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Carbon Nanofiber Toughened nc-TiC/a-C Nanocomposite Coatings

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Abstract

Producing nanocomposite films with both high hardness and toughness is a tough job but of great scientific and technical interest. Carbon nanofibers (CNFs) toughening for hard coatings is promising. This project is to try to realize *in-situ* CNF toughened nanocrystalline titanium carbide (nc-TiC) and amorphous carbon (a-C) nanocomposite coatings with high hardness and at the same time high toughness. *In-situ* growth of CNFs in amorphous carbon (a-C) and nc-TiC involves sputtering and rapid thermal processing. Influence of CNF growth on microstructure, mechanical properties and tribological properties are studied in detail.

The results show amorphous CNFs can be formed in a-C and nc-TiC to form CNF:a-C, and nc-TiC/CNF:a-C coatings by this sputter plus rapid thermal processing. CNF:a-C means CNF embedded in a-C; nc-TiC/CNF:a-C stands for into CNF and residual a-C matrix surrounding nc-TiC. A longer annealing time, a higher temperature and an Al₂O₃ barrier layer can promote CNF growth. CNF formation in a-C brought in toughness increase as a result of crack bridging. *In-situ* synthesis of nc-TiC/CNF:a-C nanocomposite coatings uniformly distributes CNFs and nano sized TiC crystallites. With inclusion of CNFs, the toughness of nc-TiC coating was increased by 87 % at an expense of 24 % hardness. CNF inclusion also reduces 50 % of the friction coefficient and 65 % of the wear rate. Mechanism studies confirm that the toughness is improved by crack bridging, crack deflection and fiber pullout.

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List of Publications

- 1 Huili Wang, Sam Zhang, Yibin Li, and Deen Sun, *Bias effect on microstructure and mechanical properties of magnetron sputtered nanocrystalline titanium carbide thin films*. Thin Solid Films, 2008. 516(16): p. 5419-5423.
- 2 Sam Zhang, Huili Wang, Soon-Eng Ong, Deen Sun, and Xuan Lam Bui, *Hard yet Tough Nanocomposite Coatings - Present Status and Future Trends*. Plasma Processes and Polymers, 2007. 4(3): p. 219-228.
- 3 Sam Zhang, Huili Wang, Soon-Eng Ong, Yibin Li, and Jun Guo, *Growth of hard and tough carbon nanofiber/nanocrystalline titanium carbide coatings*. Carbon, Submitted.
- 4 Huili Wang and Sam Zhang, *Toughness and Toughening of Hard Nanocomposite Coatings*, in *Handbook of Nanostructured Thin Films and Coatings*, Edited by S. Zhang. CRC Press Taylor & Francis Group, 99-146, 2010
- 5 Sam Zhang, Huili Wang, *Hard and tough nanocomposite coatings: design, synthesis and characterization*, in *Nanocomposite Coatings and Nanocomposite Materials* Edited by A. Ochsner, W. Ahmed, N. Ali, Published by Trans Tech Publications, 195-238, 2008
- 6 Huili Wang, Sam Zhang, Yibin Li, Soon-Eng Ong, Jun Guo and Deen Sun. *The role of hydrogen in the growth of carbon nanotubes by rapid thermal processing of carbon film*. In preparation.

- 7 Huili Wang, Sam Zhang, Yibin Li, and Soon-Eng Ong, *Role of barrier layer on carbon nanofiber growth by rapid thermal processing*. In preparation.
- 8 Huili Wang, Sam Zhang, Soon-Eng Ong and Yibin Li, *Tribological behaviour of nanocrystalline titanium carbide/carbon nanofiber: amorphous carbon nanocomposite coatings*. In preparation.

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Symbols and Abbreviations

Symbols

CPR	Scratch crack propagation resistance
D	The average grain size
E	Young's modulus
FWHM	Full width half maximum
H	Hardness
K	The Scherrer's constant
K_b	Bulk modulus
K_{IC}	Fracture toughness
G	Shear modulus
P	The applied indentation load
sp^2	Interaction between one 2s and two 2p orbital to give three linear combinations lying in a plane, at 120° angles from one another (graphite-like bonding)
sp^3	Interaction between one 2s and three 2p orbital to give four linear combinations at the corners of a tetrahedron (graphite-like bonding)
V	The wear volume
ΔU	The stain energy difference responsible for the cracking
δ	An empirical constant for toughness measurement that depends on the geometry of the indenter
ν	The Poisson's ratio

θ The peak position

Abbreviations

a-C	Amorphous carbon
a-C:H	Hydrogenated amorphous carbon
CNF	Carbon nanofiber
CNT	Carbon nanotube
DLC	Diamond-like carbon
GIXRD	Grazing incidence X-ray diffraction
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
HRTEM	High-resolution transmission electron microscopy
MDP	Microhardness dissipation parameter
nc	Nanocrystalline
PACVD	Plasma-assisted chemical vapor deposition
PVD	Physical vapor deposition
RF	radiofrequency
RTP	Rapid thermal processing
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TiC	Titanium carbide
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Chapter 1 Introduction

1.1 Overview

In recent years, nanophase and nanostructured materials, as a new branch of materials research, are attracting a great deal of attention because of their potential applications in areas such as electronics, optics, catalysis, ceramics, and magnetic data storage. The unique properties and the improved performances of nanomaterials are determined by their microstructures. A nanocomposite coating comprises of at least two phases: a nanocrystalline phase and an amorphous phase or two nanocrystalline phases. Nanocomposite coatings represent a new class of materials, whose mechanical and tribological properties are not subjected to volume mixture rules but depend on grain boundary effects and synergetic interactions of the composite constituents owing to the size effect [1]. Hard materials usually refer to materials with hardness greater than 20 GPa, materials with hardness above 40 GPa are classified as superhard, and those with hardness above 80 GPa are often called ultra-hard materials. Hard, superhard or even ultra-hard nanocomposites have been a hot research topic recently [2-5]. Nanocomposite coatings with superhardness from 40 to 80 GPa or even above 100 GPa have been frequently reported recently [6-10]. Hard materials are used in many applications, from cutting and polishing tools to wear-resistant coatings. However, for engineering applications, the hardness must be combined with toughness which is as important as hardness [11-13]. Therefore, it is vitally important to master the formation of hard films with high toughness. Toughness is an important mechanical property related to the materials resistance against shock loads, and it describes the

resistance against the formation of cracks resulting from stress accumulation in the vicinity of structure imperfections. From a energy view, toughness is the ability of a material to absorb energy during deformation up to fracture [11]. According to this definition, toughness encompasses the energy required both to create the crack and to enable the crack to propagate until fracture.

1.2 Objective

Although hardness and toughness are both very important, compared with extensive studies on high hardness, there are not enough systematical attentions paid to the toughness of coatings. This project will study the preparation of amorphous carbon (a-C) and nanocrystalline titanium carbide (nc-TiC) coatings, and characterization of the coating hardness and toughness. To improve the toughness of brittle nc-TiC coatings, CNFs will be *in-situ* synthesized by sputtering and subsequent rapid thermal processing (RTP).

1.3 Scope

In this project, hardening and toughening mechanisms for nanocomposite thin films and the relationships between microstructure, hardness and toughness will be focused. Two kinds of thin films including a-C and nc-TiC will be synthesized with magnetron sputtering technique. In order to improve the toughness of nc-TiC without great sacrifice of hardness, as an effective toughening agent, CNF will be prepared through Ni catalytic induced growth in RTP and finally incorporate nc-TiC into the coating. The mechanical response of the CNF inclusion will be evaluated.

1.4 Major Contributions of the Thesis

As a result of the research work, the following original contributions have been made.

1. Through stress approach via microindentation, substrate bias effect on the toughness of nc-TiC coatings has been investigated.
2. The relationships between process parameters (for example annealing time, temperature, and the barrier layer) and CNF growth have been studied.
3. A new concept of CNF toughened nc-TiC coatings has been developed. Using the two-step deposition approach, CNFs with residual a-C have been uniformly embedded into nc-TiC coatings.
4. The newly formed nc-TiC/CNF:a-C nanocomposite coatings have high toughness and maintain high hardness simultaneously. It has also much better tribological performance than nc-TiC coating.

1.5 Organization of the Thesis

The second chapter reviews current status of hard and tough nanocomposite thin films, including hardening and toughening approaches, and toughness characterizations. Project overview, coating synthesis and characterizations are presented in the third chapter. The fourth chapter shows the results of the chemical composition, microstructure, mechanical and tribological properties for a-C, nc-TiC, CNF:a-C and nc-TiC/CNF:a-C coatings. Toughness measurement, CNF formation mechanism in nanocomposite coatings and CNF toughening mechanism are

discussed in the fifth chapter. At last, the sixth chapter draws the conclusions from the studies and the last chapter figures out recommendations for further study.

Chapter 2 Current Status of Hard and Tough Nanocomposite Coatings

Nanostructured or nanocomposite coatings are a new branch of materials that possess unique physical and mechanical properties. Hard, superhard or even ultra-hard nanocomposites have been a hot research topic recently [2-10]. However, for engineering applications, hardness must be complimented with toughness which is a property of equal importance as hardness [11-13]. Toughness and hardness do not usually go hand-in-hand. Usually trade-off between hardness and toughness takes effect (see Fig. 2-1).

Fig. 2-1 Classification of nanocomposites according to their hardness and toughness [14]

Toughness is an important mechanical property related to the materials resistance against shock loads, and it describes the resistance against the formation of cracks

resulting from stress accumulation in the vicinity of structure imperfections. In energy context, toughness is the ability of a material to absorb energy during deformation up to fracture [11]. According to this definition, toughness encompasses the energy required to create crack and to enable the crack to propagate until fracture. Therefore, a high toughness coating has high resistance to formation of cracks under stress and in the mean time, high energy absorbance to deter crack propagation, whereby preventing chipping, flaking or catastrophic failure.

Creating tough, fracture-resistant ceramics has been a focal point of ceramics research for decades. Ceramics have inherently low fracture toughness and are thus subject to brittle fracture (in comparison with ductile metals, which are much tougher because of the plasticity induced by dislocation motion). It is known that mechanical properties of a solid depend strongly on the density of dislocations, interface-to-volume ratio and grain size. An enhancement in damping capacity of a nanocomposite solid may be associated with grain-boundary sliding [15] or with energy dissipation mechanism localized at interfaces [16]. A decrease in grain size significantly affects the yield strength and hardness. The grain boundary structure, boundary angle, boundary sliding and movement of dislocations are important factors that determine the mechanical properties of the nanocomposites. In most cases, coatings are applied to protect surfaces from the consequences of mechanical loads. A greatly simplified examination of the abrasive wear resistance in a variety of materials as a function of fracture toughness (as applied to bulk materials) reveals a dependence – maximum wear resistance results from a specific favorable combination of hardness and toughness [17].

2.1 Hardening Mechanisms in Nanocomposite Coatings

Hardness is defined as the resistance of a material to plastic deformation. Plastic deformation of crystalline materials occurs predominantly by dislocation movement under applied load. That means a material with enhanced hardness has a higher resistance to dislocation movement. Very often, several of the classical hardening or strengthening mechanisms are active in hard coatings deposited by plasma-assisted vapor deposition techniques. Such hardening mechanisms work by providing obstacles for dislocation movement, which can also be applied to some extent to hard coatings. Hindering of dislocation movement can be achieved by: (i) grain boundary hardening, (ii) solid solution hardening, (iii) age hardening and (iv) compressive stress hardening.

2.1.1 Grain Boundary Hardening

In a recent review [18], Veprek has analyzed the design criteria to produce superhard or even ultrahard nanocomposite coatings. From material-selection point of view, combinations of nanocrystalline transition-metal nitrides, e.g. TiN, W₂N and VN, with amorphous Si₃N₄ or BN as the grain boundary phase, have a potential to achieve coating hardness exceeding 40–50 GPa. This hardening behavior, especially in the regime where the crystallite size $d < 10$ nm, is because in case of a thin amorphous grain boundary, the tiny crystallites will restrict the grain boundary sliding [2]. One of the best known theories based on dislocation pile-up, described by the Hall-Petch equation [19, 20]. The relationship indicates the hardness of the material is inversely proportional to the square root of the grain size. However, as grain sizes are reduced to the nanometer scale and the percentage of grain boundary

atoms increases correspondingly, this traditional view of dislocation-driven plasticity in polycrystalline metals needs to be reconsidered. In a sample with grain diameters of 20 nm, 10% of atoms are located at grain boundaries. Dislocation sources and pileup are hardly expected to exist in such a material and deformation is believed to be carried mostly by the grain boundaries via a certain accommodation mechanism [21].

For very small grains, the numbers of atoms at inter-granular boundaries and inside grains become comparable. In this case, softening may happen via inter-granular slip as inter-granular boundaries cease to be barriers for the motion of dislocations [22].

The search for very hard materials is coupled to the study of low-compressibility solids, which have high values of the bulk (K_b) or shear (G) modulus. Transition-metal-containing compounds have large cohesive energies and high K_b , associated with the distribution of their valence electrons between bonding and anti-bonding states within the partly filled electronic bands. Transition metal carbides, nitrides, borides, or oxides have very low compressibility and also often possess high hardness.

Based on thermodynamically driven spinodal segregation in a binary or ternary system, Veprek et al. proposed a design to achieve superhard or even ultrahard coating; a highly thermal stable nanocomposite structure with ≤ 10 nm crystallites of the transition metal nitride separated by about one monolayer of α - Si_3N_4 was synthesized (see ref. [2] and references therein). The approximately one monolayer thin tissue of Si_3N_4 acts as a “glue” for the MeN nanocrystals, thus avoiding reverse

Hall- Petch effect, to achieve an ultra-hardness. Though the original value given was 103 GPa, more recently studies show that the Fischerscope used normally gives too high a hardness value for superhard coatings [23]. Besides, experimental and theoretical evidences show in some cases, the tissue layer can be also crystalline [24]. Nevertheless, the design concept should be on the right track. Subsequently, many superhard similar nanocomposites with similar design have been synthesized, but none approaches the hardness of diamond (about 80-100 GPa) [25]. Fig. 2-2 shows the hardness of nc-TiN/a-Si₃N₄ coatings deposited by close-field unbalanced magnetron sputtering as a function of silicon nitride fraction. Silicon-free TiN forms elongated crystallites that are several hundreds of nanometers long and tens of nanometers wide (inset A in Fig. 2-2) [26, 27]. TiN crystallites become very small at increased Si₃N₄ contents. At 15–20 at.% Si₃N₄, the mean grain size of TiN does not exceed 7 nm; this size is too small for dislocation activities. Therefore, under mechanical loading, such a material can react only by grain-boundary sliding (i.e., by moving single, undeformed TiN nanocrystallite against another). This process requires more energy than deformation by dislocation movement; hence a higher hardness can be achieved for such a coating structure. Estimations of the mean grain separation at this composition show that only a few monolayers of silicon nitride separate the nanocrystallites (inset B in Fig. 2-2). At high silicon nitride fractions, the mean grain separation becomes so wide that ordinary crack propagation in Si₃N₄ takes place, and the hardness approaches that of Si₃N₄ (inset C in Fig. 2-2).

Fig. 2-2 Hardness of nc-TiN/a-Si₃N₄ as a function of silicon nitride fraction [26, 27].

In sets illustrate the schematic nanostructure at different compositions

2.1.2 Solid Solution Hardening

Solid solution hardening comes from the lattice distortion as a result of insertion of atoms of alloying element in the interstitial location or substitution for some of the host atoms. This is, perhaps, one of the oldest hardening methods in bulk materials. In thin films or coatings, the same principle works too. TiCN [28], TiAlN [29], CrAlN [30] and CrZrN [31] are a few popular examples. Formation of a non-equilibrium supersaturated solid solution of B in TiN may contribute to further strengthening of the material [32], since the gliding of dislocations eventually formed inside the crystallites is hindered by the strain exerted by insertion of B. To increase the solubility of B in TiN, non-equilibrium growth processes, such as

physical vapor deposition (PVD) or plasma-assisted chemical vapor deposition (PACVD) have been used, where a maximum B solubility of 17.4 at.% has been reported for PACVD [32] with hardness up to 43 GPa. For reactive arc evaporation from Ti-B compound targets, the highly ionized flux of film-forming species was utilized to synthesize a promising nanocrystalline metastable supersaturated solid solution of B in TiN at lower nitrogen fractions [33]. The maximum in hardness (34.5 GPa) is obtained when the crystallites are 6–8 nm in size, and are strained by the formation of a substitutional solid solution of B in TiN. The formation of a metastable solid solution was confirmed by XRD-observed widening of the lattice upon B substitution of N as compared to TiN. Therefore, the mobility of deformation-induced dislocations is hindered in these small crystallites that are initially dislocation-free. At high N₂ fractions, the substitutional B sites in the TiN crystallites are replaced with additional N to form energetically favorable unstrained TiN crystals. This unstrained TiN crystals combined with high fraction of less strongly bonded BN amorphous phase lead to a hardness drop (Fig. 2-3). Another example is the superhard Ti–Al–Si–N film (maximal harness ~ 55 GPa) synthesized by a hybrid coating system of arc ion plating and sputtering method [34]. Based on XPS and XRD results, it was suggested that the Ti–Al–Si–N films were a composite consisting of solid-solution (Ti,Al,Si)N crystallites and amorphous Si₃N₄.

Fig. 2-3 Indentation hardness and reduced modulus values for Ti-B-N coatings under different N₂ fraction [33]

2.1.3 Age Hardening

Age hardening is yet another “aged” hardening mechanism in strengthening bulk materials (for example Al alloys and steels). Age hardening achieves higher hardness through precipitation over time of a small and uniformly distributed strengthening phase in the form of particles from a supersaturated solid solution. This works equally well in hard coatings, as demonstrated in ref. [35-37]. Supersaturated phases can be easily obtained by non-equilibrium deposition techniques such as PVD or PACVD due to limited atomic kinetics during deposition. As-deposited (TiAl)N [36] and Ti(BN) [37] films show a dense columnar microstructure of a supersaturated NaCl structured phased based on fcc TiN whose Ti location is partly substituted by Al to form (TiAl)N, and N is partly substituted by B to form Ti(BN). During annealing, (TiAl)N and Ti(BN) coatings

undergo spinodal decomposition and transform into coherent cubic-phase nanometer-size domains, resulting in hardness increase.

2.1.4 Compressive Stress Hardening

Ion bombardment during deposition at low temperatures has been utilized to increase the density and modify the morphology of the films [38]. During growth, stresses are generally induced by energetic particle bombardment. The lattice defect arrangements induced by impinging energetic ions are responsible for the stress. As the incoming ion or knock-on atoms possess enough kinetic energy, they knock atoms out of their lattice positions and create secondary collisions. In this way, collision cascades. The atom first knocked absorbs most of the energy. The resulting strong atomic motion along the trajectory of the ions leads to a rearrangement of the lattice atoms [39]. The hardness enhancement results from a complex synergistic effect of the decrease of crystallite size, densification of grain boundaries, and compressive stress upon ion bombardment. Musil et al. reported enhancement of hardness of TiN (up to 80 GPa) and (TiAlV)N (up to 100 GPa) during deposition by means of unbalanced magnetron sputtering at negative substrate bias [40] where a correlation between the hardness enhancement and biaxial compressive stress exists [41]. However, upon annealing at a certain temperature, when the induced defects are annealed and the compressive stress relaxes, the hardness may decrease back to “normal”.

2.2 Toughening Mechanisms in Nanocomposite Coatings

In order to obtain high hardness in nanocomposite coatings, usually plastic deformation is designed to be prohibited, dislocation movement and grain boundary sliding are prevented, thus loss in ductility. Ductility is related to toughness which is very important for hard coatings to avoid catastrophic failure. Using Vickers indenter, Veprek [42] indented a 6-10 μm thick coating on a soft steel substrate with a high load of 1000 mN and found no cracks. This, however, does not necessarily mean it has high “fracture toughness”: the classical definition of “fracture toughness” measures the resistance to crack propagation – a crack exists first, then how difficult it is to make the crack propagate. The coating in the above example is “damage tolerant” owing to the difficulty in generating a crack (but once a crack is generated, it might propagate in a catastrophic manner and thus results in a brittle failure if it is not truly “tough”). To increase toughness, it is vital to study the toughening mechanisms. In bulk ceramics, various toughening methods are in use: ductile phase toughening, fiber and whisker toughening, transformation toughening, microcrack toughening, etc [43]. In hard coatings, however, investigation on toughening mechanisms lags far behind. The following sections discuss different toughening approaches.

2.2.1 Ductile Phase Toughening

In order to toughen hard ceramic coatings, a straightforward method is to incorporate a ductile phase. Ductile phase toughening arises from two major mechanisms: relaxation of the strain field around the crack tip through ductile phase yielding and bridging of cracks by ligaments of the ductile phase. These two

mechanisms can increase the work for plastic deformation. Zhang et al. [44] doped Al into a-C films by co-sputtering of graphite and Al. The composite films exhibit a reduction in residue stress and also improvement in toughness. However, this came at huge expense of hardness, where nanoindentation hardness dropped from 31.5 to 8.8 GPa. In order to restore the hardness, nanocrystalline TiC (or nc-TiC) was embedded into the a-C matrix doped with Al to form nc-TiC/a-C(Al) nanocomposite film. The hardness is restored to ~20 GPa, while toughness remained high (indentation plasticity of 55 %) and residual stress low (only 0.5 GPa) [45]. Although toughness is not measured due to lack of proper measurement facilities for such a high toughness coating, the nc-TiC/a-C(Al) nanocomposite film is evidently very tough: the optical comparison of scanning scratch tracks between nc-TiC/a-C (Fig. 2-4a) film and nc-TiC/a-C(Al) (Fig. 2-4b) shows that without doping of Al, the coating basically fails in a brittle way (Fig. 2-4a); with doping of Al, however, the scratching tip ploughs into the coating causing the scanning amplitude to reduce along the scratch direction (Fig. 2-4b). Co-sputtering of Ti, TiNi and Si₃N₄ targets produced nanocomposite coatings where amorphous metallic Ni increases the toughness of nc-TiN/a-SiN_x coating [46]. Doping from 0 to ~ 40 at.% Ni brings about an increase in toughness from 1.15 to 2.60 MPa·m^{1/2}, but at an expense of hardness from 30 to 14 GPa.

Fig. 2-4 Optical image of scratch tracks on coatings: (a) nc-TiC/a-C and (b) nc-TiC/a-C(Al) [45]

2.2.2 Phase Transformation Toughening

Some phase transformation occurs under stress and that accompanies absorption of large quantity of energy thus could be used to toughen a material. Transformation from tetragonal to monoclinic phase takes place under stress. The process occurs in the stress field around the tip of the crack and is accompanied by a volume increase of about 4 %. The resultant strain during the transformation relieves the stress field

and absorbs the fracture energy, whereby toughens the material. ZrO_2 toughened ZrB_2 is an example [47]. In order to facilitate the phase transformation, retention of the high-temperature tetragonal phase is the key, which can be easily realized during deposition. Sprio et al. [48] deposited thin zirconium oxide films by radiofrequency (RF) magnetron sputtering. The films have a mixture of tetragonal and monoclinic zirconia phases. It was shown that increasing substrate bias power disrupted columnar grain growth. Transmission electron microscope (TEM) confirmed a reduction in intergranular porosity but also an increase in lateral defects [49]. These defects are hypothesized to be stress-induced microcracks caused by a tetragonal to monoclinic phase transformation. Tetrahedral zirconia has a high toughness and is proposed to increase properties of brittle substrates[50]. Trinh et al [51] prepared $\gamma\text{-Al}_2\text{O}_3\text{-ZrO}_2$ thin films by RF magnetron sputtering with hardness up to 30 GPa. However, owing to the lack of proper toughness measurement instrumentation, toughness was not measured in this work.

2.2.3 Compressive Stress Toughening

Generally cracking is initiated by tensile stress, thus compressive residual stress has to be overcome first before a crack is initiated in tension. When a coating has a high compressive residual stress to start with, the coating will be able to take more tensile strain before fracture, as is demonstrated in Zr-Cu-O coatings (c.f. Fig. 2-5) [52]. Halitim et al. [132] found the toughness was increased by compressive residual stress due to ion implantation. Abe et al. [133] performed oxidation of $\text{NiAl}/\text{Al}_2\text{O}_3$ and noticed that NiAl_2O_4 was formed accompanied by volume expansion resulted in the compressive stress. A compressive stress of about 127

MPa efficiently improved the toughness from 3.91 to 6.22 MPa m^{1/2}. Although certain level of compressive stress increases toughness, excessively large compressive stress does cause coating delamination or cracking [53].

Fig. 2-5 Comparison of Vicker's indenter impressions into Zr-Cu-O with different residual stress (a) 0.3 GPa, (b) -0.1 GPa, and (c) -0.3 GPa [52]

2.2.4 Nanotube/Nanofiber Toughening

The discovery of carbon nanotube (CNTs) has opened up new avenues in producing unique carbon-based materials. Novel mechanical tests on individual CNF/CNTs [54-56] and atomistic calculations [57-60] suggest that CNF/CNTs have ultra-high elastic moduli of approaching 1 TPa, and exceptional tensile strengths, in the range of 20-100 GPa. Due to their outstanding properties, carbon nanotubes have

attracted growing interest and are considered to be the most promising materials of applications in nanoengineering [11, 61-67]. Toughness enhancement can be obtained through crack deflection, crack bridging and CNT pull-out. CNT toughened bulk ceramics are attractive and outstanding results have been successfully achieved, for instance, in Al_2O_3 matrix [67] and BaTiO_3 matrix [68]. However, nanotube toughened thin films have gained few attentions, due to difficulties in controlled alignment, interface reaction and reasonable volume fractions.

Xia et al. [65, 69] anodized aluminum to obtain an amorphous alumina matrix having pores in 30-40 nm diameters in which multiwall carbon nanotubes were grown by CVD to realize CNT/alumina composite layer of 20 to 90 μm in thickness. Crack deflection at the CNT/matrix interface (Fig. 2-6a), crack bridging by CNT (Fig. 2-6b), CNT pull-out (Fig. 2-6c) are all observed.

(a)

(b)

(c)

Fig. 2-6 Micrographs of deformation in CNT-alumina composites fabricated using ordered porous alumina templates: (a) transverse crack deflection at the CNT/matrix interface; (b) CNTs bridging longitudinal matrix cracks; (c) nanotube pullout, and subsurface nanotube bridging [65, 69]

Using *in-situ* growth of CNTs, by catalytical chemical vapor deposition (CVD) technique and plasma spray, 0.5 wt% CNT/Al₂O₃ coating (400 μm thick) were grown on the steel substrate [70]. *In-situ* CNTs grown in Al₂O₃ shows a promising enhancement in hardness (from ~ 8 GPa to 9 GPa) and fracture toughness (from 4.14 to 4.62 MPa m^{1/2}) in the plasma-sprayed coating. Well defined CNT structures were preserved in the coating and the retention of CNT structure is beneficial for the enhancement. The uniform occurrence of CNT bridges indicates a sound toughening effect.

Chen et al. fabricated CNT reinforced hydroxyapatite (HA) composite coatings by surface laser surface alloying [70-73]. HA (Ca₁₀(PO₄)₆(OH)₂) is a widely used biomaterial similar to apatite crystallites in bone tissues with poor mechanical properties. CNTs were used as a reinforcement agent. TEM observations confirmed the preservation of CNTs in the laser surface alloyed coating. HA matrix crystal was also confirmed by the selected area diffraction pattern. Nanoindentation was used to measure the coating hardness and Young's modulus. The results show remarkable increase of coating hardness and slight increase of Young's modulus with increasing of CNT content. However, no toughness characterization was carried out. Instead, scratch tests were conducted. As shown in Fig. 2-7, the morphology of the scratch track for the as-alloyed HA coating is very deep and many fine cracks emanates from the trace of diamond tip. These indicate the brittleness of HA coating. When the amount of CNTs was increased, the depths of the scratch track became smaller than that of pure HA coating and the crack number decreased, as indicated in Fig. 2-7b.

Fig. 2-7 FESEM images of morphologies of the scratch tracks (scratch direction from left to right) of HA/CNT coatings with different CNT contents (a) 0 wt%, (b) 5 wt%, (c) 10 wt%, and (d) 20 wt% [72]

HA/CNT composite coatings have also been prepared by plasma spray [74, 75]. Toughness (measured by Vickers indentation) improvement up to 56% ($0.61 \text{ MPa}\cdot\text{m}^{1/2}$) is obtained.

2.2.5 Composition or Structure Grading Toughening

Graded inter-layering is a known effective method to reduce crack concentration and enhance adhesion between coating and substrate. In gradient design, the substrate is first coated with a high adhesion layer, and then the coating constituents

are allowed to vary homogeneously or heterogeneously while the coating thickness builds up. With bias graded (varying substrate bias voltage while coating thickness builds up) in magnetron sputtering, Zhang et al. [76] prepared 1.5 μm a-C gradient coating on tool steels with moderately high hardness (25 GPa) but very high toughness (plasticity 57.6 %). During deposition, substrate bias gradually increased from -20 to -150 V during deposition, and a graded sp^2/sp^3 was achieved through coating thickness. The bottom layer has the highest sp^2/sp^3 fraction for high adhesion whereas the top layer possesses the highest sp^3 fraction to render a high hardness. Bias-graded coating design enhances the toughness and the adhesion of the coating on tool steel (Fig. 2-8). The adhesion strength increased more than two times as compared to the same coating deposited at constant bias (-150 V).

Fig. 2-8 Scratch adhesion strength of the non-hydrogenated DLC deposited under various constant bias or bias-graded conditions [76]

Pei et al. [77, 78] changed substrate bias to change the microstructure of nc-TiC/a-C:H coatings prepared by close field unbalanced magnetron sputtering. Increasing bias resulted in a clear transition from columnar to glassy microstructure in coating (Fig. 2-9). Substrate bias also simultaneously and greatly enhanced coating hardness, toughness and adhesive strength. The coating with glassy microstructure exhibits substantial toughening (however, a word of caution on the actual toughness value given in the paper – the value – in few tens of $\text{MPa}\cdot\text{m}^{1/2}$ – is unbelievably high, as also pointed out by the authors, due to experimental limitation). Ion bombardment can densify the structure and prevent the formation of columns which are detrimental in terms of microcrack initiation and propagation under load. The induced residual stresses grow as bias increasing.

Fig. 2-9 SEM micrographs showing the fractured cross-sections of nanocomposite coatings deposited at different substrate bias: (a) floating, (b) -60 V , (c) -100 V and (d) -150 V [77]

2.3 Toughness Characterization

In classical definition, toughness measures the ability of a material to resist crack propagation until fracture. For bulk materials and very thick films, toughness can be easily measured according to ASTM standards [79, 80]. For thin films, there is no a proper definition for toughness, since in thin films or coatings, the cracks do not necessarily pre-exist, and thus energy has to be used to initiate the crack. In measurement, thin film toughness measurement is difficult or tedious due to the thickness limitation. Although many proposed methods can be used in some cases, till now, a standard procedure or universally accepted methodology does not exist for ceramic thin film or coating toughness measurement. Qualitatively, toughness can be simply estimated by plasticity [81, 82], MDP (microhardness dissipation parameter) [83, 84], and scratch crack propagation resistance [85, 86].

The plasticity or MDP are measured as the ratio of the plastic over the total displacement or work. The scratch crack propagation resistance, or *CPR* is determined by measuring the lower critical load, i.e. cohesive failure load L_{c1} and the upper critical load or adhesion failure load L_{c2} and then calculated by $CPR = L_{c1}(L_{c2} - L_{c1})$. The CPR measures the scratch resistance to crack initiation and propagation.

More detailed quantitative measurement of toughness via bending, buckling, indentation and tensile methods can be found in literature [86]. The most widely used in assessment of thin film toughness is indentation. When the stress exceeds a critical value during indentation, a crack or spallation is generated. Failure of the coating is manifested by the formation of a kink or plateau in the load–

displacement curve or crack formation in the indent impression. The length c of radial cracks is related to the fracture toughness K_{IC} through [87]:

$$K_{IC} = \delta \left(\frac{E}{H} \right)^{1/2} \left(\frac{P}{c^{3/2}} \right) \quad (2-1)$$

where P is the applied indentation load; E and H are the Young's modulus and hardness of the coating, respectively; δ is an empirical constant which depends on the geometry of the indenter. Major uncertainties in this method come from crack formation threshold, the substrate effect and the crack length measurement.

A somewhat different approach was illustrated by Li et al. [88, 89], in which the dissipated energy during cracking was determined through a controlled-load indentation measurement. The fracture of thin film was simplified into three stages (c.f. Fig. 2-10) [90]: the first ring-like through-thickness crack forms around the indenter by high stress in the contact area; delamination and buckling occur around contact area at the film/substrate interface by high lateral pressure; a second ring-like through-thickness crack forms and spalling is generated by high bending stresses at the edges of the buckled thin films.

Fig. 2-10 Schematic diagram of three stages in nanoindentation fracture for film/substrate system [88]

The work performed during elastic-plastic deformation of the film/substrate system is the area under the load-displacement curve. The strain energy released in the first/second ring-like cracking and spalling can be calculated from the corresponding step in the loading curve. Fig. 2-11 shows a schematic diagram of load-displacement curve. $OACD$ is the loading curve and DE is the unloading curve. Area under curve ABC presents the energy difference before and after the ring-like cracking, which is released as strain energy to create the ring-like through-thickness crack. The fracture toughness of the film is then written as

$$K_{Ic} = \left(\frac{E}{(1 - \nu_f^2) 2\pi C_R} \frac{\Delta U}{t} \right)^{1/2} \quad (2-2)$$

where, E is the Young's modulus of the thin film, ν_f the Poisson's ratio of film, $2\pi C_R$ the crack length in the coating plane, t the film thickness, and ΔU the strain energy difference before and after cracking. In this method, both the cube corner indenter and the conical indenter are preferred because the through-thickness cracking of thin films can be accomplished at low load. This method was successfully used to assess the toughness of thin amorphous carbon films [90, 91]. However, errors could be easily introduced in the energy (ΔU) determination and the crack length ($2\pi C_R$) measurement due to the irregular crack shape.

Fig. 2-11 Schematic diagram of a load-displacement curve, showing a step during the loading cycle and associated energy release [86]

Tensile testing of free-standing thin films with a pre-crack induced by indentation recently was used to measure the toughness of 0.52 and 1 μm tetrahedral amorphous diamond-like carbon (ta-C) [92]. During preparation of the stand-alone

film, wet etching of SiO₂ interlayer between the coating and silicon substrate has been employed. This method has difficulties in obtaining freestanding film without curling, precrack sharpness and accurate measurement of the precrack dimension. A simple two-step tensile method, based on strain energy difference between two tensile processes is proposed by Zhang, et al. [93]. The “two-step” tensile method extends a very elastic substrate coated with ceramic film in question until coating fracture. A kink is observed in load-extension curve. The load is then released to zero but re-loaded to the previous extension. The energy difference is considered the energy used in creating the fracture. In this method, nc-TiN/a-SiN_x nanocomposite with thickness of 3.0 μm gives a toughness value of 2.6 MPa·m^{1/2}. The method requires very good elasticity of the substrate (so that when the coating is fractured the substrate is still in elastic deformation regime), and the thickness of the substrate be thin enough (for the kink to be visible), plus, there should not have coating delamination during tension.

Currently, there are relatively few toughness data available for thin nanocomposite films due to the difficulties in forming a sensible crack while reducing the substrate effect in the thin films. Toughness values of some nanocomposite are listed in Table 2-1.

Table 2-1 Toughness values of some hard coatings

Materials	Toughness (MPa·m ^{1/2})	Measurement Method	Reference
TiC _x N _y /SiCN	1.0	Indentation	[94]
TiN/SiN _x	1.15	Indentation	[46]
Ni-doped nc-TiN/a-SiN _x	2.60	Two-step tensile	[93]
YSZ/Au	1.6	Indentation	[95]
Nanolayered Cr/a-C	1.81-3.49	Indentation	[96]
Ni/Al ₂ O ₃	2.4	Indentation	[97]
ta-C	4.25~4.4	Tensile with precrack	[92]

2.4 Summary

Hardness can be enhanced by grain boundary hardening, solid solution hardening, age hardening, compressive stress hardening and etc. For engineering applications, however, the zest for sole superhard coating will subside while a combination of hardness and toughness will be pursued more by academics driven by industrial needs. The key to toughness enhancement is to design and create a structure that absorbs as much fracture energy as possible. Ductile phase toughening, phase transformation toughening, compressive stress toughening, composition or structure grading toughening and more recently carbon nanotube toughening achieve this goal in varying degree. *In-situ* growth of carbon nanotube in a hard or superhard

coating is very promising and may be one of the keys in realization of combining hardness and toughness in one.

Due to the small dimension in thickness, toughness measurement for thin films/coatings is still a big challenge. Currently there is neither standard procedure nor methodology available in assessing toughness of hard thin films or coatings even though a spectrum of methods are in use (bending, buckling, scratch, indentation and tensile) with no comparability. There is an urgent need to develop an internationally acceptable methodology and test procedure for measurement of fracture toughness in ceramic films and coatings.

Chapter 3 Experimental

3.1 Project Overview

Even though hard or even superhard coatings have been widely reported recently, most of applications do not require high hardness alone. For the benefit of long time stability, a high toughness is in a great need.

As a potential toughening agent, CNF/CNT can be synthesized in various ways, such as arc discharge, laser vaporization or plasma-enhanced chemical vapor deposition (CVD). CNT growths from a-C via Rapid Thermal Processing (RTP) [98] and conventional CVD [99] have also been reported. CNF growth via RTP is fast and simple. In this project, CNF coatings were grown via sputtering and RTP.

In this project, a new concept of toughening solution for coatings categories has been proposed and materialized. CNF will be incorporated into nc-TiC to form *in-situ* nc-TiC/CNF:a-C nanocomposite coatings through a two-step process i.e. magnetron sputter and subsequent rapid thermal processing. To gain better knowledge, a-C, CNF and nc-TiC coating will be studied first and then combining the above three into nc-TiC/CNF:a-C nanocomposite coatings. The four different coatings will be characterized including chemical composition, microstructure, hardness, toughness, adhesion and etc. The scheduled study is presented in Fig. 3-1.

Fig. 3-1 Schedule for the study of nc-TiC/CNF:a-C nanocomposite coatings

3.2 Experimental Procedure

As shown in the project overview section, different types of coatings will be synthesized using magnetron sputtering and RTP. Effect of process parameters, like substrate bias, process temperature, annealing time and etc, on composition, microstructure, mechanical properties and tribological properties will be examined.

3.2.1 Coating Preparation

There are two coating preparation techniques involved in the project, including sputtering and post thermal annealing.

3.2.1.1 Sputtering System

Deposition process for the different coatings including a-C, CNF:a-C, nc-TiC, and nc-TiC/CNF:a-C, is carried out using E303A magnetron sputtering system (Penta Vacuum, Singapore). It is equipped with one RF (1500 W) and two DC (1500 W) power sources. The system includes four 4-inch planar water-cooled magnetrons and a heated rotatable substrate holder. The substrate can be heated up to 500°C by two heaters. Besides, the substrate holder can be grounded, floated or powered by a 600 W RF generator. Vacuum of the chamber is maintained by incorporation of a 800 l/s cryogenic UHV pump and 12 m³/h two-stage rotary backing pump. Gas flow control is via mass flow control valves on three gas lines, with pressure control set point achieved by automatic close throttle valve control. A loadlock is fitted in order to keep the deposition chamber at high vacuum. During deposition, the dominant process parameters are target power density, deposition temperature, substrate bias and process pressure.

Two types of substrates have been used, including silicon wafer (100) and tungsten carbide/cobalt cermet (WC/Co, 10 wt.% Co). For any batch, several pieces of diced Si (100) monocrystalline single side polished wafers (100 mm diameter, 450 µm thickness, 0.2 nm R_a) were deposited. In order to reduce the thermal stress effect on CNF composite coatings for toughness measurement, WC/Co tool substrates were

also used. The substrates were ultrasonic cleaned in acetone for 20 min, the acetone was renewed every 5 min interval. And they were ultrasonically cleaned in ethanol for 10 min. The substrates were then blown dry with nitrogen gas.

These substrates were placed in the sputtering chamber. Before the actual deposition, the substrates were Ar plasma cleaned for 15 min at a radio frequency (RF) induced substrate bias of 300 V to remove the surface oxide. The sputtering targets were then pre-sputtered for 10 min. Thereafter, the actual deposition began.

To deposit a-C coatings, a pure graphite (99.999 %) target was employed. Co-sputtering of graphite and pure metallic titanium targets (99.995 %) was carried out to deposit nc-TiC/a-C nanocomposite coatings. Co-sputtering of graphite, pure metallic titanium and nickel targets was used to prepare nc-TiC/CNF:a-C composite coatings. The targets (100 mm in diameter and 5.5 mm in thickness) were located at a distance of about 70 mm above the substrate holder. Before deposition, the chamber was evacuated to a base pressure of 2×10^{-4} Pa. Argon was fed into the chamber as the plasma gas. The argon flow during sputtering was maintained constant at 50 sccm (standard cubic centimeter per minute). The power density of graphite was fixed at 10.5 W while Ni, Ti power density varied. The sputtering process parameters are summarized in Table 3-1.

To improve the CNF quality, Al₂O₃ barrier layers have been deposited for CNF:a-C and nc-TiC/CNF:a-C coatings. 100 nm thick amorphous Al₂O₃ interlays were sputtered onto Si substrate by reactive sputtering of Al target. Table 3-2 summarized the sputtering process parameters for Al₂O₃ barrier layer deposition. To avoid target poisoning, RF power is used.

Table 3-1 Sputtering process parameters for the coating deposition

Parameters	a-C	CNF:a-C	nc-TiC	nc-TiC/CNF:a-C
Base pressure (Pa)	2×10^{-4}			
Process pressure (Pa)	0.6			
Substrate to target distance (cm)	70			
Ar gas flow rate (sccm)	50			
Carbon DC power density (W/cm^2)	10.5			
Titanium DC power density (W/cm^2)	NA		4.2	3.6,4.0
Nickel RF power density (W/cm^2)	NA	0.1	NA	0.1
Substrate temperature ($^{\circ}\text{C}$)	RT to 300	RT		
Substrate bias (-V)	20-150	150		
Deposition time (minute)	90	60	60-120	180

Table 3-2 Sputtering process parameters for Al_2O_3 barrier layers

Parameters	Conditions
Base pressure (Pa)	2×10^{-4}
Process pressure (Pa)	0.6
Gas flow rate (sccm)	30/30 for Ar/ O_2
Al RF power density (W/cm^2)	3.7
Substrate temperature ($^{\circ}\text{C}$)	RT
Substrate bias (V)	- 150
Deposition time (minute)	60

3.2.1.2 Rapid Thermal Processing

Rapid thermal annealing/processing (RTP) was used to obtain the CNF imbedded nc-TiC/CNF:a-C nanocomposite coatings where CNF can toughen the coatings. The samples were annealed in Jipelec Jetfirst rapid thermal processor with the heating lamps on the top of the chamber. The temperature was measured by a thermocouple when the annealing temperature is below 500 °C and by a pyrometer when the annealing temperature is above 500 °C. The temperature was ramped up at 60 °C/sec, and held at up to 1100 °C for up to 180s before ramping down at around 6 °C/sec. The process pressure was maintained at 0.1 MPa with N₂ flow rate of 2000 sccm.

3.2.2 Coating Characterization

Different properties including coating surface, thickness, chemical composition, microstructure, hardness, toughness, interfacial adhesion and wear performance have been characterized. These characterization techniques applied in the project will be described in this section.

3.2.2.1 Thickness

In order to determine the deposition rate of the coatings, a distinct step was created by masking half of the diced silicon wafer with a mask tape. After film deposition, the tape was removed and the surface was cleaned in acetone. A contact mode surface profilometer (Dektak³ ST Surface Profiler) with a diamond stylus in 2.5 μm radius was used to measure the height of the step to measure the film thickness. The scanning distance, scanning speed, and data resolution are 1000 μm, 12

seconds/scan and 4000 data points/scan). At least three readings were taken to get an average value.

3.2.2.2 Composition

The chemical composition and bonding state were determined by X-ray photoelectron spectroscopy (XPS). The spectra of binding energy can be used to determine the elements present, relative quantity of each element and chemical state of the elements present. Kratos AXIS XPS using a monochromatic Al-K alpha (1486.71 eV) X-ray radiation, operating at 15 kV and vacuum of 10^{-6} Pa was employed to characterize the coatings. To remove the surface contamination layer, Ar ion bombardment was carried out using a differential pumping ion gun (Kratos MacroBeam) with an accelerating voltage of 4 keV. The bombardment was performed at an angle of incidence of 45° with respect to the surface normal. Because of preferential sputtering, the etch duration can not be too long and in literature it is a few minutes to fifteen minutes [46, 100-102]. In this project, all the etch time is kept at 10 min. First a survey scan between 1250 eV to 0 eV with a step size of 1.0 eV was done to determine the elements present in the film. It was followed by a narrow scan of step size 0.1 eV at the binding energy range covering the peak position of the detected elements. The atomic concentrations of the elements were calculated based on the integrated peak area ratio. The deconvolution of the C 1s peak was done by Kratos program using the Gaussian distribution function. The respective contribution of the various bonding configurations was calculated based on the deconvoluted peak area ratio. The quantification uncertainty for coating compositions is about 15% [103].

3.2.2.3 Microstructure

3.2.2.3.1 *SEM & TEM*

Surface morphology of the coatings was observed by two scanning electron microscopes (SEM, JEOL-JSM-5600LV), field emission scanning electron microscope (FESEM, JEOL-JSM-6340F) and high resolution transmission electron microscope (TEM, JEOL-JSM-2010F). SEM, FESEM and HRTEM were operated with the operation voltages of 20, 5, and 200 kV. The TEM samples were prepared by sand paper polishing and subsequent ion milling.

3.2.2.3.2 *Raman spectroscopy*

The Raman spectroscopy is a nondestructive method where information about the bonding structure of a-C that can be determined through the peak shift and width. Fig. 3-2 displays Raman spectra of diamond, graphite and some disordered carbons [104]. Diamond has a single Raman active mode at 1332 cm^{-1} , which is a zone center mode of T_{2g} symmetry. Single crystal graphite has a single Raman active mode at 1580 cm^{-1} labeled “G” for “graphite”. Disordered graphite has a second mode at around 1350 cm^{-1} labeled “D” for ‘disorder’. It corresponds to breathing vibrations of rings at the K zone boundary [105].

Renishaw Raman Spectroscope RM1000 using a HeNe laser source with an excitation wavelength of 633 nm, and the scan area was about $3.14\text{ }\mu\text{m}^2$ was used for the characterization. The data acquisition region is from $2000 - 1000\text{ cm}^{-1}$, and the laser power used was $\sim 1\text{ mW}$. In order to decrease the noise, 3 scanning accumulations were used. The peak deconvolution was done by the GRAMS/32

program. The fitted curves have a reduced Chi-square of 1.2 or less to ensure convergence. The I_D/I_G ratio estimates the sp^3 fraction in the a-C.

Fig. 3-2 Raman spectra of some carbon materials [104]

3.2.2.3.3 *Crystal structure*

X-ray Diffractometry is an excellent method for the characterization of crystal structures. Information like the crystal type, orientation and grain size can be determined from the patterns. The systems used were Philips PW3710 and Rigaku Ultima 2000, using Cu-K α 40 KV/30mA x-ray sources (wavelength $\lambda = 0.15406$ nm). The scanning was conducted from 20° to 90° at step size 0.01° and 0.5

seconds per step. An incidence angle of 2° was used in grazing incidence x-ray diffraction (GIXRD) operation.

To estimate the grain size through XRD measurement, Scherrer formula [106] or Williamson-Hall plot [107] analysis can be done. Scherrer formula considers only grain size effect on the peak broadening while Williamson-Hall plot takes microstrain broadening into account. Therefore, Williamson-Hall plot is preferred and grain size and microstrain can be estimated by

$$\frac{\beta_i \cos \theta_i}{\lambda} = \frac{K}{D} + \varepsilon \frac{4 \sin \theta_i}{\lambda} \quad (3-1)$$

where β_i is the integral breadth (in radius, 2θ) of the i th Bragg reflection positioned at $2\theta_i$. K is a constant ($K = 0.89$), D the average grain size and, ε is the microstrain. In W-H plot, the reciprocal of the intercept with y-axis and the slope of the line relate the grain size and microstrain, respectively.

3.2.2.4 Adhesion Strength

Scanning micro scratch tester (Shimadzu SST-101) was used to study the adhesion strength. A diamond tip stylus with $15 \mu\text{m}$ in radius was dragged on the coating with a gradually increased load. The scanning amplitude was set at $50 \mu\text{m}$ at a speed of $10 \mu\text{m/s}$. As increasing the load applied to the test sample, the coefficient of friction (here in terms of output voltage rate) increased. Upon peeling-off (fracture) of the coating starting to occur, fractured pieces of the coatings cause the fluctuation of the cartridge output signal. Thus the peeling load can be used as the adhesion value of the coating.

3.2.2.5 Hardness and Young's modulus

The hardness and Young's modulus were determined using a nanoindenter (XP, MTS) with a Berkovich diamond indenter. The indentation depths were set less than 10 % of the coating thickness to minimize substrate effect. For each sample, 10 indentations were made at random locations and the results were an average of these readings.

As shown schematically in Fig. 3-3, the method uses indentation load-displacement data obtained during loading and unloading to determine the hardness, modulus and plasticity. The symbols P and h are used to denote loads and displacements, respectively. The plasticity is estimated by the ratio of the residual displacement after full unloading to the maximum displacement. The hardness and Young's modulus are computed from three measured parameters: the peak load, $P_{\max}$, the peak displacement, $h_{\max}$, and the contact stiffness, $S = dP/dh$. The first two quantities are taken directly from the load-displacement data, and the third is determined by curve fitting the upper portion of the unloading curve and measuring its slope at peak load. With these measured parameters, the first step in the computational process is to determine the contact depth, h_c , defined as the depth along which the indenter and specimen make contact at peak load. The contact depth is determined from the relation

$$h_c = h_{\max} - \varepsilon \frac{P_{\max}}{S} \quad (3-2)$$

where ε is constant with a value of about 0.75 for a Berkovich indenter [108].

Equation (3-1) is based on the assumption that at peak load, the edge of the contact is vertically displaced relative to the initial position of the surface in a manner that can be modeled by the indentation of an elastic half space by a rigid axisymmetric indenter. The projected area of contact, A , is then deduced from an empirically determined shape function $A = F(d)$ which describes the cross-sectional area of the indenter at a distance, d , back from its tip; more specifically, the contact area is determined by evaluating the shape function at the contact depth, i.e., $A = F(h_c)$. Once the contact area is known, the hardness follows from its normal definition

$$H = \frac{P_{\max}}{A} \quad (3-3)$$

and the effective Young's modulus or reduced modulus, E_{eff} , which accounts for elastic displacements in both the specimen and the indenter, is evaluated from

$$E_{\text{eff}} = \frac{1}{\beta} \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A}} \quad (3-4)$$

where β is a constant with a value of 1.034 for a Berkovich indenter [109]. Finally, the Young's modulus of the specimen, E , is extracted from the effective modulus using

$$\frac{1}{E_{\text{eff}}} = \frac{(1-\nu^2)}{E} + \frac{(1-\nu_i^2)}{E_i} \quad (3-5)$$

where E_i is the modulus of the indenter, and ν and ν_i are Poisson's ratio for the specimen and the indenter, respectively. The values $E_i = 1141$ GPa, $\nu_i = 0.07$, are used in all computations.

Fig. 3-3 Typical curve of load versus indentation displacement showing the parameters needed to determine hardness and Young's modulus

3.2.2.6 Toughness

Toughness was estimated by two approaches based on indentation method. The first was using microindenter with Vicker's tip to indent the coatings to obtain well-defined radial crack on silicon wafer substrate. To ensure the occurrence of the required crack, different loads were applied to the coating. For each load, at least three readings were obtained. In order to reduce the substrate effect, the coating toughness was linearly extrapolated to about 10% of the coating thickness. The fracture toughness K_{IC} can be calculated by equation (2-1). As for Vickers' indentation, δ equals to 0.016.

The second approach was using energy-release: the energy difference before and after through-thickness cracking is believed responsible for the coating fracture.

The fracture toughness of the film can be calculated by equation (2-2).

3.2.2.7 Residual stress

Residual stress was measured using a Talyscan 150 laser system by testing the curvature changes of silicon substrate before and after coating deposition. At least five measurements were performed for each sample at different orientation of silicon wafer. The residual stress σ can be calculated through Stoney's equation [110]

$$\sigma = \frac{Et_s^2}{(1 - \nu)6 R t_c} \quad (3-6)$$

where $E/(1-\nu)$ is the biaxial elastic modulus of the substrate, t_s and t_c are thickness of the substrate and coating, respectively. R is the substrate radius of curvature, which is calculated through:

$$R = \frac{1}{\left(\frac{1}{R_2} - \frac{1}{R_1}\right)} = \frac{R_1 R_2}{(R_1 - R_2)} \quad (3-7)$$

where, R_1 and R_2 are the radius of silicon substrate before and after coating deposition.

3.2.2.8 Tribotest

Ball-on-disk tests in dry condition (ambient environment: 75% humidity, 22 °C) were performed to determine the friction and wear characteristics. The sliding speed was set 20 cm/s under a load of 5 N and stainless steel (100Cr6) balls of diameter 6 mm were used as counterpart.

The wear rates were then calculated using the relation, wear rate $k = V / (W * S)$, where V is the wear volume in mm³, W is the normal applied load in Newton and S is the sliding distance in meters. The wear volumes of the steel balls were calculated from the ball geometry changes. The wear scar diameter, d (shown in Fig. 3-4) was measured using an optical microscope. The wear volume can be calculated using the equation

$$V = \frac{\pi t^2 (3R - t)}{2} \quad (3-8)$$

where R is the ball radius, t can be retrieved from the trigonometric relation $t = R - \sqrt{R^2 - (d/2)^2}$. Finally, the ball wear rate was calculated.

Fig. 3-4 Diagram for calculating the wear volume of Geometry of stainless steel ball

Chapter 4 Results

Through magnetron sputtering and RTP, different coatings including a-C, nc-TiC, CNF:a-C, and nc-TiC/CNF:a-C have been synthesized and the microstructures, mechanical properties and wear performance will be discussed in this chapter.

4.1 Composition and Microstructure

The properties of the coatings are affected by the microstructure and composition. Therefore, it is necessary to study the microstructure first.

4.1.1 a-C

XPS analysis was conducted to study the atomic bonding state of the a-C coatings. Fig. 4-1 shows the survey scans of the a-C coating deposited at -100 V. During deposition, there was no intentional heating, i.e. the process was conducted at room temperature. From XPS figures, it is shown that the major element is C 1s (~285 eV), and minor traces of O 1s (~531 eV), Ar 2p (~242 eV) and Ar 2s (~319 eV). The presence of oxygen was due to surface contamination, and after etching for 10 minutes, most of the oxygen was etched away with the evidence that O 1s peak became much weaker.

Fig. 4-1 XPS survey scans of a-C coating deposited at -100 V before and after etching for 10 minutes. A small amount of oxygen is present on the surface of a-C film due to surface contamination, and Ar is implanted during the sputtering process (deposition and/or Ar gas etching)

Fig. 4-2 shows XPS C 1s of a-C coating deposited at -100 V whose full width at half maximum (FWHM) is about 2 eV. The FWHM of a-C is much larger than pure graphite (FWHM = 0.7 eV) and diamond samples (FWHM = 1.0 eV). The peak can be deconvoluted with Gaussian distribution function. The peaks are fitted using binding energy interval values from the literature and three kinds of bonds are obtained: C-C sp^2 bonding at 284.7 eV, sp^3 bonding at 285.7 eV and C-O bonding at 288.3 eV [111, 112]. The concentrations of the different bonds are calculated and the sp^2/sp^3 ratio are derived and listed in Table 4-1. The sp^3/sp^2 ratio increased slightly from 0.35 to 0.43 after etching due to removal of surface absorption of hydrocarbon (mainly sp^2 bonded) and graphitized surface. However, long time

etching is not desirable because argon ion bombardment of the a-C surface may greatly change the bonding state of carbon. So the etching time is maintained at 10 minutes for all the studied pure a-C coatings.

(a)

(b)

Fig. 4-2 XPS detail scans for C 1s of a-C coatings deposited at -100 V (a) before and after etching for 10 minutes (b)

Table 4-1 C 1s XPS deconvoluted peaks for the a-C coating deposited at –100 V

Bonding		C-C sp ²	C-C sp ³	C-O
Before etching	Peak Position (eV)	284.6	285.7	288.0
	FWHM (eV)	1.22	1.59	4.15
	Percentage (%)	66.74	23.50	9.76
	sp ³ /sp ² ratio	0.35		NA
After etching	Peak Position (eV)	284.6	285.6	288.0
	FWHM (eV)	1.19	1.80	3.19
	Percentage (%)	62.39	27.04	10.57
	sp ³ /sp ² ratio	0.43		NA

To obtain a good quality of a-C coatings, it is vitally important to gain a high sp³/sp² ratio to achieve a very hard coating. Fig. 4-3 shows substrate bias effect on sp³/sp² of a-C coatings. Sp³/sp² ratio grows gradually as substrate bias increases. The maximum sp³/sp² ratio is almost doubled. It is well known that electrically biasing the substrate can influence the sputtered ion energy and provide ion bombardment of the growing film during deposition. The relationship between sputtered ion energy and substrate bias follows [113]:

$$E_i \propto \frac{V_b}{p^{1/2}} \quad (4-1)$$

Where E_i is sputtered ion energy, V_b substrate bias voltage, and p is the process pressure. The explanation for high sp³ fraction of high bias voltage coatings are high degree of ion impingement and re-sputtering of carbon atoms from graphite

clusters. Consequently, the formation of graphite clusters in the coatings is hindered. The bias voltage should not be too high since high bias voltage will yield high residual stress and delamination will occur. Hence in experiments, the substrate up limit of -150 V is selected.

Fig. 4-3 sp^3/sp^2 ratios of a-C coatings deposited under difference substrate bias (sp^3/sp^2 ratios are obtained by deconvolution of XPS C 1s peaks)

Raman spectrum of the a-C film under substrate bias 150 V is shown in Fig. 4-4. The broad peak was deconvoluted into two Gaussian bands at $\sim 1530\text{ cm}^{-1}$ (G peak) and 1350 cm^{-1} (D peak). As shown in Fig. 4-5, the G peak is the stretching vibration of any pair of sp^2 sites, whether in C=C chains or in aromatic rings while the D mode is the breathing mode of those sp^2 sites only in rings, not in chains [104]. The sp^3/sp^2 ratio was qualitatively estimated by the ratio of G and D peak intensity [114], i.e. a higher I_D/I_G means a lower sp^3/sp^2 ratio. Therefore, the I_D/I_G

trend with increasing the substrate bias follows the inverse trend of sp^3/sp^2 ratio (cf Fig. 4-6), i.e. the higher the substrate bias voltage, the lower the I_D/I_G ratio.

Fig. 4-4 Raman spectra of the film deposited under substrate bias -150 V

Fig. 4-5 Carbon motion in (a) G mode due to the relative motion of sp^2 carbon atoms and can be found in chains as well; (b) D mode due to sp^2 disordering [104]

Fig. 4-6 I_D/I_G ratio of a-C coatings as a function of substrate bias and higher bias voltage results in lower I_D/I_G ratio

The a-C coatings have been grown at different substrate temperatures in order to study the resulted bonding structure. Fig. 4-7 shows the Raman spectra under different substrate temperatures. With increasing temperature, the D peak becomes more and more obvious, which means the growth of I_D/I_G ratio. By fitting curves, the resulted I_D/I_G ratio is plotted in Fig. 4-8. The increase of the I_D/I_G ratio indicates the drop of sp^3/sp^2 . In addition, the order of the sp^2 hybrids is promoted with temperature as revealed by the decrease of FWHM of the G peak (Fig. 4-9) as discussed in ref. [104]. It can be concluded that the bonding structure evolves from a diamond-like structure to a graphitic-like structure as the substrate temperature increases, as in the case of tetrahedral a-C prepared by filter cathodic vacuum arc (FCVA) system [115].

Fig. 4-7 Raman spectra for a-C coatings deposited at different substrate temperatures

Fig. 4-8 Raman intensity ratio of the D to G peaks of a-C coatings at different substrate temperatures

Fig. 4-9 FWHM of G peak for a-C coatings at different deposition temperatures

4.1.2 CNF:a-C

After gaining some knowledge of a-C synthesis and its microstructure evolution upon different sputtering parameters, it is possible to grow CNF from a-C. To optimize the microstructure of CNFs, the effects of annealing temperature, annealing time and Al₂O₃ barrier layer have been examined.

The effects of annealing, time temperature and barrier layer on CNF coating microstructures are evaluated. Due to the equipment limit of RTP, the longest annealing time and highest temperature are 180s and 1100 °C, respectively.

4.1.2.1 Effect of Annealing Temperature

The a-C coatings were annealed at different temperatures (800-1100 °C) to examine the effect of annealing temperature on CNF growth. Fig. 4-10 shows plain view of the surface morphologies. At the temperature 800 °C, the surface is quite smooth and there is no any feature that can be observed (Fig. 4-10a). When the temperature is increased to 900 °C, there are a few CNFs grown with the lengths of about a few microns (Fig. 4-10b). Further increase of the annealing temperature (1000-1100 °C) leads to a dense distribution of CNFs (Fig. 4-10C&d), especially at the highest temperature. The CNFs are randomly distributed and in the length of a few tens of microns. Some of the nanoparticles are possibly Ni catalyst. It can be noticed that many of CNFs are not straight, and have spaghetti like structures.

(a) 800 °C

(b) 900 °C

(c) 1000 °C

(d) 1100 °C

Fig. 4-10 SEM images of the CNF:a-C coatings annealed for 180s at different annealing temperatures (a) 800 °C; (b) 900 °C; (c) 1000 °C; and (d) 1100 °C

4.1.2.2 Effect of Annealing Time

In order to study the effect of annealing time on the growth of CNFs, a-C films were annealed for different durations (30-180s) at 1100 °C in nitrogen atmosphere. Fig. 4-11 shows the morphologies for the CNF:a-C coatings annealed at different time. Except the coating annealed for 15s (Fig. 4-11a), all the other coatings have fiber-like structures and some coatings have nanoparticles. For the coating annealed at 15s, CNF is absent because the time for carbon diffusion into the catalyst particle is too short. For the coating with CNFs, they show random distribution and most CNFs are bundled together. The lengths are at least a few microns. For the coating annealed for 30s, there are a few CNFs observable and therefore CNF density is quite low. Increasing the annealing time significantly promotes CNF growth and increases CNF density and CNF lengths. The coating annealed for 180s contains much more CNFs and longer than the one annealed for 30s. During annealing, rapid achievement of high temperature allows carbon atoms to diffuse into Ni particles. Based on the above results, for the temperature of 1100 °C, the best annealing time is about 180s. In the following part, the annealing time will be fixed at 180s. From SEM observation, it can be seen some amorphous cluster is present together with CNF. The estimation of CNF purity will be done by Raman analysis.

(a) 15s

(b) 30s

(c) 45s

(d) 60s

(e) 90s

(f) 120s

(g) 180s

Fig. 4-11 SEM images of CNF:a-C coatings grown at 1100 °C with different dwell time (a) 15s, (b)30s, (c) 45s, (d) 60s, (e) 90s, (f) 120s and (g) 180s

Raman spectra have been used to study the bonding state evolution during annealing. Fig. 4-12 shows the evolution of the Raman spectra of the CNF:a-C coatings with increasing the annealing time. The coatings show typical D ($1320\text{--}1340\text{ cm}^{-1}$) and G ($\sim 1580\text{--}1590\text{ cm}^{-1}$) peaks [116]. The G peak position of CNF:a-C is close to that of graphite (1580 cm^{-1}). The upshift of G peak position comparing with those of annealed a-C ($\sim 1530\text{ cm}^{-1}$), also conforms the enhanced graphitization at high temperature annealing.

Fig. 4-12 Evolution of the Raman spectra of the CNF:a-C coatings with increasing the annealing time

The variation in FWHM and the ratio of D to G peak intensity with increasing the annealing time are presented in Fig. 4-13 and Fig. 4-14, respectively. As shown in Fig. 4-13, the FWHM of Raman G peak decreases when the annealing time increases. The decrease of FWHM of Raman G peak is due to the graphitization/crystallization of disordered carbon. I_D/I_G increases when the annealing time increases (Fig. 4-14). Though the I_D/I_G ratio is not direct indicate of sp^2 or sp^3 bonding fraction, the I_D/I_G ratio is inversely proportional to sp^3/sp^2 fraction [114]. Thus the increase of I_D/I_G signals an increase of sp^2 hybridization. Therefore, the longer the annealing time is, the higher sp^2 ordering of the coating will be.

Fig. 4-13 The Raman G peak FWHM of CNF:a-C coatings with increasing annealing time

Fig. 4-14 Raman intensity ratio of the D to G peaks of CNF:a-C coatings with increasing annealing time

4.1.2.3 Effect of Barrier Layer

As is shown in the previous results, a longer annealing time and a higher annealing temperature can promote CNF growth and lead to denser CNFs. Due to our RTP limitation, the annealing time can not exceed 180s and the annealing temperature is at most 1100 °C. To promote CNF growth, a small amount of ethanol vapor was introduced into the RTP chamber [117]. The results show that introduction of ethanol vapor during the thermal annealing process can promote the yield of the CNF. It was proposed by the researchers that ethanol can enhance the CNF growth by the following CVD reaction:

where O_2 comes from the gas impurity.

The newly formed H_2O is a weak oxidizing agent[118] which can etch the a-C encapsulating the catalyst to release more catalytic particles into action.

This treatment, however, brings in a CVD process actually, where it is originally a transformation process from a-C to CNF via RTP. In CVD process, the carbon source is gas. Thus one question still exists: can this transformation be improved by some other way?

For CVD synthesis of CNF/CNTs, the role of barrier layers is an important issue. The barrier layer is defined as the layer between catalyst and substrate. Different materials, such as SiO_2 , TiO_2 , TiN , MgO , Al_2O_3 and etc have been investigated by many researchers [119-121]. Among them, Al_2O_3 is usually very effective [122, 123]. The Barrier layer effect, however, has not been studied for RTP grown CNFs.

As shown in Fig. 4-15, with the utilization of Al_2O_3 barrier layer, there are denser CNFs and the fiber-like structures are straighter than those without any barrier layer. No any spaghetti like structures can be observed. It should be pointed out that there are still impurities attached to the nanofibers. The results prove that the Al_2O_3 barrier layer has a strong positive effect on the CNF:a-C coating morphology. The possible reason may be due to the block of diffusion and reaction between carbon and silicon. The detailed discussion is given in section 5.2.

(a)

(b)

Fig. 4-15 FESEM images of CNF:a-C coatings grown at 1100 °C for 180 s with a Al_2O_3 barrier layer: (L) low magnification and (R) high magnification

Fig. 16(a) shows TEM low magnification image of CNF:a-C grown at 1100 °C with Al_2O_3 barrier layer. The diameters of CNFs are about 20-50 nm and the CNF lengths are at least a few microns. At the end of CNFs, there are 30-50 nm particles which are Ni catalyst. Black clouds are possibly a-C/carbonaceous impurity.

(a)

(b)

(c)

Fig. 4-16 TEM images (a)&(b) and selected area diffraction (SAD) pattern (c) of CNF:a-C coating grown at 1100 °C 180 s with an Al₂O₃ barrier layer

4.1.3 nc-TiC

After studying a-C and then CNF:a-C grown from a-C, the next step is to investigate hard single phase coating. The hard nc-TiC is chosen due to its outstanding properties like high hardness and good affinity to CNF:a-C phases. The formation of nc-TiC will be possible to provide hardness for CNF:a-C.

The substrate bias influence on deposition rate of TiC coatings is shown in Fig. 4-18. The deposition rate decreases gradually from 11.3 to 6.8 nm/s when substrate bias increases from -20 V to -200 V. The drop in deposition rate is caused by back-

sputtering of the as-deposited film, i.e., kicking off the adatoms of growing surface by the incoming ions.

Fig. 4-17 Effect of substrate bias on deposition rate of nc-TiC coatings

Fig. 4-18 and Fig. 4-19 plot the XPS spectra of C 1s and Ti 2p for nc-TiC films under different substrate bias, respectively. The peak at the binding energy of 281.8 eV is TiC peak. No peak at about 284.6 eV, i.e. no C-C bond was formed. The Ti 2p_{3/2} peak of Ti in TiC is at 454.9 eV and that of metallic Ti is at 453.8 eV [124]. The Ti 2p_{3/2} peak is at 461.0 eV for Ti in TiC and 459.9 eV for metallic Ti [124]. Almost no metallic Ti 2p_{3/2} and Ti 2p_{1/2} peaks are detectable. Therefore the structure of the film was virtually 100 % TiC.

Fig. 4-18 XPS spectra of C 1s of nc-TiC coatings deposited under different substrate bias

Fig. 4-19 XPS spectra of Ti 2p of nc-TiC coatings deposited under different substrate bias

XPS result shows that Ti/C ratio differs only a little from 1:1 as the substrate bias increases (c.f. Table 4-2). Unlike reactive sputtering through input of hydrocarbon gas, co-sputtering of titanium and graphite target has the advantage of easier composition control, i.e. Ti/C ratio does not significantly affect the composition when substrate bias is varied.

Table 4-2 nc-TiC Coating composition

Substrate bias (-V)	Composition (at.%)		
	Ti	C	Ti/C ratio
20	51.1	48.9	1.04
100	49.8	50.2	0.99
150	49.5	50.5	0.98
200	51.3	48.7	1.05

XRD analysis was conducted on the films and the results are shown in Fig. 4-20. The peak around 69° is from the Si (100) substrate underneath the film. No peak of Ti or carbon was found. Peaks at 35.9° , 41.7° , and 76.1° were attributed to (111), (200) and (222) diffraction mode of TiC. All these patterns exhibited relatively broad peaks and have a dominant orientation of the (111) plane. Although existing of the stress effect on microstraining will affect XRD peak width, the effect would be small. Using equation 3-1, Williamson-Hall plot has been drawn as shown in Fig. 4-21. Through Williamson-Hall plots, grain size and microstrain for nc-TiC coatings have been calculated, and the results are illustrated in Fig. 4-22. The calculated grain size of the TiC crystallite drops slightly from ~ 15 nm to 13 nm and the microstrain increases as the substrate bias grows, possibly due to enhanced ion bombardment at high substrate bias.

Fig. 4-20 X-ray diffraction results for nc-TiC coatings at different substrate bias

Fig. 4-21 Williamson-Hall (W-H) plot for nc-TiC coating with various substrate bias

Fig. 4-22 Calculated grain size & microstrain variation for nc-TiC coatings at various substrate bias

Scanning electron micrographs of cross sections of the films deposited at different substrate bias is shown in Fig. 4-23. Regardless of various substrate bias, the morphology shows columnar structure. But the morphology is more refined at higher substrate bias which agrees with the calculated finer grain size. At bias -200 V, the film has smaller columnar structure compared with the film at lower substrate bias. TiC has a melting temperature (T_m) of 3340 K [125] while the deposition temperature (T_s) is 473 K, which give rise to a homologue temperature T_s/T_m of only ~ 0.14 . Therefore, the TiC film should possess a Zone I (equiaxial small grain) structure, according to Thornton model [126]. However, at different bias (-20 V to -200 V), the TiC film shows a Zone T structure. With a negative substrate bias applied to the substrate, the ionized argon in the plasma increases. Intense substrate ion bombardment (bias sputtering) can deliver a high energy to the

as-deposited film and result in a dense film. The mechanism is primarily a sputter-induced redistribution of coating material.

(a)

(b)

(c)

(d)

Fig. 4-23 FESEM micrographs showing the cross-section of nc-TiC coatings deposited at different substrate bias: (a) -20V, (b) -100V, (c) -150V and (d) -200V

4.1.4 CNF Formation in nc-TiC/a-C

After knowing the process conditions for CNF:a-C and nc-TiC, the final stage is to combine them to form nc-TiC/CNF:a-C nanocomposite coatings. The nc-TiC/CNF:a-C dedicates there are nc-TiC, CNF phases and some residue a-C phase. Till now, there has been no published method to produce such in-situ growth of one dimensional hard nanocomposites coating. Magnetron sputtering and rapid thermal processing were chosen in this thesis work due to their wide availability in industry, high cost effectiveness, easy scalability, friendly environmental effect and etc.

C 1s XPS spectra of the coatings with and without nanotubes are shown in Fig. 4-24. The deconvolution of the spectra gives rise to two components at binding energies of 281.8 and 284.2 eV. The peak at 281.8 eV is carbon bonded to titanium in TiC phase (the Ti-C bond) and 284.2 eV is that of carbon bonded to carbon (the C-C bond), which agrees with previous study [102]. As reported in literature, a fourfold coordinated sp^3 configuration of carbon has a binding energy of 285 eV while graphite or CNF characterizes a threefold coordinated sp^2 configuration with binding energy of 284.3 eV [111, 127]. Thus in the coatings, C-C bond is mainly of sp^2 configuration due to high temperature annealing. The coating without CNF has no C-C bond detected thus is purely nc-TiC coating. In coatings with CNF, some carbon atoms are bonded to titanium as estimated by fitting two peaks of Ti-C and C-C.

Fig. 4-24 C 1s XPS spectra of nc-TiC (C0) and nc-TiC/CNF:a-C (C1&2) coatings

4.1.4.1 Composition

Based on XPS results, the compositions for the coatings can be calculated. For these two coatings, Ni concentration is too low to be detected by XPS. The results are showed in Table 4-3. The coating C0 is pure nc-TiC while C1 and C2 contain certain amounts of C-C so they are nc-TiC/CNF:a-C. For C1 and C2, CNF:a-C concentrations are ~5 at.% and ~10 at.%, respectively. Considering the purity of CNF (45 at.%) in CNF:a-C (details will be discussed in chapter 5), CNF concentrations are ~2.3 at.% and ~4.5 at.%, respectively.

Table 4-3 Chemical composition of nc-TiC and nc-TiC/CNF:a-C coatings

Coating	Ti/C ratio	Coating structure
C0	0.99	nc-TiC
C1	0.95	nc-TiC/(CNF:a-C) _{0.05}
C2	0.91	nc-TiC/(CNF:a-C) _{0.10}

4.1.4.2 Microstructure

Fig. 25 shows SEM cross-section view of coating C0, C1 and C2. For C0, there is no any nanofiber like structure present and it is a typical columnar structure. For C1 and C2, some fibers are shown inside the coating. Some long nanofibers (at least a few microns) was grown in the coating and for C2, quite a few short tips of nanofibers can be observed. From SEM observation, nanofiber distribution in the coating is uniform. When CNF:a-C was included, there was no columnar structure, indicating the secondary phases break down the column growth.

(a)

(b)

(c)

Fig. 4-25 SEM micrographs showing the cross-section of nc-TiC and nc-TiC/CNF:a-C coatings. C0: nc-TiC, C1: nc-TiC/(CNF:a-C)0.05 and C2: nc-TiC/(CNF:a-C)0.10

After TEM examination, for annealed nc-TiC C0, there is no any fiber like structure observed. But for nc-TiC/ CNF:a-C C1&2, fiber like structures are present. Fig. 4-26 (a) shows uniform distributed CNFs observed by TEM for nc-TiC/CNF:a-C coating (C1). Fig. 4-26 (b) shows a nanofiber structure where the nanofiber is surrounded by nanoparticles. No graphite layer can be observed. HRTEM imaging (Fig. 4-26 (c) shows TiC crystallite with a lattice spacing of $2.14 \text{ \AA}$, which matches the interplanar spacing of TiC (200) plane, (JCPDS card No. 73-0472). The crystallite sizes of nc-TiC are in the range of 5-8 nm. Rapid ramping of heating avoids the over-growth of nc-TiC. The nanofiber diameter is about 50 nm, and the length is at least $1 \text{ }\mu\text{m}$. The image reveals that the nc-TiC grains are well attached to the tube, likely due to C-C or Ti-C bond between crystallite and the tube surface.

A good interfacial reaction is vital for load transfer across the CNF/TiC interface. Computational modeling of the interface between Al_2O_3 and CNF shows partial bonding of Al-terminated Al_2O_3 with carbon [128].

(a)

(b)

(c)

Fig. 4-26 HRTEM images of C1: nc-TiC/(CNF:a-C)_{0.05} coating showing (a) uniformly distributed CNFs, (b) a single carbon nanofiber and (c) nc-TiC crystallites well adhered to the fiber; inset: enlarged TEM image, taken from one nc-TiC

Fig. 4-27 shows GIXRD plots for the nc-TiC and nc-TiC/CNF:a-C coatings. Aside from the WC/Co substrate peaks, TiC's (111), (200) and (220) peaks were observed, which agrees well with the TEM observation. The graphite peak (located at $\sim 26-26.5^\circ$) is absent which confirms the amorphous state of CNF. It is possibly due to relatively low annealing temperature. Using Williamson-Hall plots [107] (c.f. equation 3-1), the calculated crystallite size and lattice strain were 18 nm and 0.13 % when no CNF is present (see Fig. 4-28). When CNF is imbedded, the crystallite size was decreased to 14 nm and lattice strain was about the same 0.12~0.15 %. As a second phase, CNF can constrain the grain growth. The relatively low strains indicate that the strain can be minimized upon annealing due to the reduction in the concentration of lattice imperfections. Due to some affecting factors like residual stress and texture, the grain sizes deduced from XRD analysis are slightly bigger than TEM observations but still comparable. TEM observations provides direct imaging of nanocrystalline structures but the information from TEM represents only a local region and it needs many images to get average. However XRD is able to provide the mean grain size in the entire sample. Even though Williamson-Hall plot considered the microstrain broadening, some defects such as dislocation [129], deformation faulting [130], stacking faults [131] may also contribute to the peak broadening of XRD peaks.

Fig. 4-27 GIXRD spectrum of nc-TiC and nc-TiC/CNF:a-C coatings. C0: nc-TiC, C1: nc-TiC/(CNF:a-C)_{0.05} and C2: nc-TiC/(CNF:a-C)_{0.10}

Fig. 4-28 Williamson-Hall plot of C0: nc-TiC, C1: nc-TiC/(CNF:a-C)_{0.05} and C2: nc-TiC/(CNF:a-C)_{0.10} coatings

4.2 Hardness and Young's Modulus

For pure a-C coatings, the hardness and Young's modulus are mainly governed by sp^3 fraction, i.e. the higher sp^3 fraction, the higher the hardness and Young's modulus. Fig. 4-29 shows the substrate bias can increase the hardness and Young's modulus. The maximal hardness and Young's modulus of a-C deposited at 150 V bias reaches 31.6 GPa and 303.4 GPa. At elevated substrate temperature, the hardness and Young's modulus are decreased greatly as seen in Fig. 4-30. When substrate temperature is up to 300 °C, the hardness and Young's modulus drop to 11.3 GPa and 117.7 GPa, respectively. Further increasing the substrate temperature is not conducted because a too low hardness of a-C coating is undesirable and out of actual application interest.

Fig. 4-29 Hardness and Young's modulus of a-C coatings deposited under different substrate biases

Fig. 4-30 Hardness and Young's modulus of a-C coatings deposited at different substrate temperatures

Hardness and Young's modulus of the nc-TiC films at different substrate bias is shown in Fig. 4-31. As expected from microstructure and morphology analysis, the substrate bias enhances the hardness and Young's modulus of the nc-TiC films. At -20 V bias, the hardness and Young's modulus of the film are only 13.9 GPa and 208.6 GPa, respectively. At -200 V bias, the hardness and Young's modulus are improved to 28.8 GPa and 302.5 GPa, respectively.

Fig. 4-31 Hardness and Young's modulus of nc-TiC coatings as a function of different substrate bias

4.3 Toughness

Coating toughness has been characterized using indentation technique and the effect of process conditions will be discussed.

4.3.1 a-C

The toughness of a-C coatings is measured by nanoindentation energy approach. Substrate bias effect and substrate temperature effect on a-C coating toughness were investigated using a modified Michel model (Fig. 4-32a&b) by considering the Si substrate effect. In Fig. 4-32a, the toughness of a-C coatings deposited at room temperature increases as the substrate bias grows. At lowest substrate bias (-20 V), the toughness is about $2.9 \text{ MPa}\cdot\text{m}^{1/2}$, while at -150V bias, the toughness

grows about 40 % to $4.9 \text{ MPa}\cdot\text{m}^{1/2}$. That means both toughness and hardness of a-C coatings shows the same growing trend as the substrate bias increases. It is similar to the results of a-C:H reported by Michel et al [132], but the reason is not clear. In Fig. 4-32b, substrate temperature effect on toughness shows that under constant substrate bias, toughness drops down as substrate temperature increases. At 300°C , the toughness decreases to about $2.8 \text{ MPa}\cdot\text{m}^{1/2}$ which contradict the scratch results. The toughness and hardness also hold the same trend.

(a)

(b)

Fig. 4-32 (a) Effect of substrate bias on toughness of a-C coatings; (b) effect of substrate temperature on toughness of a-C coatings

4.3.2 CNF:a-C

Mechanical properties of CNF:a-C coatings annealed at 1100 °C with different annealing time are examined. Coating hardness and Young's modulus have been measured by nanoindentation. The coatings annealed for longer than 30 s shows can not be measured because these coatings have porous rather than dense film. The results for the coating annealed at 1100°C for 15 s (a-C) and 30 s (6%CNF:a-C) are shown in Table 4-4. The hardness and Young's modulus of 6% CNF:a-C after annealing are much lower than those annealed a-C coatings, due to the significant graphitization. A longer annealing duration further slightly reduces coating hardness and Young's modulus.

Nanoindentation energy approach can not be used to characterize the coating toughness due to the absence of the ring crack formation but radial cracks are present. Microindentation stress approach based on the radial crack length is used. The toughness values of a-C and CNF:a-C coatings are also shown in Table 4-4. CNF:a-C coating has a toughness of $3.65 \text{ MPa}\cdot\text{m}^{1/2}$ which is about 55 % higher than that of a-C ($2.35 \text{ MPa}\cdot\text{m}^{1/2}$) while the hardness is decreased .

Table 4-4 Mechanical properties of a-C and CNF:a-C coatings annealed at 1100 °C for 15 and 30 s, respectively

Coating	Hardness (GPa)	Young's Modulus (GPa)	Toughness ($\text{MPa}\cdot\text{m}^{1/2}$)
a-C	3.12 ± 0.38	28.5 ± 2.2	2.35 ± 0.35
6%CNF:a-C	2.63 ± 0.48	24.8 ± 3.4	3.65 ± 0.44

4.3.3 nc-TiC

The toughness characterization was carried out to investigate the bias effect and the results are shown in Table 4-5. The film deposited at -20 V bias was fractured greatly even at 98 mN indentation load (the minimum load in our instrument) and was unable to be used for toughness calculation. While at -200 V bias, the crack load threshold is increased at least 20 times, that means the load capacity is increased. For those films deposited at -200 V bias, the toughness is also improved by about 60 % compared with at low bias -100 V. All the toughness data is comparable and falls into the range of $\sim 1\text{-}2 \text{ MPa}\cdot\text{m}^{1/2}$ which is lower than reported bulk indentation toughness value $2.5 \text{ MPa}\cdot\text{m}^{1/2}$ of TiC [133].

For a hard coating, when the hardness is increased through restricting the dislocation movement and grain boundary sliding, the plastic deformation will be prohibited. Therefore the ductility will be lost. However, in our case of nc-TiC films, the enhanced hardness at high bias is due to ion energy bombardment and it promotes more crystallites while keeping them relatively small. Higher ion energy can eliminate the shadowing effect which is typical in zone I structure and surface diffusion will dominate. Recently, Pei et al [77, 78] studied the substrate bias effect on nc-TiC/a-C:H coatings prepared by close field unbalanced magnetron sputtering (CFUMS). Increasing bias changed the coating microstructure, showing clear transition from columnar to glassy microstructure in the nanocomposite layer. Substrate bias also simultaneously and greatly enhanced coating hardness, toughness and adhesive strength (although the toughness values are unbelievably high due to experimental limitation, which is pointed out by the authors). The toughness trend indicates the coating with a glassy microstructure exhibiting substantial toughening effects. Ion bombardment can densify the structure and prevent the formation of voids and large columnar boundaries which are detrimental in terms of microcrack initiation and propagation under load. Therefore, in our case, nc-TiC toughness can be further enhanced if the nano-column structure of nc-TiC is evolved to glassy microstructure.

Another possible contribution to the bias enhanced hardness and toughness is compressive stress [11, 40]. Bias plays a big role and leads to an increase in compressive residual stress [134]. Since cracking is generally initiated by tensile stress, compressive residue stress has to be overcome first. However, the compressive stress effect on TiC toughness is difficult to be separated from

microstructure evolution. In our case, too high substrate bias is detrimental to the adhesion strength as shown in the adhesion strength results.

Table 4-5 Crack load threshold and toughness at different substrate bias

Substrate bias (-V)	Crack threshold load (mN)	Toughness K_{IC} (Mpa·m ^{1/2})
20	98	NA
100	490	1.19±0.34
150	980	1.60±0.19
200	1960	1.89±0.45

4.3.4 nc-TiC/CNF:a-C

The mechanical properties of three coatings on WC/Co substrates measured by nanoindentation and microindentation are shown in Table 4-6. For nc-TiC/CNF:a-C, hardness drops from 30.97 GPa to 25.93 and 23.44 GPa, and Young's modulus from 626.04 GPa to 435.67 and 463.52 GPa. Measurement of toughness of ceramic films or coatings is still an unresolved controversy where currently no unified methodology is available [86]. Though indentation for toughness is arguably inaccurate, it still provides a quick self comparison if it is used properly [135, 136]. Without CNF, the toughness of nc-TiC coating is 3.25 MPa·m^{1/2}, which is comparable with literature toughness data for bulk TiC [137] but higher than the coatings measured on silicon substrate, possibly due to the difficulty of totally excluding the substrate effect. After CNF growth, i.e., nc-TiC/CNF:a-C, the toughness increases to 5.54 and 6.09 MPa·m^{1/2}. In other words, at a cost of 16 %

and 24 % hardness reduction the toughness improved by 70 % and 87 % due to CNF:a-C incorporation.

Table 4-6 Mechanical properties of nc-TiC and nc-TiC/CNF:a-C nanocomposite coatings

Coating	Hardness [GPa]	Young's Modulus [GPa]	Toughness [MPa·m ^{1/2}]
C 0 (nc-TiC)	30.97±4.98	626.04±40.11	3.25±0.20
C1 (nc-TiC/(CNF) _{0.05})	25.93±4.46	463.52±23.76	5.54±0.23
C2 nc-TiC/(CNF) _{0.10})	23.44±3.04	435.67±21.88	6.09±0.11

4.4 Adhesion

The adhesion strength of a-C is a major obstacle for its application, especially for a thick (~ a few microns) a-C coating. Low adhesion strength arises from its high compressive stress and low plasticity due to ion bombardment. The high residual stress weakens the adhesion and leads to peeling off. The lack of plasticity results in a brittle fracture of the coating due to crack propagation even at low applied loads. The coatings were deposited at a power density of 10.5 W/cm², process pressure of 0.6 Pa and substrate bias of -150 V. The thickness was about 0.5 μm. The critical loads obtained from the tests for a-C deposited on Si substrates are plotted in Fig. 4-33. The adhesion strength increases with increasing substrate temperature. The coating deposited without any intended external heating has the poorest adhesion. When substrate temperature increases to 300 °C, the critical load increases to the highest value of 481 mN.

Fig. 4-33 Effect of deposition temperature on the critical load for a-C coatings. The critical load increases as deposition temperature increases

Fig. 4-34 shows the optical images of the scratches on the coatings which are sputtered on Si after the tests. For all coatings, the low critical load (the load at which the damage starts to occur) and high critical load (the load at which the coating is totally damaged) were not distinguishable. At relatively low deposition temperature (room temperature to 150 $^{\circ}\text{C}$), a brittle fracture happens as chipping is present. However, on the surface of coatings deposited at 200 and 250 $^{\circ}\text{C}$ there are less cracks. The coating deposited at 300 $^{\circ}\text{C}$, exhibits no fracture or interfacial failure was observed, and the diamond tip ploughs into the coating causing a gradual decrease in scanning amplitude, indicating good adhesion and high ductility.

Fig. 4-34 Scratch images of a-C coating deposited at different substrate temperature:

- (a) room temperature, (b) 100 $^{\circ}\text{C}$, (c) 150 $^{\circ}\text{C}$, (d) 200 $^{\circ}\text{C}$, (e) 250 $^{\circ}\text{C}$, and
(f) 300 $^{\circ}\text{C}$

The adhesion strength of nc-TiC coatings is shown in Fig. 4-35. The film deposited at bias -20 V, exhibited the lowest adhesion (58 mN). As the bias increased, the adhesion grew up greatly and reached the maximum (252 mN) at bias -100 V. Further rise of bias leads to the drop of adhesion. At substrate bias -200 V, the critical load is 190 mN.

Fig. 4-35 Scratch adhesion strength of nc-TiC coatings on Si substrates at different substrate bias

As can be clearly seen from the optical micrographs of the scratch tracks in Fig. 4-36, nc-TiC coatings deposited on Si substrates under different substrate bias all show delamination in a brittle manner and the lower critical load and the higher critical load were not distinguishable. However, at lowest substrate bias (-20V), the coating fails at a very low load of 58 mN. The substrate bias can promote the intermixing of TiC coating and substrate, indicating the positive role of substrate

bias [138]. However, the substrate bias can not be too high, because too high overstressed film will decrease the adhesion.

Fig. 4-36 Optical micrographs of scratch tracks on nc-TiC coatings deposited at different substrate bias (a) - 20 V, (b) - 100 V, (c) - 150 V, and (d) - 200 V

4.5 Residual Stress

For a-C coatings, high residual stress is a big drawback, which limits the coating thickness and adhesion strength thus limits its applications [139, 140]. Fig. 4-37 shows the measured residual stress as a function of substrate bias and temperature. At -20 V substrate bias, the residual stress was about 0.9 GPa. When the bias was increased to 150 V, the residual stress increased to 4.2 GPa. This agrees with observation of the relationship between the I_D/I_G ratio and substrate bias, as when the bombardment is high, more sp^3 can be formed in the a-C coating. For the substrate temperature effect, the residual stress decreased from 4.2 GPa for the coating deposited at room temperature to 0.8 GPa for that deposited at 300 °C. It indicates at high temperature, residual stress can be thermally released, accompanied by the graphitization transformation.

(a)

(b)

Fig. 4-37 Compressive residual stress in a-C coatings as a function of (a) substrate bias and (b) deposition temperature

4.6 Wear Performance

Unlike other carbon-based materials, such as graphite [141], diamond [141], fullerene [142], amorphous carbon [143], CNF/CNT coatings show diverse friction coefficient. Some research groups have investigated the tribological properties of CNT coatings either aligned or non-aligned. Vertically aligned CNT coatings exhibit high COF (coefficient of friction), and it is attributed to bending of CNTs. Dickrell et al. [144] have discussed the orientation effect on CNT coating friction coefficients. COFs of CNT coatings will decrease from high value 0.795 for vertically aligned CNTs to very low value 0.090 for flat aligned CNTs on the contact plane [144].

To determine the CNF/a-C effect on the tribological performance, tribotest was conducted in dry condition. In this study, the doping of CNF decreased the COF from 0.39 to 0.21 (Fig. 4-38). It is well known that a-C coatings offers low or even super low (~ 0.01) friction coefficients [104]. During contact and wear, the a-C at the contact area can be transformed into graphitic layers which behave as a solid lubricant [145]. Water intercalation between the graphite layers lowers the friction coefficient.

The diameter of the wear scars were also decreased significantly. As shown in Fig. 4-39, the wear scar diameter for nc-TiC coating C0 is about 919 μm while after CNF growth, they are decreased to 672 μm and 542 μm for nc-TiC/CNF/a-C coatings C1 and C2. Based on the wear scar diameters, the wear rates of the stainless steel have been calculated (see Fig. 4-40). For the wear rate of 100Cr6 steel counterparts from $19.9 \times 10^{-14} \text{ m}^3/\text{Nm}$ to $6.9 \times 10^{-14} \text{ m}^3/\text{Nm}$. In another word, the wear rate of the stainless steel ball was decreased by $\sim 65\%$ when CNF was incorporated. The results support the CNF has good lubricant property and is possible to be applied in tribological applications.

The reason of the good lubricant property is possibly due to the carbon sp^2 riched transfer film generated during wear test. It was reported that nc-TiC/a-C:H coatings showed the self-lubricating behavior by the formation of transfer films on the surface of the ball counterpart [146]. The removal of transfer layers at high sliding speed, caused a sudden jump of COF in the wear test [146]. Fig. 4-41 indicates after tribotest, there are Raman characteristic peaks (D peak and G peak) for the stainless steel ball, similar to those of the coating. Some parts of the coatings were

attached to the steel to form carbon rich film which benefited the coating lubricant properties and improved the wear performance.

Fig. 4-38 Coefficient of friction for the coatings sliding against stainless steel balls after 1 km ball-on-disc tribotests in ambient air (22 °C, 75% humidity). Coating C0 is nc-TiC coating, C1 nc-TiC/(CNF:a-C)_{0.05} and C2 is nc-TiC/(CNF:a-C)_{0.10}

(a) C0: nc-TiC

(b) C1: nc-TiC/(CNF:a-C)_{0.05}

(c) C2: nc-TiC/(CNF:a-C)_{0.10}

Fig. 4-39 Wear scars of stainless steel balls for coatings (a) C0, (b)C1 and (c) C2

Fig. 4-40 Wear rates of the stainless steel balls (a) and coating (b), when sliding against C0: nc-TiC, C1: nc-TiC/(CNF:a-C)_{0.05} and C2: nc-TiC/(CNF:a-C)_{0.10} coatings

(a)

(b)

Fig. 4-41 Raman spectra for C2 nc-TiC/(CNF:a-C)_{0.10} coating (a) and the wear ball after tribotest (b)

4.7 Summary

For sputtered a-C coatings, deposition parameters (e.g. substrate bias, deposition temperature) of a-C significantly affected the coating properties. An increase in bias voltage (or decrease in deposition temperature) induced an increase in the energy of ion bombarding the substrate which promotes a high sp^3 fraction up to $\sim 48\%$. CNFs were grown through a two-step process: co-sputtering of graphite and nickel and post-annealing at $1100\text{ }^\circ\text{C}$. Increase of the annealing time and the annealing temperature and using Al_2O_3 barrier promoted CNF growth and increased the purity of CNF by promoting graphitization. Co-sputtering of graphite and Ti formed nanocrystalline TiC. The size of the nanograins, and mechanical properties were influenced by substrate bias. As the substrate bias was increased from 0 to -200 V , the crystallite size decreased from 26 nm to 17 nm and the columnar structures became smaller. *In-situ* growth of CNFs in nc-TiC/a-C coating was realized. The distribution of CNFs was uniform. The diameters of CNFs were $\sim 50\text{ nm}$ and the crystallite sizes of nc-TiC were $\sim 5\text{-}8\text{ nm}$. No clear interfacial region between CNF and nc-TiC was observed.

For a-C coatings deposited with the highest substrate bias (-150 V), the high hardness (31 GPa) can be obtained. However, such high energy bombardment sacrificed the adhesion. Based on indentation energy approach, toughness values of a-C coatings under different substrate biases were calculated in the range of $2.8\text{-}4.9\text{ MPa}\cdot\text{m}^{1/2}$ which are comparable with literature. 6% CNF concentration improved the toughness of a-C by 55% from $2.35\text{ MPa}\cdot\text{m}^{1/2}$ to $3.65\text{ MPa}\cdot\text{m}^{1/2}$ while the hardness decreased by 16% from 3.12 GPa to 2.63 GPa . For nc-TiC coatings, the

hardness, Young' modulus, load capacity and toughness were enhanced by substrate bias. But too high substrate bias led to the deterioration of adhesion strength. The toughness of the TiC coatings was 1.19-1.89 MPa·m^{1/2} which is low but comparable to TiC bulk toughness.

Due to the high thermal stress during annealing, instead of Si substrate, WC/Co substrate had to be used for toughness measurement of nc-TiC/CNF:a-C. CNF inclusion increased toughness of the coating in a big way, but at some cost of hardness: the toughness of nc-TiC enhances by 87% from 3.25 MPa·m^{1/2} without CNF to 6.09 MPa·m^{1/2} with CNF, while hardness decreased by 24 % from 30.97 GPa to 23.44 GPa. Toughness and hardness of these magnitudes in a ceramic coating at the same time have not been reported before. Besides, the CNF incorporation also promotes good tribological properties such as friction coefficient and wear rate of stainless steel balls.

Chapter 5 Discussions

In this chapter, the toughness measurements for a-C, CNF:a-C, nc-TiC, and nc-TiC/CNF:a-C will be discussed in detail. Then it is followed by CNF growth mechanism and finally by CNF toughening mechanism in the nanocomposite coatings.

5.1 Toughness Measurement

As discussed in the literature review (Section 2.3), it is still a big challenge to characterize the coating toughness due to the size/geometry limitations. Indentation stress and energy approaches are the most popular. The stress approach is based on radial crack length and the energy approach is based on fracture energy absorbed during cracking. These two approaches will depend on the coating's fracture behavior, i.e. what kind of crack happens. Hence it is necessary to study the fracture behavior of a-C coating during indentation. The SEM micrographs and load-displacement curves of indentation made at 300, 400 and 500 mN peak indentation loads using the Berkovich tip are shown in Fig. 5-1. The sample was deposited at room temperature, with -20 V substrate bias, graphite target power density 10.5 W/cm², and process pressure 0.6 Pa. The hardness and Young's modulus are 14.1 GPa and 138.0 GPa, respectively. The thickness of the samples was ~500 nm. When peak indentation load is 300 mN, there is no any discernable crack happening (Fig. 5-1 (a)). In Fig. 5-1 (a) & (b), the pop-out event (sudden drop of the indentation displacement upon unloading) is present which can be attributed to silicon substrate phase transformation [147, 148]. Depending on the experimental process, silicon exhibits a phase transition from cubic diamond (Si-I) into a tin

structure (Si-II), accompanied by a volume decrease of 22 % [149]. However, the Si-II structure is not stable at ambient pressure. During unloading, the pressure release can lead to a transition from the metallic Si-II structure to a nonmetallic low pressure polymorph, accompanied by a sudden volume increase. When peak indentation is increased to 400 mN, lateral cracks and three very short radial cracks emanating along the indentation residual corner are observed. These lateral and radial cracks result in the discontinuities in the load-displacement curves. Recall equation (2-1) in section 2.3, the toughness can be calculated $0.113 \text{ MPa}\cdot\text{m}^{1/2}$ which seems too low and may be due to the effect of brittle silicon substrate (bulk silicon toughness $\sim 0.9 \text{ MPa}\cdot\text{m}^{1/2}$). Further increasing the peak indentation load to 500 mN, delamination and chipping phenomena around the indentation happen, and correspondingly, there is a large step (pop-in event) in the load-displacement curves. Therefore, it is applicable to use the energy approach to calculate the toughness of a-C under different process parameters.

(a) 300mN

(b) 400mN

(c) 500mN

Fig. 5-1 a-C coating's fracture behavior and respective load-displacement curves under different peak indentation load

According to Michel et al. [132], the fracture energy can be estimated by analyzing and subtracting the load-displacement curve of the silicon substrate. In our experiment, indentation has been conducted on the bare Si (100) without any coating. The peak indentation load is selected as 733 mN (the maximal indentation load in load control mode of MTS nanoindentation system). The result is shown in Fig. 5-2. Although there is chipping on the Si surface, no pop-in event can be observed in the load-displacement curve.

It is desirable to know the quantitative relationship between indentation load and depth to predict the Si substrate deformation behavior during indentation process. Hainsworth et al. [150] showed that the loading curve of homogenous samples could be well-described by a linear relationship, $P = k_{\text{cal}} h^2$, between load and displacement squared. k , a constant [150], equals to

$$k_{\text{cal}} = E \left(0.194 \sqrt{\frac{E}{H}} + 0.930 \sqrt{\frac{H}{E}} \right)^{-2} \quad (5-1)$$

The H and E of Si are measured, which are $181.3 \pm 3.3 \text{ GPa}$ and 11.5 GPa , respectively. So k can be calculated to be $1.80 \times 10^{11} \text{ N} \cdot \text{m}^{-2}$ which is a little lower than the value reported in ref. [150]. Therein a higher hardness value (18.0 GPa) is used.

(a)

(b)

Fig. 5-2 (a) load-displacement curves for Si (100) substrate with 733 mN peak indentation load. (b) SEM micrograph of the fracture after indentation

After making 20 indentations, the resulted load-displacement curves are plotted in log-scale to fit these curves (one curve is shown in Fig. 5-3) to obtain k_{exp} . There is a little slope change at the initial state probably possibly due to the surface roughness and indentation size effect. Upon curve fitting, we can get $k_{exp} = (2.100 \pm 0.005) \times 10^{11} \text{ N} \cdot \text{m}^{-2}$. k_{exp} is a little higher than k_{cal} and it may be caused by unideal Berkovich indenter. The following discussion will use k_{exp} instead of k_{cal} .

Fig. 5-3 loading part and fitted curve for indentation for Si (100) substrate with 733 mN peak indentation load. Data points indicate experimental results and solid lines represent the curve fitting results.

Fig. 5-1(c) and Fig. 5-3 are combined and re-plotted in Fig. 5-4. The energy absorbed by Si substrate (U_s) dissipated during elastic and plastic deformation, can be calculated by shifting the curve to the point at the end of the step.

According to Michel et al [132], the fracture energy, U_{fr} is

$$U_{fr} = U - U_s \quad (5-2)$$

where U is the total energy during chipping stage. There is an assumption in the Michel model that the Si deformation behavior will be almost the same whether there is coating or not. This assumption needs further examination and probably needs finite element method to simulate.

Fig. 5-4 Load-displacement curve for a-C coating deposited at 0.6 Pa and -20 V bias. Solid squares correspond to an indentation on Si substrate at the same load shifted to the point at the end of the step

Based on Bound model or Michel model, the fracture energy can be calculated and listed in Table 5-1. It can be seen the fracture energy and corresponding toughness based on Michel model is much lower than those based on Bound model. To our knowledge, currently there is no literature reported for sputtered hydrogen-free a-C. Li et al. [90] used cube corner and conical indenter to measure the toughness of a-

C:H prepared by ion beam method and obtained a toughness of $5.4 \text{ MPa}\cdot\text{m}^{1/2}$ with conical indentation while $4.9 \text{ MPa}\cdot\text{m}^{1/2}$ with cube corner indentation. For cathodic arc tetrahedral amorphous carbon (ta-C) coatings with cube indentation, a much higher toughness of $10.9 \text{ MPa}\cdot\text{m}^{1/2}$ was also measured. However, their calculation of fracture energy was argued by Toonder [151]. Michel et al. [132] measured the toughness of a-C:H deposited by CVD under cube corner indentation. The results showed the toughness values varied from $1.9\sim 3.6 \text{ MPa}\cdot\text{m}^{1/2}$ depending on the substrate bias. Although the magnitudes of such toughness data are diverse, most of them fall into the same order. Later Michal model is confirmed to be consistent for Berkovich and cube corner indentations [152]. To be comparable, the following discussion will only use the Michel model to calculate the toughness.

Table 5-1 Fracture energy and toughness of a-C coatings deposited at 0.6 Pa, bias - 20 V based on bound model and Michel model

Fracture energy U_{fr} (nJ)			K_{IC} ($\text{MPa}\cdot\text{m}^{1/2}$)		
Bound model		Michel model	Bound model		Michel model
Lower limit	Upper limit		Lower limit	Upper limit	
69.18	103.77	17.47	5.76	7.05	2.89

As a first estimation of the toughness, the plasticity is often used. For example, plasticity decreases with increasing bias [76]. But it is found that the plasticity does not agree well with the trend of the toughness of a-C coatings. Based on the fact that a higher sp^3 fraction carbon exhibits the outstanding properties of diamond, Li et al. supposed the possible reason to the higher sp^3 content. However, to the best of

our knowledge, there is no literature discussing the residual stress and sp^3 content effect on the toughness of a-C, mainly due to no standard data available. Essentially, toughness increase can be summarized to increasing the material's ability to absorb energy, as illustrated in Fig. 5-5. Toughness can be considered as the total area under stress-strain axis ABC. Raising yield and/or tensile strength or maximum strain may result in a larger area under curve and hence increase the toughness.

Fig. 5-5 Illustration of stress-strain curve obtained from tensile testing, showing starting point A, yielding point B and break point C [11]

Fyta et al. [153] used tight-binding molecular dynamics simulations to compare the different stress-strain behavior (at temperature 0 K) of amorphous diamond (a-D), nanocrystalline-diamond/a-C nanocomposite (n-C/a-C), ta-C and a-C. The results of tensile stress strain curve are shown in Fig. 5-6. The yield stress and area of ta-C is moderately larger than those of a-C but rather smaller than those of a-D with 100 % sp^3 . Hence the toughest material should possess the highest sp^3 content

although higher sp^2 content is liable to larger plastic deformation. It will be very complex to include defects. Our experimental results are consistent with the simulation.

Fig. 5-6 Simulated tensile stress-strain curve for amorphous carbon and diamond.

The ta-C and n-D/a-C contain 80% sp^3 ; a-C contains 50% sp^3 . Lines are fits to the data points [153]

It is known that residual stress affects the toughness. The coatings under compression present a higher intensity stress factor. Future work will be done by post annealing to study the sp^3 content and residual stress effect on coating toughness.

5.2 CNF Formation Mechanism

Even though various one dimensional material such as nanofibers, nanowires and nanotubes has been recognized for more than ten years and different mechanisms have been proposed, they are still under debate. The growth mechanisms of CNF/CNTs may depend on the synthesis method [154-159].

During ramping and holding at 1100 °C, a-C can diffuse into the Ni nanoparticles to form a solid-solution. Upon saturation, the excess C must precipitate out of the Ni. From phase diagram of bulk Ni-C (Fig. 5-7), the solubility limit of C in Ni can be estimated to be ~ 1.1 at.%. Through catalytic reaction, the precipitated C atoms nucleate on the surface of the catalysts and CNFs start growing from the nuclei. The bulk of the precipitation or CNF growth takes place during the cooling stage where the solubility of C in Ni reduces as temperature is reduced. Tip-growth theory brought forward that metal catalyst particles are floating. The carbon atoms will segregate towards the substrate and thus the catalyst will be lifted up [160]. In root-growth, the tube grows away from the substrate, without lifting the catalyst particles [158]. Tip-growth is favored when the Ni nanoparticles is small (~100 nm or less), and root-growth is dominant when the Ni particle is larger. In current process condition, Ni nanoparticles is kept quite small (only about 50-60 nm or even smaller). Therefore, the tip-growth mode may dominate.

Fig. 5-7 The Ni-C binary phase diagram [161]

When the temperature ramps from room temperature to high temperature, Ni nanoparticle can be formed and carbon atoms from a-C will diffuse into Ni nanoparticles via diffusion. During diffusion process, the carbon atom motion is thermally promoted and therefore the diffusion rate increases with increasing temperature, which explains why annealing temperature significantly affects the CNF growth (c.f. Fig. 5-7).

As prepared CNF coatings are often a mixture of CNFs and impurities like the catalyst and carbonaceous materials. Due to the exceptionally low concentration of the catalyst Ni in these coatings, carbonaceous or a-C impurity is of the major concern. Qualitatively SEM can estimate the purity of CNFs and it is preferred due to ease of use. Although thermo gravimetric analysis (TGA) can easily determine

the catalyst content, it is tedious to provide a-C content [162] and it often requires a large amount of coatings. Recently, the purity of CNT containing a-C has been successfully measured using Raman spectroscopy [163]. The behavior of Raman peak ratio of I_D/I_G versus different known purities of CNT was investigated. A linear relationship between I_D/I_G and CNT purity has been established. Borrowing this idea, we can write the purity of CNF, Y as followed,

$$Y = -k(I_D/I_G) + b \quad (5-3)$$

where k and b are constants.

To determine k and b , it is necessary to know two sets (I_D/I_G , Y). From SEM observation (Fig. 4-11), it has been found there is no any CNF inside the coating annealed at 1100 °C for 15s (Fig. 4-11a). Another extreme case is pure CNT, i.e. no any a-C included, where no defect will be present. In that case, I_D/I_G will be zero. Based on the above conditions, k and b can be estimated as 57.14 and 100. Equation (4-4) can be rewritten as

$$Y = -57.14(I_D/I_G) + 100 \quad (5-4)$$

The estimated CNF purities of the coating versus different annealing time are shown in Fig. 5-8. CNF purity increases as the annealing time increases. The highest CNF purity is about 38 ± 8 % which is obtained upon 180 s annealing time.

Fig. 5-8 CNF purities of CNF:a-C coatings with increasing annealing time

To investigate further the Al_2O_3 barrier layer effect, XRD (Fig. 5-9) and Raman spectra (Fig. 5-10) have been done to obtain detailed information about the microstructure change. Due to their main intrinsic nature, CNF's XRD pattern is close to the one of graphite [162]. Fig. 5-9 shows the graphite peak (002) at $\sim 26.5^\circ$. For the coating grown without any barrier layer, this graphite (002) peak is exceptionally weak while the one with Al_2O_3 barrier layer is a little stronger, indicating higher graphitization when Al_2O_3 barrier layer is used. Raman spectroscopy is one of the most powerful tools to examine CNFs [164]. Fig. 5-10 shows the microstructures of CNF coatings with and without Al_2O_3 barrier layer. The characteristic peaks are present as following: D peak ($\sim 1350\text{ cm}^{-1}$), the G peak ($\sim 1580\text{ cm}^{-1}$) and the G' peak ($\sim 2700\text{ cm}^{-1}$). The D peak indicates the defects in the CNF coating, for example impurities with sp^3 bonding, broken sp^2 bonding at the

sidewalls. The G peak is due to the graphitic nature of the coating and the G' peak is an indicative of long range order of graphite lattice. It is noted that G peak is up shifted compared to that of as deposited a-C, indicating enhanced graphitization [165]. Both coatings have these three characteristic peaks and it means they contain disordered and ordered graphitic structures. The much stronger peak of G' peak for the coating prepared by Al_2O_3 barrier layer further proves that the barrier layer promotes graphitization during annealing [163] and therefore the CNF growth. I_D/I_G is calculated to be 0.96 ± 0.18 and based on equation 4-5 the purity is estimated about $\sim 45 \pm 6\%$ which is higher than that ($38 \pm 8\%$) of the CNF:a-C without Al_2O_3 barrier layer.

Fig. 5-9 XRD patterns for CNF:a-C coatings with and without Al_2O_3 barrier layer

Fig. 5-10 Raman spectra for CNF:a-C coatings with and without Al_2O_3 barrier layer

The possible reason for this enhancement due to the barrier layer may result from the restriction of the interaction between the coating and silicon substrate. Beyond 300 °C, nickel catalyst can diffuse into silicon substrate which will deteriorate the catalytic effect for CNF growth [166, 167]. Besides, silicon may react with carbon to form SiC during annealing process [168]. The formation of SiC will retard the CNF growth by reducing the source of carbon atoms in annealing. Even though for bulk, the reaction between silicon and graphite needs high temperatures (for example above 1500 °C [169]), the temperature for thin films may be much lower. It was found that silicon substrate can react with C_{60} films when the annealing temperature is above 700 °C [170].

5.3 CNF Toughening Mechanism

To study CNF toughening mechanisms, two types of coatings including CNF:a-C and nc-TiC/CNF:a-C are discussed.

For CNF:a-C coatings, Fig. 5-11 shows the fracture surface of CNF:a-C coating after indented at 5 N. The radial cracks are clearly present. Many parts of the crack are bridged. No other toughening mechanisms have been observed for CNF:a-C. The crack bridging is responsible for the toughness improvement.

(a)

(b)

Fig. 5-11 Fracture surface of CNF:a-C after microindentation at a load of 5N at low magnification (a) and high magnification (b)

For nc-TiC/CNF:a-C coatings, fractured surface was examined by FESEM, as illustrated in Fig. 5-12. Without CNF, the crack paths of nc-TiC coating are obviously straight (Fig. 5-12 (a)&(b)). With CNF inclusion (Fig. 5-12 (c)-(e)), however, the fracture paths become much more zigzag when compared at the same magnification. Obviously, the existence of the CNF whiskers helped to deflect the crack propagation (thus costing more fracture energy). It is also observable that the crack of the coating with CNF is as smooth as that in the coating without CNF. At places, CNF-sticking out is also observable. All these contribute to toughness improvement. In this stage, it is not certain which effect is the most significant. The

interface between CNF and nc-TiC crystallite is not clear from the TEM observations. However, it is possible that the bonding between the tube and the nc-TiC crystallites exists. Therefore, the load can be effectively transferred between nc-TiC and CNFs. Similar behaviors were observed for specially designed highly ordered parallel array of 20 and 90 μm amorphous Al_2O_3 /CNF composite thick coatings [65, 69]. In here, the coating thickness is much less than those of Al_2O_3 /CNF composite thick coatings. But the mechanisms underlining the mechanical property improvement after inclusion of *in-situ* CNFs are still due to crack bridging, crack deflection and CNF pullout. Once the load is borne by the CNFs, the required fracture energy is increased when CNFs form a bridge between nc-TiC nanoparticles. When there are CNF pullouts, the interface between nc-TiC and CNF will consume energy which promotes adsorption of fracture energy.

(a)

(b)

Fig. 5-12 FESEM image of the fracture surface of nc-TiC coating C0 (a&b) and C1: nc-TiC/CNF:a-C_{0.05} coating (c-e) at indentation load of 198 N

Although indentations provide insights and direct observations for fracture mechanisms in CNF:a-C and nc-TiC/CNF:a-C coatings, a-C contribution into the toughness should not be ignored. During the discussion of a-C and nc-TiC coatings, it has been found the a-C coatings on silicon substrate have higher toughness values ($2.8\sim 4.9 \text{ MPa}\cdot\text{m}^{1/2}$) than nc-TiC coatings on silicon substrate ($1.19\sim 1.89 \text{ MPa}\cdot\text{m}^{1/2}$). From rule of mixture, it would be possible for nc-TiC/a-C to have higher toughness than nc-TiC. To check whether a-C can lead to such significant toughness enhancement or not, the toughness of unannealed nc-TiC/a-C (un-C1) coating on WC/Co substrate has been measured by the same method for nc-TiC/CNF:a-C. The mechanical properties including hardness, Young's modulus and toughness for un-

C1 coating is shown in Table 5-2. The values of hardness and Young's modulus of nc-TiC/a-C are comparable with each other. But the toughness increases after CNF formation upon annealing are 40 % (from 3.84 to 5.54 MPa·m^{1/2}) and 43% (from 4.25 to 6.09 MPa·m^{1/2}). Since during the annealing process, the compressive residual stress inside the coating can be released and a-C becomes more sp² like, the compressive and a-C contributions for toughness enhancements will be decreased. Therefore, the increase of coating toughness for nc-TiC/a-C can be attributed to CNF formation.

Table 5-2 Mechanical Properties of nc-TiC/a-C (un-C1&2) coating

Coatings	Hardness [GPa]	Young's Modulus [GPa]	Toughness [MPa·m ^{1/2}]
un-C1: nc-TiC/a-C _{0.05}	26.67±3.04	485.35±57.72	3.84±0.35
un-C2: nc-TiC/a-C _{0.10}	24.32±5.18	415.67±34.86	4.25±0.28

5.4 Summary

For indentation method for toughness characterizations, different coatings have to be used based on the crack types. For a-C coatings, indentation induced ring like cracks are often present. The formation of ring like cracks corresponds to the step (pop-in) in the curve of load-displacement curve. Based on Michel model for the calculated energy responsible for coating fracture, a-C coating toughness under different deposition conditions has been characterized and the results show that the sp³ content and residual stress strongly affect the measured values. For CNF:a-C, nc-TiC and nc-TiC/CNF:a-C coatings, there are well defined radial cracks after

microindentation, and therefore the coating toughness can be estimated by linear extrapolation. This method gives a fast estimation for coating toughness and satisfies the purpose of comparison.

CNF can be formed inside nanocomposite coatings via annealing. The morphologies and purity of CNFs are strongly influenced by annealing temperature, time and Al_2O_3 barrier layer. *In-situ* growth of CNFs realized the uniform distribution.

CNFs can enhance the toughness of brittle nc-TiC greatly due to crack bridging, crack deflection and CNF pullout. For CNF:a-C, the dominant toughening mechanism is crack bridging while for nc-TiC/CNF:a-C, all three toughening mechanisms exist.

Chapter 6 Conclusions

Amorphous carbon (a-C), nanocrystalline titanium carbide (nc-TiC), carbon nanotube (CNF), and nc-TiC/CNF:a-C nanocomposite coatings were fabricated by magnetron sputtering and thereafter rapid thermal processing (RTP). Their microstructure, mechanical properties and tribological properties were characterized.

Based on the experimental results obtained, the major conclusions are as follow:

1. Novel *in-situ* grown nc-TiC/CNF:a-C nanocomposite coatings with excellent mechanical properties were synthesized via magnetron sputtering and RTP. CNFs were uniformly distributed with residual a-C. The growth of CNFs showed a promising enhancement: brings 87 % toughness increase, 50 % friction coefficient reduction and 65 % wear rate decrease with a cost of 24 % hardness. Promotion of mechanical and tribological properties was attributed to crack bridging, crack deflection and CNF pullout. This novel CNF based nanocomposite showed great potential for tribological applications.
2. Growth of CNFs via sputtering and RTP was controlled by process parameters and Al₂O₃ barrier layer. Increase of annealing time and temperature allowed more carbon atoms diffuse into nickel catalysts thus result in dense and straight CNFs. Utilization of an Al₂O₃ barrier layer significantly and uniformly distributed CNFs. Through optimization, the purity of CNFs was improved to 45 %.

3. The choice of stress and energy approaches via indentation depended on the type of induced cracks for the measured coating systems. Toughness of a-C coatings was characterized by calculating the fracture energy while that of nc-TiC and nc-TiC/CNF:a-C was estimated by measuring crack lengths and extrapolating method to minimize the substrate effect.
4. The microstructure and mechanical properties of amorphous carbon coatings strongly depended on deposition parameters e.g. substrate bias and deposition temperature. An increase in substrate bias (or decrease in deposition temperature) raised sp^3 content and therefore increased the hardness and toughness but degraded the coating adhesion.
5. The deposition rate and grain size of sputtered nc-TiC films decreased with increase of substrate bias. The TiC films had (111) preferential orientation. All nc-TiC films had a columnar structure but the column became refined at high substrate biases. The hardness, Young's modulus, load capacity and toughness of the TiC films were enhanced by substrate bias but too high substrate bias led to the deterioration of the adhesion strength. The toughness of the TiC films was $1.19\text{-}1.89 \text{ MPa}\cdot\text{m}^{1/2}$, comparable to TiC bulk toughness value. The toughness enhancement was attributed to the compressive stress and restrained columnar growth due to ion bombardment.

Chapter 7 Recommendations

This project has successfully synthesized hard and tough nc-TiC/CNF:a-C nanocomposite coatings through a novel two-step fabrication method including magnetron sputter and RTP. The research findings have shown it is a promising way to toughen brittle ceramic coatings by *in-situ* growth of CNFs. There are still a number of unexplored aspects to gain thorough understanding of CNF toughened hard coatings.

1. Design of microstructure

For bulk applications, the distribution of CNF, the properties of CNF, and the interface between CNF and the matrix have been found out to be key factors for the toughening effect. The CNF distribution, the diameter and length of CNF, and interfacial reaction between CNF and nc-TiC can be controlled by manipulating the sputtering and RTP process parameters. Due to the new birth of CNF/CNF toughened coatings, it lacks detailed studies for this aspect. Other hard phases such as TiN, SiC, AlN and etc can also be used instead of TiC phase. To further promote the growth of CNF, bimetallic catalyst system (for example, Ni-Co, Co-Pt) can be examined.

2. Understanding of CNF toughening mechanisms

Examination on the mechanisms of CNF toughening is of fundamental importance. Although crack bridging, crack deflection and fiber pull-out have been observed for CNF nanocomposite coatings, these three mechanisms are still to be fully studied through theoretical and experimental analysis. Research

on this part can be performed to gain more knowledge about CNF applications in hard coatings.

3. Development of toughness methodology

Currently there are many different toughness-evaluation methods. However, no any standard test procedure or a standalone methodology for the assessment of coating toughness is available. The substrate effect on the crack formation is very difficult to be fully excluded. One possible way is to release the coating from the substrate and then to test the coating without any substrate to obtain the toughness data. Further study should be focused on the experimental and theoretical designs.

4. Practice in field testing

To bring nc-TiC/CNF:a-C nanocomposite coating into industry, further work should be done on field testing, for example, in the application of cutting/drilling tools.

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