient H$_2$O to form the MoO$_3$ thin layer during sliding process. The MoO$_3$ layer can function as a solid lubricant to reduce direct contact
between the coating surface and Ti ball\textsuperscript{[99,100,101,102]}. The COF of ternary coatings are in the range of between binary CrN and MoN coatings.

While wasn't shown here, with the increase of normal load, the coefficient of friction decreases slightly, which can probably be explained by wear debris and generating of lubricating surface layer with the increase of normal load. The long term coefficient of friction remains a stable value.

![Coefficient of Friction (COF) of Cr\textsubscript{1-x}Mo\textsubscript{x}N\textsubscript{y} coatings deposited at 200 °C](image)

Fig.4.27 Coefficient of Friction (COF) of Cr\textsubscript{1-x}Mo\textsubscript{x}N\textsubscript{y} coatings deposited at 200 °C

As shown in Fig. 4.28, for the coatings deposited at 400°C, the COF of as-deposited films behavior very similar to the coatings deposited at 200°C, decreased from 0.65 for CrN to 0.42 for MoN. The coating with Cr/Mo targeted ratio of 1/1 has the lowest COF among the ternary films. After the coatings were annealed in air atmosphere at 600°C and 700°C, the COF remains stable under the oxidation and delamination threshold.
Fig. 4.28 Coefficient of Friction (COF) of Cr$_{1-x}$Mo$_x$N$_y$ coatings deposited at 400 °C

Conclusion:

Ternary chromium molybdenum nitride Cr$_{1-x}$Mo$_x$N$_y$ films coatings were deposited on silicon wafers by using a dual rf-magnetron sputtering system. While all films had low roughness and were highly adherent to Si substrate, with lower roughness observed in the films which were deposited at higher temperature. The overall properties of the coatings deposited at higher temperature were improved compared with the coatings deposited at
room temperature. Table 4.5 shows the selected properties overview of the samples deposited at 400°C.

Table 4.5 Selected properties overview of the Cr-Mo-N coatings deposited at 400°C

<table>
<thead>
<tr>
<th>Films with real composition</th>
<th>Delamination /Cracking @600°C</th>
<th>Hardness increase @600°C</th>
<th>Smooth surface @600°C</th>
<th>Delamination/ Cracking @700°C</th>
<th>Hardness increase @700°C</th>
<th>Smooth surface @700°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a2)Cr&lt;sub&gt;57.4&lt;/sub&gt;N&lt;sub&gt;40.6&lt;/sub&gt;</td>
<td>NO</td>
<td>YES</td>
<td>YES</td>
<td>NO</td>
<td>NO</td>
<td>YES</td>
</tr>
<tr>
<td>(b2)Cr&lt;sub&gt;39.1&lt;/sub&gt;Mo&lt;sub&gt;10&lt;/sub&gt;N&lt;sub&gt;49.5&lt;/sub&gt;</td>
<td>NO</td>
<td>YES</td>
<td>YES</td>
<td>NO</td>
<td>NO</td>
<td>NO</td>
</tr>
<tr>
<td>(c2)Cr&lt;sub&gt;16.1&lt;/sub&gt;Mo&lt;sub&gt;34.9&lt;/sub&gt;N&lt;sub&gt;47.1&lt;/sub&gt;</td>
<td>NO</td>
<td>YES</td>
<td>YES</td>
<td>NO</td>
<td>YES</td>
<td>YES</td>
</tr>
<tr>
<td>(d2)Cr&lt;sub&gt;8.1&lt;/sub&gt;Mo&lt;sub&gt;44.7&lt;/sub&gt;N&lt;sub&gt;46.1&lt;/sub&gt;</td>
<td>NO</td>
<td>NO</td>
<td>YES</td>
<td>YES</td>
<td>NO</td>
<td>NO</td>
</tr>
<tr>
<td>(e2)Mo&lt;sub&gt;51.5&lt;/sub&gt;N&lt;sub&gt;46.9&lt;/sub&gt;</td>
<td>YES</td>
<td>NO</td>
<td>NO</td>
<td>YES</td>
<td>NO</td>
<td>NO</td>
</tr>
</tbody>
</table>

Only Cr-rich materials with the Cr/ Mo ratio of more than 16.9/34.9 were able to withstand thermal treatment in air up to 700 °C. The MoN and Mo-rich ternary films were completely oxidized and delaminated after annealing in air at 600 °C and 700°C for one hour. The hardness of the films was below the expectation and this was assigned to the porosity of Cr-containing films. However, Cr-rich films thermally processed at up to 600 °C show an increase both in hardness and Young’s modulus. The hardness of Cr<sub>1</sub>-xMo<sub>x</sub>N<sub>y</sub> coatings which with Cr/Mo ratio of more than 3.91 increased by about 20% after annealing, at the same time, the surface roughness of the films was reduced. Desired mechanical properties were achieved in binary CrN and MoN films deposited at higher temperature (400°C). Although the desired mechanical properties were not reached in
ternary films, the adjustment of Cr/Mo ratio during the deposition process allows to obtaining ternary Cr$_{1-x}$Mo$_x$N$_y$ coatings with the properties between those of binary CrN and MoN.
CHAPTER 5
DISCUSSION AND CONCLUSION

For the low temperature deposition, all the films contain a single fcc phase. For the high temperature deposition, the ternary films crystallize in mainly F.C.C phase with a strong texture in the (111) direction. The molybdenum nitride films contain mainly the γ-Mo$_2$N phase and the chromium nitride films crystallize in the fcc CrN and hexagonal Cr$_2$N phase. The phase formation difference is probably due to the rephrase from the deposition temperature. The phase transformation can be further discussed with reference to the phase diagram of the Cr-Mo-N system, which is given in Fig. 5.1.

![Fig. 5.1 Chromium-Molybdenum-Nitrogen ternary alloy phase diagram (based on 1991 Frisk K.)](image)
The formation of hexagonal Cr$_2$N has a much narrow window of condition compared to the formation of F.C.C CrN. Increasing the deposition temperature leads to densification of porous column boundaries, defect incorporation, and enhanced renucleation rate from ion bombardment-induced surface defects leading to a suppression of the columnar-type growth. These high-energy ions effectively bombard the growing film and a densely packed morphology results. The hardness increases in CrN system if the content of the hexagonal phase increases. While the crystallites of all coatings consist of crystallites of up to 23 nm. Apart from the crystal size, the morphology does not change significantly for all films over the whole parameter range of this study.

Nanoindentation measurements revealed a maximum hardness value of about 22 GPa observed in MoN film, while the films with about equal amounts of chromium and molybdenum appear to be softer ~hardness values in 11 GPa. The chromium nitride thin films show hardness values of 18 GPa, which are significantly higher in comparison with those of CrN deposited at lower temperature. Tensile stresses up to 1.23 GPa were measured for the binary film, while the ternary films exhibit tensile stresses in lower range. The values for the elastic modulus were in the range of 330 (MoN) and 185 GPa (Cr$_{18}$Mo$_{32}$N$_{50}$). The different hardness values of the binary and the ternary films are mainly due to changes in the bonding character. Also, softening may caused by the grain boundary sliding which is mainly attributed to the large amount of defects in the grain boundaries that allows fast diffusion of atoms and vacancies with the applying of stress.

A solid solution is formed when two metals are completely soluble in liquid state and also completely soluble in solid state. In other words, when homogeneous mixtures of two or more kinds of atoms (of metals) occur in the solid state, they are known as solid
solutions. The more abundant atomic form is referred as solvent and the less abundant atomic form is referred as solute\textsuperscript{104}. If the atoms of the solvent or parent metals are replaced in the crystal lattice by atoms of the solute metal then the solid solution is known as substitutional solid solution.

Hume Rothery formulated certain rules which govern the formation of substitutional solid solutions. These are:

\textit{(a) Crystal structure factor:} For complete solid solubility, the two elements should have the same type of crystal structure \textit{i.e.}, both elements should have either F.C.C. or B.C.C. or H.C.P. structure.

\textit{(b) Relative size factor:} As the size (atomic radii) difference between two elements increases, the solid solubility becomes more restricted. For extensive solid solubility the difference in atomic radii of two elements should be less than about 15 percent. If the relative size factor is more than 15 percent, solid solubility is limited. For example, both silver and lead have F.C.C. structure and the relative size factor is about 20 percent. Therefore the solubility of lead in solid silver is about 1.5 percent and the solubility of silver in solid lead is about 0.1 percent. Copper and nickel are completely soluble in each other in all proportions. They have the same type of crystal structure (F.C.C.) and differ in atomic radii by about 2 percent.

\textit{(c) Chemical affinity factor:} Solid solubility is favored when the two metals have lesser chemical affinity. If the chemical affinity of the two metals is greater than greater is the tendency towards compound formation. Generally, if the two metals are separated in the periodic table widely then they possess greater chemical affinity and are very likely to form some type of compound instead of solid solution.
(d) **Relative valence factor:** It is found that a metal of lower valence tends to dissolve more of a metal of higher valence than vice versa. For example in aluminum-nickel alloy system, nickel (lower valance) dissolves 5 percent aluminum but aluminum (higher valence) dissolves only 0.04 percent nickel.

In the sputtered ternary \(\text{Cr}_{1-x}\text{Mo}_x\text{N}_y\) films, the Cr and the Mo atoms are randomly distributed over the metal sublattice. CrN and MoN both have F.C.C structures, Mo atoms may substitute for Cr atoms without disturbing the F.C.C structure of CrN, which was shown in the XRD results. The films still have some secondary phase precipitates due to the solid solubility of these two materials. The octahedral coordination can be deformed, leading to local modifications of the covalent/ionic bonds between metal and nitrogen atoms. Consequently, the charge distribution and covalence level of these bonds are changed. Additionally, due to the distorted lattice (molybdenum) has larger covalent and ionic radii compared to chromium, and nitrogen vacancies, metallic bonds are reinforced\(^{[105,106]}\). The number of metal–nitrogen bonds with covalent/ionic character is diminished.

In conclusion, the adjustment of Cr/Mo ratio during the deposition process allows to obtaining ternary \(\text{Cr}_{1-x}\text{Mo}_x\text{N}_y\) coatings with the properties between those of binary CrN and MoN. Good thermal stability, low surface roughness and tribological properties have been achieved by the desired Cr/Mo ratio of 16.1/34.9.

The mechanical properties were significantly improved by the multilayer CrN/MoN coatings, and the surface roughness were comparable to those of the monolayer Cr-Mo-N coatings. Further investigation of the multilayer CrN/MoN coatings, such as the thermal stability and oxidation resistance, need to be conducted. The complex structure can show
advantages in the mechanical properties due to the overcome of the boundary defects and dislocations. However, for the specific cutting tool application, whether multilayer coating designs are really advantageous regarding the cutting performance will have to be evaluated for each application. For example, the multilayer structured TiN/TiCN coatings had negative effects on the cutting performance of cemented carbides, such as the reduction of the thermal conductivity and a decrease of the resistance against abrasive wear. It seems that for cutting operations with a high load of tribo-oxidation of the multilayer coatings with oxide top layers have a high potential. The optimization of the process to improve the mechanical properties with high thermal stability is the obvious next step for the multilayer CrN/MoN coatings.
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