Hard yet tough nc-CrAlN/a-SiNx nanocomposite coatings

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**NANYANG
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**HARD YET TOUGH nc-CRALN/a-SiNx
NANOCOMPOSITE COATINGS**

**WANG YUXI
SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING
2013**

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**Hard yet Tough nc-CrAlN/a-SiN_x
Nanocomposite Coatings**

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Table of Contents

Abstract	i
List of Publications	iii
List of Figures	v
List of Tables	xvi
List of Symbols and Abbreviations	xvii
Chapter 1 Introduction.....	1
1.1 Prelude	1
1.2 Objective	2
1.3 Scopes	3
1.4 Major contributions	4
1.5 Organization of the thesis	5
Chapter 2 Literature Review	7
2.1 Nanocomposite coatings	7
2.1.1 Chromium aluminum nitride and its nanocomposite coatings	12
2.1.1.1 CrAlN coatings	12
2.1.1.2 nc-CrAlN/a-SiN _x nanocomposite	22
2.2 Toughness measurement.....	27
2.2.1 Qualitative evaluation	33
2.2.1.1 Indentation plasticity.....	34

2.2.1.2 Scratch toughness	35
2.2.2. Quantitative evaluation	37
2.2.2.1 Stress approach to the coating/substrate system.....	38
2.2.2.2 Energy approach to the coating/substrate system	40
2.2.2.3 Stress approach to the free-standing coatings	46
2.3 Toughening methodology	49
2.3.1 Incorporation of the toughening agent	50
2.3.2 Toughening through architecture modification	56
2.4 Comments on the reviewed literatures	62
Chapter 3 Problem Statement and Proposal	64
Chapter 4 Experimental Details	66
4.1 Overview	66
4.2 Experimental procedure.....	67
4.2.1 Coating preparation.....	67
4.2.1.1 Sputtering system	68
4.2.1.2 Coating deposition	69
4.2.2 Microstructure characterization	75
4.2.2.1 Chemical concentrations.....	75
4.2.2.2 Bonding state.....	78
4.2.2.3 Morphology.....	79
4.2.2.4 Crystalline structure	81
4.2.3 Mechanical properties	83
4.2.3.1 Hardness & Young's modulus	83

4.2.3.2 Toughness.....	87
4.2.3.3 Residual stress.....	92
4.2.3.4 Tribology.....	93
Chapter 5 Effect of Negative Bias Voltage on pc-CrAlN Coatings	94
5.1 Deposition rate	94
5.2 Chemical composition and bonding state.....	95
5.3 Crystalline structure.....	96
5.4 Microstructure.....	101
5.4.1 Cross-sectional morphology	101
5.4.2 Surface roughness.....	104
5.5 Mechanical properties.....	105
5.5.1 Residual stress	106
5.5.2 Hardness and Young's modulus.....	109
5.5.3 Toughness	110
Chapter 6 Influence of Si on nc-CrAlN/a-SiN_x nanocomposite.....	116
6.1 Effect of Si content on the nc-CrAlN/a-SiN _x nanocomposite	116
6.1.1 Deposition rate.....	116
6.1.2 Chemical concentration and bonding state	118
6.1.3 Crystalline structure	120
6.1.4 Microscopic morphology	124
6.1.5 Hardness and toughness.....	127
6.2 Influence of gradient distribution of Si on nc-CrAlN/a-SiN _x nanocomposite	132
6.2.1 Chemical composition and microstructure	132

6.2.2 Mechanical properties	137
Chapter 7 Toughening Effect of Ni on nc-CrAlN/a-SiNx Nanocomposites ..	139
7.1 Chemical concentration	139
7.2 Microstructure	141
7.3 Mechanical properties	148
Chapter 8 Influence of Bilayer Thickness on [pc-CrAlN]/[nc-CrAlN/a-SiNx] Multilayers.....	150
8.1 Chemical composition	150
8.2 Crystalline structure.....	151
8.3 Morphology and microstructure.....	154
8.4 Mechanical properties	158
8.5 Tribological performance	163
Chapter 9 Conclusions and Suggestion for Further Work	167
9.1 Conclusions	167
9.2 Suggestions for further work	170
References.....	172

Abstract

In the past decades, hard or even super-hard ceramic coatings have been vigorously developed to satisfy the various requirements of practical applications in the machining industry. It is increasingly recognized that the enhanced hardness must be complemented by a proper toughness to avoid the catastrophic fracture when the coatings are subjected to an intensive contact force as in harsh conditions. However, results of the recent researches indicate that the increasing toughness is usually accompanied with a large sacrifice of the hardness.

In this project, the state-of-the-art nitride hard coatings (*i.e.* CrAlN) and their nanocomposite variants (*i.e.* nc-CrAlN/a-SiN_x, nc-: nanocrystalline, a-: X-ray amorphous) are fabricated using magnetron sputtering. The effect of the negative bias voltage on the CrAlN and the role of the Si content on the nc-CrAlN/a-SiN_x are studied. The obtained results show that the bias voltage and the Si content are essential factors in determining the coating's microstructure, and thus the mechanical properties. A proper bias voltage is beneficial for achieving a simultaneous improvement of the hardness and toughness since a dense microstructure and higher compressive stress are ready to be obtained. However, the increasing Si content leads only to a drop of toughness although a significant increase of hardness.

To overcome the brittleness of the nc-CrAlN/a-SiN_x nanocomposite, the distribution of the doped Si is varied and the influence of the distribution behavior is investigated. With the homogeneous and heterogeneous grading of Si,

the toughness of brittle nc-CrAlN/a-SiN_x is restored but still at an expense of hardness to different extents. Heterogeneous grading is more effective due to the laminated structure. It is believed that the inner layer with less Si provides the good toughness and adhesion while the outer layer with more Si offers the great resistance to the plastic deformation. On the other hand, a conventional toughening method by adding the ductile phase Ni is also evaluated. The obtained results indicate that with proper concentration of Ni (4.3 at.%), the toughness of the nc-CrAlN/a-SiN_x nanocomposite is improved by 200% at an expense of 18% hardness drop.

Based on the analyses of the above monolayers, a new routine in achieving hard-yet-tough ceramic coatings is proposed. A multilayers consisting of soft-tough CrAlN and hard-brittle nc-CrAlN/a-SiN_x is fabricated. The dependence of the microstructure and mechanical properties on the bilayer thickness is revealed. Detailed studies on the microstructure indicate that the mixture of nanograins with different crystallographic orientations, the complex atomic configuration at the layer interface and the reduced grain size governed by the bilayer thickness are beneficial to achieve the enhanced toughness and high hardness. At bilayer thickness of 20 nm, the optimum toughness of the multilayers is improved by 5 times as compared to the nc-CrAlN/a-SiN_x monolayer. Moreover, the hardness of multilayers also increases, and thus the achievable hard-yet-tough ceramic coatings.

List of Publications

Journal papers

1. Y. X. Wang, S. Zhang, J. W. Lee, W. S. Lew, B. Li, Toughening Effect of Ni Doped nc-CrAlN/a-SiN_x nanocomposites, *Applied Surface Science*, 265 (2013) 418-423
2. Y. X. Wang, S. Zhang, J. W. Lee, W. S. Lew, D. Sun, B. Li, Influence of Bias Voltage on the Hardness and Toughness of CrAlN Coatings via Magnetron Sputtering, *Surface and Coatings Technology*, 206, (2012), 5103-5107
3. Y. X. Wang, S. Zhang, J. W. Lee, W. S. Lew, D. Sun, B. Li, Toward Hard yet Tough CrAlSiN Coatings via Compositional Grading, *Surface and Coatings Technology*, 2012, DOI: 10.1016/j.surfcoat.2012.03.036 (In Press)
4. Y. X. Wang, S. Zhang, J. W. Lee, W. S. Lew, D. Sun, B. Li, Hard Yet Tough Ceramic Coating: Not a Dream Any More—I. Via Nanostructured Multilayering, *Nanoscience and Nanotechnology Letters*, 4, (2012), 375-377
 - Cover article
5. Y. Qiu, S. Zhang, B. Li, Y. Wang, J. W. Lee, F. Li, D. Zhao, Improvement of Tribological Performance of CrN Coating via Multilayering with VN, *Surface and Coatings Technology*, 2012, DOI: 10.1016/j.surfcoat.2012.03.010 (In Press)
6. Y. X. Wang, S. Zhang, J. W. Lee, W. S. Lew, D. Sun, B. Li, Hard Yet Tough Ceramic Coating: Not a Dream Any More—II. Microscopic Studies, *Nanoscience and Nanotechnology Letters*, 2012 (submitted)

Conference papers

1. Y. X. Wang, S. Zhang, J. W. Lee, W. S. Lew, D. Sun, B. Li. Role of Si and Layered Structure in Hard yet Tough Ceramic Coating, *6th International Conference on Technological Advances of Thin Films & Surface Coatings (ThinFilms2012)*, 2012, Singapore
2. Y. X. Wang, S. Zhang, J. W. Lee, W. S. Lew, D. Sun, B. Li. Hard yet Tough Coatings via Magnetron Sputtered Multilayers of Nanocomposite and Polycrystalline Architecture, *39th International Conference on Metallurgical Coatings and Thin Films (ICMCTF)*, 2012, San Diego, USA
3. Y. X. Wang, S. Zhang, J. W. Lee, W. S. Lew, D. Sun, B. Li. Toward Hard yet Tough CrAlSiN coatings via Compositional Grading, *International Thin Films Conference (TACT2011)*, 2011, Taiwan
4. Y. X. Wang, S. Zhang, W. S. Lew, D. Sun. The role of Si in morphology evolution of magnetron sputtered CrAlSiN Thin Films, *12th International Conference in Asia (IUMRS-ICA)*, 2011, Taiwan
5. Y. X. Wang, S. Zhang, H. L. Wang. Toughness Evaluation of nc-TiC/a-C (Ni) through Nanoindentation with Energy Approach, *5th International Conference on Technological Advances of Thin Films & Surface Coatings (ThinFilms2010)*, 2010, Harbin, China

List of Figures

Figure 1. 1 Classification of nanocomposites according to their hardness and toughness (revised from ref. ¹)	2
Figure 2. 1 A schematic representative of the crystal atoms (solid black) and boundary atoms (open circle) ¹¹	8
Figure 2. 2 Schematic representation of material hardness as a function of grain size d ⁷	9
Figure 2. 3 Hardness of nc-TiN/a-Si ₃ N ₄ as a function of silicon nitride volume fraction (insets show the schematic nanostructure of different compositions) ¹ .10	
Figure 2. 4 Structural organization of the nanocomposites with different hardness: (a) columnar, (b) nanograins embedded in a matrix with larger dispersed separation (c) nanograins embedded in a matrix with compact separation ⁷	11
Figure 2. 5 Dependence of hardness of nc-TiN nanocomposite on the Si content (a) fabricated by PCVD and (b) fabricated by reactive sputtering ⁷	11
Figure 2. 6 Structure zone diagram proposed by (a) Movchan-Demchishin ¹³ (b) Thornton ¹⁴ (c) Messier ¹⁵ and (d) Grovenor ¹⁶	15
Figure 2. 7 Hardness (•) and Young's modulus (⊙) of the as-deposited CrAlN coatings as a function of Al/Cr atomic ratio ²⁸	17
Figure 2. 8 (a) XRD spectra of various CrAlN coatings ($0 < x < 1$); (b) Lattice parameter of various CrAlN coatings ($0 < x < 1$) ²²	17
Figure 2. 9 Hardness as a function of different working pressures during CrAlN deposition ³⁵	19

Figure 2. 10 XRD diffraction patterns of CrAlN prepared at different negative substrate bias voltages (Dashed lines stand for cubic CrN peak position and peaks labeled “s” corresponds to substrate) ¹⁹	20
Figure 2. 11 SEM micrographs of impact scar of CrAlN coatings at different bias voltage of (A) 0 V (B) 80 V (C) 120 V ³⁷	21
Figure 2. 12 High resolution TEM lattice images of CrAlN fabricated at ion energy of (a) 122 eV and (c) 188 eV, (b) and (d) are the FFT filtered image of (a) and (c), respectively ³³	22
Figure 2. 13 Electron diffraction patterns and TEM images in plane-view geometry for (a), (b) (Cr _{0.3} Al _{0.7})N and (c), (d) (Cr _{0.25} Al _{0.7} Si _{0.05})N, respectively ³⁸	24
Figure 2. 14 Dependence of (a) the stress-free lattice parameters and (b) crystallite size on the chemical composition of the CrAlN (•) and CrAlSiN (■) coatings ³¹	24
Figure 2. 15 Dark-field TEM images of (a) Cr ₃₃ Al ₁₇ N ₅₀ (b) Cr _{31.7} Al _{9.2} Si _{8.7} N _{49.6} ⁴²	25
Figure 2. 16 Surface oxygen concentration of CrAlSi _x N coatings with different Si contents at (a) various heat-treatment temperature (b) various heat-treatment period ^{46, 47}	27
Figure 2. 17 The Kitagawa-Takahashi curve ³⁹	29
Figure 2. 18 Idealization of unloaded region near crack flanks.....	30
Figure 2. 19 Schematic plot of a nanoindentation load-displacement curve ⁵⁴	34
Figure 2. 20 Surface cracks generated in a scratch test track can be classified as (a) angular cracks, (b) parallel cracks, (c) transverse semicircular cracks, (d) coating chipping, (e) coating spalling and (f) coating breakthrough ⁵⁸	36
Figure 2. 21 Typical scratch adhesion profile of nc-TiN/a-SiN _x coatings deposited on Si wafer with lower and higher critical load labeled ⁵¹	37

Figure 2. 22 Irreversibly dissipated energy W_{irr} as a function of the applied load ⁶⁷	41
Figure 2. 23 Schematic of three stages in nanoindentation fracture in a coating/substrate system ⁶⁸	42
Figure 2. 24 Schematic of a load-displacement curve, showing a step during the loading cycle and associated energy release ⁶⁸	43
Figure 2. 25 Schematic illustration of the boundaries of dissipation energy at the plateau in the indentation curve ⁶⁹	44
Figure 2. 26 Schematic drawing representing load-unloading curve of nanoindentation in a film after chipping, the area of ABH represents for the dissipation energy due to the cracking	44
Figure 2. 27 Schematic illustration of load-extension curve obtained using the two-step uniaxial tensile test (energy difference can be determined from the area differences $S_{OABCDE}-S_{ODEO}$) ⁷²	46
Figure 2. 28 Schematic representation of the three general microfabrication steps used to process the specimens ⁷⁴	47
Figure 2. 29 An optical image of a freestanding coating with both ends attached to a wafer ⁷⁴	48
Figure 2. 30 Schematic representation of the testing configuration ⁷⁵	49
Figure 2. 31 Schematic diagram of ductile phase toughening: (1) ductile phase deformation, and (2) crack bridging ⁷⁶	52
Figure 2. 32 Optical image of scratch tracks on: (a) nc-TiC/a-C and (b) nc-TiC/a-C(Al) coatings ⁸¹	52
Figure 2. 33 SEM images of (a) SWNT network encompassing some of the alumina grains (SWNT 5.7 vol.%) (b) tangled rope network of SWNT ⁸⁴	54

Figure 2. 34 Low- and high- magnification SEM micrographs showing top views of Vickers indentation sites: classical radial cracks can be seen in (a) the dense Al_2O_3 and (b) the porous Al_2O_3 ; no evidence of classical radial cracks in (a) the SWNT/ Al_2O_3 composite or (d) the graphite/ Al_2O_3 composite ⁸⁵	54
Figure 2. 35 (a) SEM micrograph of as-fabricated CNT/ceramic composite viewed from the top, showing high degree of hexagonal order (b) Crack deflection around the CNTs along the interface (c) Crack bridging the gap between the crack surfaces (d) CNTs pulling out with longitudinal delamination and residual holes ⁸⁶	55
Figure 2. 36 Basic ideas for the development of gradient coatings ⁸⁷	56
Figure 2. 37 (a) Hardness of graded DLC coatings (b) scratch adhesion strength of the non-hydrogenated DLCs deposited under various constant bias voltage or bias-graded conditions ⁵⁵	57
Figure 2. 38 Toughening mechanism in ceramic multilayer materials ⁹⁵	58
Figure 2. 39 Surface view of the indentation with a load of 20 N showing dependence of edge cracking on layer spacing: (a) monolayer TiN (b) multilayer TiN/TiAlN with bilayer thickness of 650 nm (c) multilayer TiN/TiAlN with bilayer thickness of 130 nm ⁹⁶	59
Figure 2. 40 Cross-sectional images of the indentation under 5 N showing inclined shear cracks: (a) monolayer TiN (b) multilayer TiN/TiAlN with bilayer thickness of 650 nm (c) multilayer TiN/TiAlN with bilayer thickness of 130 nm ⁹⁶	59
Figure 2. 41 Scratch channels (a) and (b) and indent marks (c) and (d) of monolayer $(\text{Ti}_{0.5}\text{Al}_{0.5})\text{N}$ and TiN/ $(\text{Ti}_{0.5}\text{Al}_{0.5})\text{N}$ multilayer coatings using ⁹⁷	60

Figure 2. 42 Variation of hardness, critical load for cracking and fracture toughness for a number of coatings: 1. TiN; 2. TiCN, 3. TiAlN, 4. TiAlN(M), 5. TiAlSiN(M), 6. TiAlCN ⁹⁸	61
Figure 2. 43 Cross-section TEM micrograph showed the propagation of nanocracks in nc-TiAlN/a-Si ₃ N ₄ nanolaminate coatings with $\Lambda=20\text{nm}$ ¹⁰⁵	62
Figure 3. 1 Schematic of the novel multilayers, where one layer is soft-tough nitride coating and one layer is the hard-brittle nanocomposite formed from the soft one.....	65
Figure 4. 1 Methodological overview.....	67
Figure 4. 2 Overview of the sputtering system	69
Figure 4. 3 SUS420C and Si wafer square used in experiments.....	70
Figure 4. 4 Schematic of nc-CrAlN/a-SiN _x with gradient Si distribution	73
Figure 4. 5 Schematic of the multilayer structure	74
Figure 4. 6 TEM cross-sectional sample preparation	81
Figure 4. 7 William-Hall plot of CrAlN coating prepared at bias voltage of 160 V ⁸³	
Figure 4. 8 (a) Schematic representation from a cross-section through an indentation, showing the maximum indentation depth h_{max} , contact depth h_c , minimum indentation depth h_{min} and sinking-in condition (b) Schematic representation of a typical load versus indent displacement for an indentation experiment.....	87
Figure 4. 9 Characteristic radial traces of the cracks left on the specimen surface after unloading (a) Vickers indent impression (b) Cubic-corner or Berkovich indent impression.....	88

Figure 4. 10 Schematic representation of coating failure modes in the scratch test in profile and plan views: (a) spalling failure (b) buckling failure (c) chipping failure (d) conformal cracking (e) tensile cracking ¹²⁰	90
Figure 4. 11 (a) Schematic of the scratch test (b) experiment layout of the scratch tester.....	91
Figure 4. 12 A typical scratch profile with information of normal load, acoustic emission signal and friction force.....	92
Figure 4. 13 Equipment layout for a ball-on-disk tester, where F is the normal force applied to the ball, r is the ball diameter, R is the radius of the wear and w is the rotational speed of the disc.....	93
Figure 5. 1 Deposition rate of CrAlN at different value of the negative bias voltage	95
Figure 5. 2 XPS core-level spectra of (a) Cr 2p (b) N 1s (c) Al 2p	97
Figure 5. 3 GAXRD results of CrAlN coatings at different bias voltage	98
Figure 5. 4 Referenced diffraction patterns of (a) fcc-CrN powder and (b) hcp-AlN powder.....	98
Figure 5. 5 Calculated grain size and microstrain of CrAlN coatings at different bias voltage	99
Figure 5. 6 Cross-sectional morphology at different bias voltage (a) 50 V (b) 160 V (c) 210 V (d) 260 V	102
Figure 5. 7 Barna structure zone diagrams ¹⁷	103
Figure 5. 8 TEM image of CrAlN coatings prepared at bias voltage of (a) 50 V (b) 160 V (c) 260 V.....	103
Figure 5. 9 SAD image of CrAlN coatings prepared at $V_b=160$ V	104
Figure 5. 10 Surface topography of CrAlN prepared at the different V_b	105

Figure 5. 11 Residual stress of CrAlN coatings as a function of bias voltage	107
Figure 5. 12 Hardness and Young's modulus of CrAlN coatings at different negative bias voltage	110
Figure 5. 13 Hardness as a function of grain size.....	110
Figure 5. 14 Indent marks (Berkovich indenter) on the CrAlN fabricated at $V_b=160$ V under indent force of (a) 700 mN (b) 250 mN.....	111
Figure 5. 15 Plot of calculated toughness of CrAlN coated onto a Si substrate prepared as a function of indent depth	112
Figure 5. 16 (a) Lower and (b) higher critical load of CrAlN coatings as a function of the loading rate.....	114
Figure 5. 17 Scratch tracks of CrAlN with different negative bias voltage (black arrow: L_{c1} ; white arrow: L_{c2})	115
Figure 5. 18 Crack propagation resistance and indentation toughness as a function of negative bias voltage.....	115
Figure 6. 1 Deposition rate as a function of power density on the Si target	117
Figure 6. 2 XPS core level of (a) Cr 2p (b) N 1s (c) Si 2p and (d) Al 2p in CrAlSiN-4	119
Figure 6. 3 Evaluation of the Si narrow scan as a function of Si content	120
Figure 6. 4 GAXRD pattern of CrAlSiN with varied Si content.....	122
Figure 6. 5 Grain size of Si doped CrAlN as function of Si content.....	122
Figure 6. 6 Lattice parameter and residual stress as a function of Si content	123
Figure 6. 7 Cross-sectional images of CrAlN (a) and CrAlSiN with different Si content (b) 0.4 at.% (c) 1.8 at.% (d) 5.9 at.% (e) 8.5 at.%	124
Figure 6. 8 High-resolution TEM image of CrAlSiN coatings with Si content of 8.5 at.%, inset is the corresponding SAD pattern.....	125

Figure 6. 9 Evaluation of the surface topography of CrAlSiN for different Si content (at.%) (a) 0.4 (b) 1.8 (c) 5.9 and (d) 8.5	126
Figure 6. 10 Hardness and Young's modulus as a function of Si content	128
Figure 6. 11 H^3/E^2 ratio as a function of Si content.....	129
Figure 6. 12 Brittle fracture of CrAlSiN-4 at indent force of 400 mN (a) fracture of the intent array (b) close up of the intent neighborhood.....	130
Figure 6. 13 Optical observation of micro-scratch test of CrAlSiN coating with different Si contents on SUS420 substrates (black arrow: L_{c1} , white arrow: L_{c2})	130
Figure 6. 14 Fracture behavior at the emergence of spallation of CrAlSiN with different Si content.....	131
Figure 6. 15 Plot of hardness versus CPR_s depending on Si content in CrAlSiN coatings.....	132
Figure 6. 16 Cross-sectional morphology of CrAlSiN with (a) homogeneously and (b) Heterogeneously gradient Si	134
Figure 6. 17 GDOES results of CrAlSiN with gradient Si distribution (a) CrAlSiN-GL (b) CrAlSiN-GH	135
Figure 6. 18 High-resolution TEM image of the upper part in CrAlSiN-GL.....	136
Figure 6. 19 TEM image (a) and selected area diffraction patterns (b) of the bottom layer	136
Figure 6. 20 TEM image (a) and selected area diffraction patterns (b) of the intermediate layer	137
Figure 6. 21 TEM image (a) and selected area diffraction patterns (b) of the top layer	137

Figure 6. 22 Hardness versus CPR_s of homogeneous CrAlSiN coatings with different Si and graded CrAlSiN coatings.....	138
Figure 7. 1 Al/Cr ratio of Ni-doped nanocomposite nc-CrAlN/a-SiN _x	140
Figure 7. 2 Si/(Cr+Al) ratio of Ni-doped nanocomposite CrAlSiN as a function of Ni content	140
Figure 7. 3 GAXRD pattern of Ni-doped nc-CrAlN/a-SiN _x as a function of Ni content.....	142
Figure 7. 4 Average grain size of Ni-doped nc-CrAlN/a-SiN _x as a function of Ni content.....	143
Figure 7. 5 XPS narrow scan of CrAlSiN with 12.0 at.% Ni: (a) Cr 2p (b) N 1s (c) Si 2p (d) Ni 2p and (e) Al 2p.....	144
Figure 7. 6 Tendency of the Al 2p and Ni 3p intensities as a function of the Ni content.....	145
Figure 7. 7 TEM image of Ni-doped nanocomposite CrAlSiN (Ni-12.2 at.%) (a) grain size around 3 nm imbedded in amorphous phase (b) selected area diffraction pattern	146
Figure 7. 8 SEM cross-sectional image of Ni-doped nanocomposite CrAlSiN as a function of Ni content.....	147
Figure 7. 9 Surface morphology of Ni-doped nanocomposite CrAlSiN coatings with varying Ni addition	147
Figure 7. 10 Hardeness and Young's modulus of Ni doped nanocomposite CrAlSiN coatings with varying Ni addition.....	148
Figure 7. 11 Hardness versus "toughness" (scratch crack propagation resistance) of the nanocomposites.....	149

Figure 8. 1 XRD patterns of monolayers and multilayers with different bilayer thickness	152
Figure 8. 2 Lattice parameter of multilayers as a function of period thickness ..	153
Figure 8. 3 The dependence of residual stress on the bilayer thickness of multilayers	153
Figure 8. 4 Grain size of multilayers as a function of the period thickness	154
Figure 8. 5 Cross-sectional images (BEI mode) of the multilayer coatings with varying period thickness: (a) 10 nm (b) 20 nm (c) 40 nm and (d) 60 nm	155
Figure 8. 6 TEM image of the cross-section of the multilayer coating with period thickness of 20 nm	155
Figure 8. 7 (a) HRTEM image of the multilayer coating with period thickness of 20 nm, (b) an enlarged interface at the white arrows in (a), (c) HRTEM image of the nanocomposite (<i>i.e.</i> nc-CrAlN in a-SiN _x) sub-layer and (d) the schematic representative of the sandwich structure	156
Figure 8. 8 Surface morphology of pc-CrAlN monolayer, nanocomposite monolayer and multilayers with varying period thickness	157
Figure 8. 9 (a) Hardness and (b) Young's modulus of the pc-CrAlN monolayer, nanocomposite monolayer and multilayers with varying period thickness	158
Figure 8. 10 Hardness as a function of grain size	160
Figure 8. 11 Optical observation of the micro-scratched morphology of the coatings on SUS420C substrates (black arrow: L_{c1} , white arrow: L_{c2})	161
Figure 8. 12 Optical observation at the emergence of spallation (at onset of L_{c2})	161
Figure 8. 13 Plot of hardness versus scratch toughness	162

Figure 8. 14 SEI (a)-(d) and BEI (e)-(h) observation of the wear tracks in multilayers.....	164
Figure 8. 15 Coefficient of friction of pc-CrAlN, nanocomposite monolayer and multilayer	165
Figure 8. 16 Schematic illustration of proposed wear model of monolayered (left) and nanometer scale multilayered (right) coatings ¹⁶³	166

List of Tables

Table 2. 1 Mechanical properties of CNTs as compared to those of the tradition materials ⁸²	53
Table 4. 1 Deposition parameters in fabricating CrAlN coatings	71
Table 4. 2 Deposition parameters in fabricating nc-CrAlN/a-SiN _x coatings.....	72
Table 4. 3 Deposition parameters used in fabricating nc-CrAlN/a-SiN _x nanocomposite with gradient Si content.....	73
Table 4. 4 Deposition parameters in fabricating Ni doped nc-CrAlN/a-SiN _x nanocomposite.....	74
Table 4. 5 Deposition parameters in fabricating multilayers	75
Table 5. 1 Summary of the chemical concentrations of as-deposited coatings determined by EPMA.....	96
Table 5. 2 Calculated CTE and thermal stress	108
Table 5. 3 Linear fitting of the toughness at different indentation depth	113
Table 6. 1 Summary of chemical concentration of as-deposited coatings.....	118
Table 7. 1 Chemical concentration of Ni-doped CrAlSiN nanocomposite.....	139
Table 8. 1 Summary of chemical concentration of monolayers and multilayers.....	151

List of Symbols and Abbreviations

Symbols

a	Lattice Constant
	Crack Length
	Flaw Size
a_{exp}	Experimentally Calculated Lattice Parameter
a_0	True Value of Lattice Constant
a-	Amorphous
a-C	Amorphous Carbon
d	Grain Size
d_{hkl}	Interplanar Spacing with Crystal Plane Indices
d_c	Critical Grain Size of Nanocomposites
h	Displacements of Indentation
h_f	Coating Thickness
m	Taylor coefficient of Koehler's model
nc-	Nanocrystalline
pc-	Polycrystalline
t	Coating Thickness
t_c	Coating Thickness
t_s	Substrate Thickness
A	Projected Area of Contact in Indentation Test
	Absorption Correction
	Crack Area

C	Mass Concentration of the Detected Element
C_d	Diameter of the Delamination Crack that Initiated the Chip
C_R	Radius of Circular Crack
D	Average Grain Size
E	Young's Modulus of Specimen or Coating
E_c	Young's Modulus of Coating
E_{eff}	Effective Young's Modulus
E_i	Young's Modulus of Indenter
E_s	Young's Modulus of Substrate
F	Fluorescence Correction
F_b	Backscattering Factor
F_s	Electron-stopping Power Factor
H	Hardness
H_{max}	Maximum Hardness
K_{IC}	Fracture Toughness
OA	Plastic Deformation associated with Plastic Strain
OB	Total Displacement under the Normal Force
W	Width of Specimen
	Width of Crack Mouth
	Work done by External Loads
P	Applied Indentation Load
N	Number of Chipped Areas
R_1	Curvature Radius of Substrate Before Deposition
R_2	Curvature Radius of Substrate After Deposition
S	Contact Stiffness

T_1	Temperature of Depositing Specimen
T_2	Temperature of Taking Out Specimen
T_h	Film Growth Temperature Normalized by Melting Temperature of Deposited Film Material
T_m	Substrate Temperature
T_s	Melting Temperature of Material
U	Elastic Energy stored in the System
U_{pl}	Energy Dissipated of Plastic Deformation
U_{fr}	Energy Dissipated of Coating Fracture or Chipping
V	Volume
V_b	Negative Bias Voltage
W_{irr}	Total Dissipated Energy
Y	Dimensionless Parameter depending on both the Specimen and Crack Geometry
Z	Atomic Number Correction
α_s	Coefficient of Thermal Expansion of Substrate
α_c	Coefficient of Thermal Expansion of Coating
β_i	Integral Breadth (in radians, 2θ) of the i th Bragg Reflection Positioned at $2\theta_i$
θ	Bragg Angle
δ	Empirical Constant depending on the Geometry of Indenter
ε	Strain
ε_f	Strain upon Failure
σ	Stress

σ_y	Yield Stress
σ_T	Thermal Stress
σ_g	Coating Growth Induced Stress
σ_m	Structure Mismatch Induced Stress
λ	Wavelength of X-ray
ν	Poisson's Ratio of Specimen
ν_c	Poisson's Ratio of Coating
ν_i	Poisson's Ratio of Indenter
ν_s	Poisson's Ratio of Substrate
ΔU	Strain Energy Difference before and after Cracking
Λ	Bilayer Thickness

Abbreviations

sccm	Standard Cubic Centimeter per Minute
BEI	Back-scattered Electron Image
CPR _s	Scratch Propagation Resistance
DC	Direct Current
EPMA	Electron Probe Micro-Analyzer
EDS	Electron Dispersive X-ray Spectroscopy
FCC	Face-Centered Cubic
FESEM	Field Emission Scanning Electron Microscope
FIB	Focused Ion Beam
GDOES	Glow Discharge Optical Emission Spectroscopy
GAXRD	Glancing Angle X-Ray Diffraction
HRTEM	High Resolution Transmission Electron Microscope

LEFM	Linear Elastic Fracture Mechanics
MDP	Microhardness Dissipation Parameter
MWNT	Multi-Wall Nanotube
PCVD	Plasma Chemical Vapor Deposition
RF	Radio Frequency
SEI	Secondary Electrons Image
RH	Relative Humidity
SZD	Structure Zone Diagram
SWNT	Single-Wall Nanotube
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscope
WDS	Wavelength Dispersive X-ray Spectroscopy
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

Chapter 1

Introduction

1.1 Prelude

The early example of controlling the properties of materials by merging their advantages can be tracked back to 1500 B.C., when early Egyptians and Mesopotamian settlers used a mixture of mud and straw to create strong and durable materials for buildings. In the early bronze-age, the ongoing development of materials by adding suitable elements leads to the emergence of alloys, largely improving the performance of bulk materials and greatly upgrading the productivity in the ancient times. Nowadays, integrating materials merits into a composite remains important, with current interest on size downsizing to micro- or even nano-scale.

Nanocomposite is the consequence of extending this approach to the nano-scale. Surface engineering makes use of this advance to fulfill the ever-changing demands in practical industrial applications. Generally, a nanocomposite coating comprises at least two phases: a nanocrystalline phase and an amorphous phase, or two nanocrystalline phases. With this combination, coating's mechanical properties do not obey the volume mixture rule but rely on the synergetic interactions of the constituents whilst obeying the size effect. Hard (>20 GPa) and super-hard (>40 GPa) nanocomposites with superior ability to resist deformation and wear were obtained and intensively studied in the past decades.

For engineering applications, hardness must be complemented with toughness. Usually, however, these two properties of equal importance do not go hand-in-hand. Figure 1. 1 demonstrates the challenge of synthesizing hard coatings. As shown in the image, materials with great hardness, for example the widely used machining coating TiC and TiN, multilayers TiN/VN and TiN/NbN, and nanocomposite are usually accompanied by a low toughness. While improved toughness, for example nanocomposites with soft metal matrix, leads to the reduced hardness. In this regard, toughening hard coating so that high hardness and high toughness can integrate in one unity is much desired (as shown in the dash circle in the top-right corner in Figure 1. 1).

Figure 1. 1 Classification of nanocomposites according to their hardness and toughness (revised from ref. ¹)

1.2 Objective

The objective of this project is to develop ways of toughening the hard-brittle nc-CrAlN/a-SiN_x nanocomposite with little or even no sacrifice of hardness, realizing a hard-yet-tough ceramic coating. Approaches based on the microstructural

modification, *e.g.* doping a ductile phase, changing the elemental distribution throughout the coating thickness and tailoring coating architecture, will be proposed and assessed.

1.3 Scopes

To achieve the toughened nc-CrAlN/a-SiN_x nanocomposites, this project mainly covers the following work:

- 1) Understanding the influence of the parameters of deposition via magnetron sputtering on the polycrystalline CrAlN coatings (pc-CrAlN)
Deposition parameters such as negative bias voltage are manipulated to optimize the mechanical properties. The analysis on the microstructure, hardness and toughness variation will be conducted.
- 2) Exploring the role of Si in the nc-CrAlN/a-SiN_x nanocomposites
Incorporating Si allows synthesizing hard nc-CrAlN/a-SiN_x nanocomposites. The influence of Si content on the coatings' microstructure and mechanical properties was investigated.
- 3) Determining the toughening effect of grading Si in the nc-CrAlN/a-SiN_x nanocomposites
CrAlSiN coatings with homogeneously and heterogeneously graded Si are fabricated. The influence of the Si distribution on the microstructure and mechanical properties is revealed.
- 4) Studying the toughening effect of Ni on the nc-CrAlN/a-SiN_x nanocomposites

Ni is doped as a ductile phase to verify its toughening effect on the nanocomposite. With different Ni content, the change on the microstructure and mechanical properties are investigated in detail.

- 5) Optimizing bilayer thickness in multilayers [pc-CrAlN]/[nc-CrAlN/a-SiN_x] to achieve hard-yet-tough coatings.

A [pc-CrAlN]/[nc-CrAlN/a-SiN_x] multilayer will be presented. The effect of the bilayer thickness on the microstructure and mechanical properties is presented and analyzed. The reinforcing mechanisms in hardening and toughening are investigated.

1.4 Major contributions

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

- The effects of substrate bias voltage on the microstructure, hardness and toughness of the monolayer pc-CrAlN have been revealed.
- The influence of Si content on the morphology, hardness and toughness of the monolayer nc-CrAlN/a-SiN_x nanocomposite has been presented.
- The influence of gradient Si on the microstructure and mechanical properties of the gradient CrAlSiN nanocomposite has been evaluated.
- The influence of Ni content on the microstructure and mechanical properties of the Ni doped nc-CrAlN/a-SiN_x nanocomposite has been analyzed.

- A novel toughening method by combining soft-tough layer of pc-CrAlN and hard-brittle nc-CrAlN/a-SiN_x nanocomposite to form multilayers is developed. The [pc-CrAlN]/[nc-CrAlN/a-SiN_x] multilayers show the improved scratch toughness by 5 to 7 fold as compared to the monolayer nc-CrAlN/a-SiN_x nanocomposite. And at the same time, the multilayers possesses high hardness as much as 30 GPa. In addition, multilayer coatings present better tribological performance than monolayer nanocomposite, indicating a great potential in the practical applications.

1.5 Organization of the thesis

- Chapter 1: A brief introductions of the background and the motivation of this research are presented.
- Chapter 2: A literature review on the current status of hard nanocomposite, toughening methodologies and the metrological solutions for measuring coating toughness is given.
- Chapter 3: Current challenges in toughening hard ceramic coatings are identified and a possible solution is proposed.
- Chapter 4: Procedures and methods of conducting the various experiments are described in detail.
- Chapter 5: The effect of the negative bias voltage on the CrAlN is revealed.
- Chapter 6: The influence of the Si content and distribution on the nc-CrAlN/a-SiN_x is presented.
- Chapter 7: The influence of Ni content on the microstructure and mechanical properties of the nc-CrAlN/a-SiN_x is analysed.

Chapter 8: The dependence of the microstructure and mechanical prosperities of [pc-CrAlN]/[nc-CrAlN/a-SiN_x] multilayers on the bilayer thickness is determined.

Chapter 9: Conclusions and the remarks on the future studies are given.

Chapter 2

Literature Review

2.1 Nanocomposite coatings

The emergence of the nanocomposite, which comprises at least two immiscible phases (*i.e.* nanocrystalline and/or amorphous, or their combination), has led to tremendous developments in synthesizing a new generation of hard ($H \geq 20$ GPa) or even super-hard coatings ($H \geq 40$ GPa) ². It should be noted that the existence of ultra-hard coatings ($H \geq 80$ GPa) is still a subject of considerable debate^{3,4}. In the pioneer work on the ternary nitride coating system (*i.e.* nc-TiN/a-SiN_x), the maximum hardness of around 50 GPa was achieved ⁵, significantly exceeding the value given by the rule of mixtures. Following this work, many nitride- and carbide-based nanocomposites coatings were produced. Typical examples included nc-CrN/a-SiN_x, TiC/a-C, WC/a-C, to name but a few ⁶. In these nanocomposites, the hardness was found to be largely determined by the interactions of the composite constituents owing to the size effect and grain boundary effect ¹. A schematic representative of the crystal atoms and boundary atoms is shown in Figure 2. 1. The crystal atoms are those with neighbor configuration corresponding to the lattice. The boundary atoms are those with a wide variety of interatomic spacing. In the boundary regions, the coordination between nearest neighbor atoms deviates or reduces from the one in the crystallites. Figure 2. 2 illustrates the dependence of hardness on a given grain size (d) range in the polycrystalline materials ⁷. As indicated, there is a critical

characteristic size of nanocrystallites, *i.e.* $d_c=10$ nm, at which maximum hardness could be achieved. When $d>d_c$, the strength of materials is dominated and described by the well-known Hall-Petch relation ⁸⁻¹⁰, *i.e.* $H \propto d^{-1/2}$. The Hall-Petch effect in these coarse-grained materials is attributed to the grain boundaries acting as efficient obstacles to dislocations nucleated. Consequently, a dislocation pileup can be formed against a grain boundary inside a grain. When $d<d_c$, dislocation pileups inside the grains can hardly exist and processes in grain boundary regions play a dominant role in determining the physical and mechanical properties of the coatings. It is widely accepted that the local sliding along grain boundaries, together with the creep diffusion and impurity, leads to the abnormal “inverse Hall-Petch” relationship ¹. Under this condition, the strength decreases as the grain size reduces. Based on a number of experimental tests and simulation work as reviewed in a great length in Ref. ¹¹, the softening occurs via the inter-granular slips since the inter-granular boundaries cease to be the barriers for the motion of dislocation. In this regard, it is realized that a second phase should be incorporated to impede the softening to further strengthen the materials when $d<d_c$.

Figure 2. 1 A schematic representative of the crystal atoms (solid black) and boundary atoms (open circle) ¹¹

Figure 2. 2 Schematic representation of material hardness as a function of grain size d ⁷

In the most investigated Ti-Si-N coating system, the segregated α - Si_3N_4 reinforced the grain boundaries which can lead to a tremendous increase in hardness ⁵. An example of the hardness on the dependence of the Si content is shown in Figure 2. 3, where the fraction of segregated α - Si_3N_4 governed the grain size and thus determined the strength of the coatings ^{1,12}. Without Si, TiN microstructure was dominated by columnar crystallites several hundreds of nanometers in length and tens of nanometers in width. The reduced grain size of TiN in consequence of the increased α - Si_3N_4 led to the hardness increase accordingly. It should be pointed out that when Si was in the range of 15-20 at.%, the mean grain size of TiN was less than 10 nm. But the strength did not degrade owing to a few monolayered α - Si_3N_4 , which stopped the grain boundary sliding and thus the further increased strength. However, the decrease of hardness when Si was further added was attributed to the fact that the mean grain separation (*i.e.* grain boundary de-cohesion) among TiN crystallites became sufficiently wide. At this

condition, the $\alpha\text{-SiN}_x$ no longer served as reinforcement but a weak region where the cracks could possibly propagate inside.

Figure 2. 3 Hardness of nc-TiN/a-Si₃N₄ as a function of silicon nitride volume fraction (insets show the schematic nanostructure of different compositions) ¹

The above results infer another important fact in the reinforcing mechanisms besides the chemical and electronic bonding between atoms: the nano-structure of materials. Figure 2. 4 illustrates such correlation by associating with the three different types of structural organizations:

- (1) Inferior hardness: nanocomposite composed of grains assembled in columnar structures (Figure 2. 4(a)).
- (2) Inferior hardness: nanocomposites with compact globular structure comprising nano-grains completely enclosed in a matrix material with greatly-dispersed separation (*i.e.* nano-grains disperse widely as separated by the matrix) (Figure 2. 4(b)).
- (3) Superior hardness: nanocomposites with compact globular structure of nano-grains completely enclosed in a matrix material with compact

separation (*i.e.* nano-grains dispersed in a close distance as separated by the matrix) (Figure 2. 4(c))

This correlation was verified by a number of researches in recent years, in terms of Si reinforced MeN nanocomposites (Me=Ti, W and V). Results upon different Si content are shown in Figure 2. 5 ⁷. In all these coatings, the maximum hardness was obtained when Si content was around 10 at.%.

Figure 2. 4 Structural organization of the nanocomposites with different hardness: (a) columnar, (b) nanograins embedded in a matrix with larger dispersed separation (c) nanograins embedded in a matrix with compact separation ⁷

Figure 2. 5 Dependence of hardness of nc-TiN nanocomposite on the Si content (a) fabricated by PCVD and (b) fabricated by reactive sputtering ⁷

2.1.1 Chromium aluminum nitride and its nanocomposite coatings

From the previous studies, it has been realized that achieving enhanced hardness of the nanocomposites is the result of the change in the geometry of crystallites, content of individual phases and particularly a dramatic reduction of the grain size d . Recently, this attention has been focused on the quaternary nitride since introducing one more element into the existed ternary nitride may bring about further enhanced thermal stability, lower friction and much improved wear resistance. Typical examples include the nc-TiAlN/a-SiN_x (matrix is TiAlN) and nc-CrAlN/a-SiN_x (matrix is CrAlN), which are realized by incorporating Al and Si into the traditional binary Ti and Cr based nitrides, respectively. In the following paragraphs, concerns are focused on the CrAlN and its nanocomposites since increasing researches suggest that CrAlN possesses better oxidation resistance as compared to TiAlN, indicating much more promising potential for the engineering application at severe conditions.

2.1.1.1 CrAlN coatings

Generally, the incorporation of Al into the CrN renders increased hardness in addition to the improved thermal stability. The hardening originates from the formation of solid solution alloys. In the scope of ternary nitride, the maximum strengthening effect depends on the solubility of one metal Me₁ in the Me₂N matrix. In the case of CrAlN, Me₁ is the Al and Me₂ is the Cr. It has been found that the amount of Me₁ and the solubility threshold are the essences in governing the coatings' mechanical properties. And these crucial factors are closely associated

with the operating parameters during the fabrication process. In the following, the influence of the Al content, physical vapor deposition parameters such as the working pressure (P) and working bias voltage (V_b) are reviewed. However, it is by no means that the three factors are entirely isolated. In fact, the amount of Al dissolved into CrN would be determined by P and V_b , as shown in this section later. And the effect of varying P and V_b are considered interconnected (but may not be always), since sputtering process is a kinetic effects of particle impingement on the film growth. The film growth, based on the initial structure zone diagram (SZD) proposed by Movchan and Demchishin when fabricating films using evaporation, relies on the homologous temperature, T_h , defined as the film growth temperature normalized by the melting temperature of the deposited film material (both in Kelvin). Based on analysis of many samples, Movchan and Demchishin concluded that there are three zones ¹³. As seen in Figure 2. 6(a), in zone 1 where $T_h < 0.3$, the adatom mobility is low, leading to continued nucleation of grains. A Fine grained structure of textured and fibrous grains with a high density of lattice imperfections and pores at grain boundaries can be observed. At the higher temperatures of zone 2, where $0.3 < T_h < 0.5$, surface diffusion sets in, leading to uniform columnar grains. The surface ends of the grains lead to a faceted surface. At even higher temperature, $T_h > 0.5$, bulk diffusion and recrystallization lead to dense films with large grains. When the advent of the broad use of magnetron sputtering, a new parameter is introduced: process pressure. Thornton showed a revised SZD (Figure 2. 6(b)) that the film structure being governed by two important parameters: the process pressure and the homologous temperature ¹⁴. At low pressure, sputtered particles are likely to experience no collisions before arriving at the substrate, and thus having

promoted kinetic energy for adatom rearrangement on the surface. At higher pressure, the sputtered atoms suffer collisions against the processing gas, leading to a much loss of kinetic energy. In light of this, the kinetic effect of processing gas results in the microstructural change during film growth. Later, Messier proposed a modified SZD (Figure 2. 6(c)) when doing a bias-sputtering, where the effect of bias voltage has been taken into consideration. In this diagram, the separate contribution of bombardment and adatom mobility is considered ¹⁵. In addition to the above, other researches have been carried on to refine the existed SZD. For example (Figure 2. 6(d)), Grovenor proposed a model to describe the grain growth at lower homologous temperature between zone 1 and zone T, where the interface is not sharp but change in a grading manner ¹⁶. Barna, on the other hand, stressed that a more realistic SZD should include process-induced segregation of co-deposited impurities or additive species ¹⁷. And a more recent SZD proposed by Anders, has taken into account the homologous temperature plus a temperature shift caused by the potential energy of particles arriving on the surface, the kinetic energy of bombarding particles and the net film thickness ¹⁸.

Figure 2. 6 Structure zone diagram proposed by (a) Movchan-Demchishin ¹³ (b) Thornton ¹⁴ (c) Messier ¹⁵ and (d) Grovenor ¹⁶

Effect of the Al content

CrAlN coatings can be synthesized by several means of physical vapor deposition techniques, such as cathodic arc evaporation ¹⁹, cathodic arc ion plating ²⁰⁻²², reactive magnetron sputtering ²³⁻²⁵, and beam plasma-assisted physical vapor deposition ²⁶. The strength of CrAlN was found largely dependent on the Al content, which can be directly tailored by altering power applied to the metal

source (*i.e.* targets) ^{22, 23, 27-30}. Using reactive magnetron sputtering, Ding *et al.* ²⁸ investigated the influence of Al/Cr atomic ratio (between 0 and 0.6) on the mechanical properties of CrAlN coatings. With addition of Al, coating hardness gradually increased. An optimized Al/Cr atomic ratio was around 0.4-0.5, at which the hardness reached up to ~30 GPa (Figure 2. 7). The substitution of Cr (radius of 0.139 nm) by a smaller Al (radius of 0.121 nm) atom led to the formation of solid solution fcc-CrAlN. The lattice distortion caused by the substitution rendered the solid solution hardening. However, this hardening effect was weakened when Al content was further increased. The decrease of hardness was attributed to the emergence of hcp-AlN phase, which was less strengthened than the fcc-AlN. Reiter *et al.* verified the microstructure change by varying the content of Al in CrAlN with a full range from 0 to 100 at.% ²². From their results (Figure 2. 8(a)), a threshold at 46 at.% was identified, below which the Al substituted the Cr in the fcc-CrN lattice and thus kept a fcc-CrAlN solid solution. Between 46 and 71 at.%, segregation of fcc-AlN occurred as seen from the evident peak shift. When Al content exceeded 71 at.%, the fcc-AlN completely transformed into hcp-AlN phase. The lattice parameter reduction is shown in Figure 2. 8(b). As compared to the maximum value (*i.e.* 40 GPa) of fcc-CrAlN solid solution, a considerable decrease by 47% was observed in the hardness due to the formation of the soft hcp-AlN phase. In addition, a decrease of crystalline size (*i.e.* from 11 to 6 nm) was reported by Rafaja *et al.* ³¹. In their study, an increase of mutual disorientation of the grains from 0.5 to several degrees was also found when Al content increased. So far, it has been commonly recognized that the threshold (Al/(Al+Cr) ratio) of solubility of Al in CrN is around 0.7, below which CrAlN coatings retain the fcc structure without segregation of hcp-AlN ^{22, 29, 32, 33}.

Figure 2. 7 Hardness (•) and Young's modulus (⊙) of the as-deposited CrAlN coatings as a function of Al/Cr atomic ratio ²⁸

Figure 2. 8 (a) XRD spectra of various CrAlN coatings ($0 < x < 1$); (b) Lattice parameter of various CrAlN coatings ($0 < x < 1$) ²²

Effect of the deposition pressure (P)

Deposition pressure is another factor influencing the mechanical properties of CrAlN, because it changes coatings' chemical concentrations and thus the phase composition ³⁴⁻³⁶. Nowadays, the existed studies have covered two aspects

related to the working pressure (P): the effect of the total working pressure (P_{total}) and that of the partial pressure from different gas species (P_x , x denotes different kinds of gases). Wang *et al.* found that CrAlN coatings with a large content of Al (73 at.% as calculated from Al/(Al+Cr) ratio) decreased to 65 at.% when P_{total} increased from 0.4 to 2 Pa. The chemical variation caused by the total working pressure can be understood that P_{total} is essential in determining the mean free path of the sputtered elements. With varied P_{total} , the kinetic energy of the ionized particle and fast neutrals would differ in consequence of numerous collisions among ions before arriving to the substrate. And the varied elemental ratio in turn changed the strength of the as-deposited coatings accordingly. As seen from Figure 2. 9, the hardness continuously increased when P_{total} increased from 0.4-0.8 Pa. In this range, the hcp-AlN fraction was reduced as the content of Al decreased. However, further decreased Al as a result of increased P_{total} no longer increases the hardness since the solid solution hardening was weakened. In addition, it was found that the increased N_2 partial pressure ($P_{nitrogen}$) was more detrimental for the hardness. When $P_{Nitrogen}$ increased from 0.06 to 0.17 Pa, the hardness decreased from 13 GPa to an extremely low value of 3 GPa³⁵. Similar results were also recorded by Wuhrer *et al.* that increased $P_{nitrogen}$ from 0.4 to 2.4 mTorr led to the measured micro-hardness dropped from 2800 to 1900 Hv with a formation of a rougher surface³⁴. In this regard, a small flux of N_2 input is preferred. And the use of small flux can also reduce the chance of target poison, which significantly decreases the sputtering yields.

Figure 2. 9 Hardness as a function of different working pressures during CrAlN deposition ³⁵

Effect of the negative bias voltage (V_b)

The determined influence of negative bias voltage (V_c) in fabricating coatings by using PVD methods have been verified and studied in the published results as in the diamond like carbon (DLC), carbide and nitride based coatings. The variation of V_b directly determines the energy delivered to the growing film by bombarding ions and thus governs the microstructure in the end. However compared to the numerous studies of fabricating CrAlN coatings by modifying the power density applied on the targets or working/partial pressures used during deposition, reports of the influence of negative bias voltage (V_b) were rare. Romero *et al.* once reported the dependence of coating orientation on the V_b . In the cathodic arc evaporation, the dominant orientation evolved from (111) to (220) accompanied by a progressive widening of the peak when the negative bias voltage increased

from 50 to 400 V (Figure 2. 10) ¹⁹. In the meanwhile, the hardness increased accordingly from 30 GPa to the maximum value of 40 GPa at $V_b=300$ V. Xu *et al.*, on the other hand, revealed the influence of V_b (namely, 0, 80, 120 V) on the impact resistance ³⁷. In addition to the hardness increment from 16 to 28 GPa, the impact resistance increased as well. Figure 2. 11 illustrates the impact dents after a given number of loading cycles at the load of 800 N. Coatings fabricated at the bias voltage of 120 V, which was the highest value used, exhibited the best resistance.

Figure 2. 10 XRD diffraction patterns of CrAlN prepared at different negative substrate bias voltages (Dashed lines stand for cubic CrN peak position and peaks labeled “s” corresponds to substrate) ¹⁹

Figure 2. 11 SEM micrographs of impact scar of CrAlN coatings at different bias voltage of (A) 0 V (B) 80 V (C) 120 V ³⁷

The bias voltage effects on the microstructure and mechanical are ascribed to the enhanced flux of energetic incoming ions during the sputtering process. Therefore, specific attentions on the energy of the incoming ions associated to the film growth were given in a more recent study. Lin *et al.* ³³ systematically summarized the dependence of coating morphology, residual stress, hardness and wear resistance upon the ion energy and ion flux in fabricating CrAlN coatings. When the total ion energy increased from 72 to 200 eV, the hardness increased from 34 to 48 GPa with a high residual stress up to 12 GPa. The strain hardening due to the high defect densities was considered the reason for the enhanced hardness. As shown in Figure 2. 12, the crystal lattice became more distorted when higher ion energy was achieved. It was also noticed that at the

condition where the higher ion energy was used, the defect densities became more prevalent (as reflected from the intensive lattice distortion showing from the arrow in Figure 2. 12), which are likely to reduce the coating toughness, although the value were not given.

Figure 2. 12 High resolution TEM lattice images of CrAlN fabricated at ion energy of (a) 122 eV and (c) 188 eV, (b) and (d) are the FFT filtered image of (a) and (c), respectively ³³

2.1.1.2 nc-CrAlN/a-SiN_x nanocomposite

Doping Si into the transition metal nitride, for example TiN, has been intensively investigated and widely used in the industry for different applications. As reviewed in the previous sections, the outstanding performances of the Si doped TiN coatings benefit from the formation of nc-TiN/a-SiN_x nanocomposite. In recent years, the focus extends to the CrAlN since enhanced mechanical properties can be achieved. The improvement originates from the crystal structure in its metastable state. Here, metastable state means that CrAlN can be in the forms of fcc-CrAlN, fcc-CrN/fcc-AlN, or fcc-CrN/hex-AlN depending on the Al concentration. The incorporation of Si into CrAlN would lead to the composite

much more complicated and in turn gives birth to the coatings a series of unique properties ³⁸. In the following, a review on the influence of Si on the microstructure, mechanical properties and thermal stability of the CrAlN will be given ³⁹.

Microstructure

Similar to the Ti-Si-N system, the microstructure of the Cr-Al-Si-N coating can be largely verified upon the content of Si. The most documented changes on the microstructure include the variation of phase segregation, grain size and lattice parameter ^{38, 40-42}. As seen from the selected electron diffraction patterns and TEM images in Figure 2. 13, the ring pattern became more continuous when Si content increased, indicating the random orientation and smaller size of the grains produced ³⁸. The evident effect of the Si on the microstructure was attributed to the development of the amorphous silicon nitride that interrupted the growth of the CrAlN crystallites ⁴¹. An example of this interruption is shown in Figure 2. 15, where large grains with columnar structure in CrAlN evolved into fine crystallites ⁴². Rafaja *et al.* observed the similar results that the grain size was reduced in CrAlSiN from 14 to 5 nm and a continuous decrease of the lattice parameter when the fraction of (Si+Al) was increased (Figure 2. 14) ⁴⁰. At the same time, the dominant texture direction changed from (111) to (100).

Figure 2. 13 Electron diffraction patterns and TEM images in plane-view geometry for (a), (b) $(\text{Cr}_{0.3}\text{Al}_{0.7})\text{N}$ and (c), (d) $(\text{Cr}_{0.25}\text{Al}_{0.7}\text{Si}_{0.05})\text{N}$, respectively ³⁸

Figure 2. 14 Dependence of (a) the stress-free lattice parameters and (b) crystallite size on the chemical composition of the CrAlN (•) and CrAlSiN (■) coatings ³¹

Figure 2. 15 Dark-field TEM images of (a) $\text{Cr}_{33}\text{Al}_{17}\text{N}_{50}$ (b) $\text{Cr}_{31.7}\text{Al}_{9.2}\text{Si}_{8.7}\text{N}_{49.6}$ ⁴²

It was noticed that doping certain content of Si was in favor of keeping the metastable fcc structure even the CrAlN contained high concentration of Al ⁴³. Here, it should be recalled that large content of Al normally leads to the decomposition of fcc-CrAlN into fcc-CrN and hex-AlN. From a viewpoint of the strain hardening, it is worthwhile to introduce more Al into the fcc-CrAlN since it will eventually increase the strength of the nc-CrAlN/a-SiN_x nanocomposite.

Mechanical properties

The change on the microstructure is reflected from the variation of the mechanical properties. By adding different contents of Si, Soldan *et al.* explored the tendency of the residual compressive stress in CrAlSi_xN ⁴³. When Si was 1 at.%, the residual stress was -4.5 GPa ("-" indicates compressive stress). This value decreases dramatically to -2.8 GPa at 5 at.% Si. This decrease was attributed to the sufficient a-SiN_x phase separation, which released the accumulated stress in the columnar grains caused by the defects in the crystalline structure. On the other hand, Barshilia *et al.* reported that the hardness was

optimized at 32 GPa when Si was at 7.5 at.%⁴⁴. The superior hardness was attributed to the formed nanocomposite structure consisting of nanocrystalline CrAlN and amorphous SiN_x, as confirmed by their XPS study. But the chemical environment of Si in the nanostructure is still challenging. Even higher maximum hardness of 55 GPa was reported when Si was at 8.7 at.%⁴². The above results indicate that the optimized Si in achieving good hardness is around 8 to 10 at.%. At this concentration, optimal separation between nano grains was achieved so the maximum reinforcement was obtained.

Thermal stability

Recently, the use of coatings in elevated temperature (near or higher 1000°C) poses a new challenge in developing advanced nanocomposites. These challenging applications include cutting tools for the high-speed machining, turbine blades for ground electric power stations and engines of aircrafts, and specific parts of aircrafts, to name but a few. Si doped CrAlN is considered to provide a novel and feasible way to solve this problem. Due to the existence of Cr and Al, CrAlN already possessed great thermal stability than the CrN or TiN⁴⁵. The outstanding thermal stability comes from a dense Al₂O₃ and Cr₂O₃ layers formed on the outer surface, which prevents the continuous invading of oxygen from the ambient. However, it was found that the thermal stability could be further improved by adding certain amount of Si. From the results of Chen *et al.*, the anti-oxidation capability of the nc-CrAlN/a-SiN_x could be well controlled by the Si contents and optimized at ~10 at.%. As shown in Figure 2. 16, the oxygen concentration on the surface decreased monotonically with the increase of Si

after 2 hours at annealed temperatures of 800, 900 and 1000 °C ⁴⁶. Similar tendency was observed when the annealing period was extended up to 50 hours ⁴⁷. In addition to the formation of Al₂O₃ and Cr₂O₃ dense layers, complex grain boundaries as induced by the a-SiN_x accounted for the enhanced oxidation resistance by effectively prohibiting the fast diffusion paths of oxygen. However, the limitation was that the increase of Si did not necessarily provide the best mechanical and thermal properties simultaneously. Efforts in balancing this contradiction were still on going.

Figure 2. 16 Surface oxygen concentration of CrAlSi_xN coatings with different Si contents at (a) various heat-treatment temperature (b) various heat-treatment period ^{46, 47}

2.2 Toughness measurement

In the previous part, various factors that influence the microstructure and mechanical properties such as the hardness and thermal stability of the CrAlN and its nanocomposite nc-CrAlN/a-SiN_x have been reviewed. However the published results on the toughness, which is as important as the hardness, are rare and less discussed. The limit documents on the toughness of coatings lies on

the difficulties in the measurement. In this section, a specific review of the toughness measurement for thin films is given.

Load-induced deformations of a coated surface generate surface stresses, which can lead to the surface fracture, starting from the cracking in a molecular level such as atomic bonds breaking. Normally, the fracture can be categorized as ductile cracking and brittle cracking. Ductile fracture is characterized by a large amount of plastic deformation in the vicinity of an advancing crack. For ceramic materials, brittle fracture often occurs since the cracks are spread extremely rapidly, with little accompanying plastic deformation (*i.e.* typically less than 5%).

Any fracture process involves three steps: crack nucleation, crack propagation and failure by material separation. Crack nucleation and initiation may take place according to different mechanisms depending on the material structure, geometrical features and state of applied and residual stress. For example, the dislocations in a work-hardened region are piled up by shear stresses, which can lead to the crack initiation as shown in the case of rolling bearings ⁴⁸. In ceramic coating with columnar structure, the crack nucleation is expected to occur between the columnar grains. Crack propagation theory for system with cracks longer than about 1 mm is well established based on linear elastic fracture mechanics (LEFM) ³⁹. However, crack propagation for the case of a loaded very thin-coated surface is much more complicated and no general model can be used to predict. Depending on different crack dimensions, the crack growth behavior was suggested by Kitagawa *et al.*, as shown in Figure 2. 17.

Figure 2. 17 The Kitagawa-Takahashi curve ³⁹

The term “fracture toughness” refers to the material’s inherent resistance to crack growth, which is associated with the crack length and the stress at the crack tip. In 1921, Griffith ⁴⁹ employed an energy-balance approach to quantify this term. Considering a stressed material, the strain energy per unit volume (U) is:

$$U = \frac{1}{V} \int F dx = \int \frac{F}{A} \frac{dx}{L} = \int \sigma d\varepsilon \quad (2.1)$$

V is the volume of the material

F is the applied normal force

A is the cross section area

dx/L is the extension ratio

σ is the stress

ε is the strain

If the material is linear ($\sigma = \varepsilon E$), then the strain energy per unit volume (U) is:

$$U = \frac{E\varepsilon^2}{2} = \frac{\sigma^2}{2E} \quad (2.2)$$

E is the Young’s modulus

σ is the stress

ε is the strain

When a crack has grown into a solid to a depth a , a region of material adjacent to the free surfaces is unloaded, and its strain energy released. Figure 2. 18 illustrates the idealization of unloaded region near crack flanks. The two triangular regions near the crack flanks, of width a and height βa , are completely unloaded, while the remaining material continues to bear the stress. The parameter β equals to π , to agree with the Inglis solution in the plane stress condition. The total strain energy released (U^*) can be calculated by multiplying the strain energy per unit volume and volume in both triangular regions:

$$U^* = -\frac{\sigma^2}{2E} \pi a^2 \quad (2.3)$$

σ is the stress

E is the Young's modulus

a is the width of the crack flank

Figure 2. 18 Idealization of unloaded region near crack flanks

Here, the dimension normal to the x-y plane is taken to be unity. Therefore, U is the strain energy released per unit thickness of the specimen. With creation of the crack, the surface energy S associated to the bonds breaking with a crack of length a (with unit depth) is:

$$S = 2\gamma a \quad (2.4)$$

γ is the surface energy with unit of Joules/meter²
 a is the width of the crack flank

Hence, the total energy associated with crack is then the sum of the strain energy liberated by allowing the regions near the crack flanks to become unloaded and the energy absorbed to create the new surfaces. Up to a threshold of the crack length, the crack will grow only if the stress is increased. Beyond this point, crack growth is spontaneous and catastrophic. By setting the derivative of the total energy $S+U$ to zero, the value of the critical crack length can be found.

$$\frac{\partial(S+U^*)}{\partial a} = 2\gamma - \frac{\sigma_f^2}{E} \pi a = 0 \quad (2.5)$$

$$\sigma_f = \sqrt{\frac{2E\gamma}{\pi a}} \quad (2.6)$$

S is the surface energy
 U^* is the strain energy
 σ_f is the failure stress
 a is the width of the crack flank
 E is the Young's modulus

Equation (2.6) gives the critical stress at which the catastrophic fracture occurs for pure brittle materials. Taking into consideration the ductility of the material, the released strain energy is absorbed not by creating new surfaces, but by energy dissipation due to plastic flow in the material near the crack tip. Therefore, Irwin and Orowan suggested that catastrophic fracture occurs when the strain energy is released at a rate sufficient to satisfy the needs of all these energy "sinks", and denoted this critical strain energy release rate by the parameter G_c ⁵⁰. In this regard, the Griffith equation is rewritten in the form:

$$\sigma_f = \sqrt{\frac{EG_c}{\pi a}} \quad (2.7)$$

$$G_c = -\frac{\partial(U-W)}{\partial A} \quad (2.8)$$

a is the width of the crack flank
 σ_f is the stress
 E is the Young's modulus
 G_c is the strain energy release rate
 U is the elastic energy stored in the system
 W is the work done by external loads
 A is the crack area

On the other hand, the failure stress is associated with the stress intensity factor or fracture toughness K_{IC} as:

$$K_{IC} = Y \sigma_f \sqrt{\pi a} \quad (2.9)$$

K_{IC} is the stress intensity factor or fracture toughness
 σ_f is the failure stress
 a is the crack length
 Y is the dimensionless parameter that depends on both the specimen and crack geometry

Based on the equations (2.7) and (2.9), the toughness K_{IC} and the strain release rate are connected. In the plane strain condition, the relation is deduced as:

$$K_{IC} = \sqrt{\frac{E G_c}{1 - \nu^2}} \quad (2.10)$$

E is the Young's modulus
 ν is the Poisson's ratio
 G_c is the energy release rate

According to this definition, the fracture toughness is associated to the strain energy release rate with the growth of a pre-existing crack. However, in most toughness measurements for thin films (discussed later in this chapter), no known pre-existing crack is introduced. Therefore the measured values inevitably include the energy for the crack initiation. As such, "toughness" rather than "fracture toughness" is a more preferred measurement in thin film or coatings⁵¹. In this context, the toughness is defined as the ability of a material to

absorb the energy during deformation up to fracture, *i.e.* both to create the crack and to enable the crack to grow. The fracture toughness measurements for bulk materials or sufficiently thick coatings have been well established and are based on the classical routines, such as the three- or four-point bending test. The dimensional prerequisite of using these methods to meet the plain strain condition is ⁵²:

$$t, a, (W - a) \geq 2.5 \left(\frac{K_{IC}}{\sigma_y} \right)^2 \quad (2.11)$$

t is the thickness of specimen

W is the width of specimen

a is the flaw size

σ_y is the yield stress

According to the expression, specimen thickness should be sufficiently large, while the initial crack length and the un-cracked ligament width (*i.e.* $W-a$) should not be too small. However, with a decrease in the coating thickness and the introduction of complex composition and structure, the determination of toughness becomes much more complicated. Due to the size limitation (*i.e.* a few microns thickness at most), the application of traditional measurements is impossible. Some new methods are therefore introduced to solve this problem.

2.2.1 Qualitative evaluation

As a quick evaluation, indentation plasticity and scratch toughness are often chosen since they are helpful to draw a straightforward conclusion from the characteristic testing curve or a direct observation through the microscope.

2.2.1.1 Indentation plasticity ratio

Plasticity ratio is related to the plastic deformation, in which the stress can be released⁵³. Here, plasticity ratio rather than the plasticity is used in the original literature to avoid the misunderstanding. Plasticity ratio could be assessed using an indentation and defined as the ratio of plastic displacement divided by the total displacement in the load-displacement curve of an indentation test⁵⁴. Figure 2. 19 demonstrates the typical example of the load-displacement curve used to calculate the plasticity ratio.

$$plasticity_ratio = \frac{OA}{OB} \quad (2.12)$$

OA is the plastic deformation associated with plastic strain
 OB is the total displacement under the normal force

Figure 2. 19 Schematic plot of a nanoindentation load-displacement curve⁵⁴

A DLC coating with a hardness of 60 GPa exhibited a 10% plasticity ratio determined by this method, while a nc-TiC/a-C coating with hardness of 32 GPa exhibited 50-60% plasticity ratio, hence was considered as “super tough”⁵⁵. Fox-Rabinovich *et al.*⁵⁶ proposed a “micro-hardness dissipation parameter (MDP)” in

terms of the mechanical work done during different deformation stages in the indentation test instead to better describe the toughness.

$$MDP = \frac{plastic_work}{plastic_work + elastic_work} \quad (2.13)$$

However, plasticity ratio is not the real toughness or fracture toughness. This term only depicts the capability of resisting plastic deformation rather than the ability of resisting crack propagation since no crack is produced. However, the MDP parameter was found to be related to the scratch toughness which can be used to characterize the toughness more properly ⁵⁷.

2.2.1.2 Scratch toughness

Scratch test was first developed to evaluate the strength of the adhesive bonds between the coating and the substrate. In such a test, a diamond stylus subjected to a linearly increasing load is drawn across the coatings surface. When coatings break, parts of them would be detached (*i.e.* either delamination or spallation) and the substrate material be exposed to the counter surface. Generally but not necessarily, micro-cracks may appear in the scratch track before delamination takes place. Researchers have observed different typical crack patterns produced by the moving stylus ⁵⁸. As shown in Figure 2. 20, initial angular cracks are generated at the groove edge behind the sliding (a); parallel cracks emerge at higher loading (b); angular cracks merge with the parallel cracks to transverse semicircular cracks (c). With further increased loading, slight chipping occurs at the groove edge (d), and the onset of spalling due to the poor adhesion would be

observed at even larger load. Finally, large areas of the coating are spalled off resulting in complete coating failure (f).

Figure 2. 20 Surface cracks generated in a scratch test track can be classified as (a) angular cracks, (b) parallel cracks, (c) transverse semicircular cracks, (d) coating chipping, (e) coating spalling and (f) coating breakthrough ⁵⁸

The minimum load at which the onset of crack occurs is defined as the “lower critical load” (L_{c1}). The load associated to the complete delamination is termed as “higher critical load” (L_{c2}), as illustrated in Figure 2. 21. With these two parameters, Zhang *et al.* ⁵⁹ proposed a new parameter termed as “scratch propagation resistance” (CPR_s) to semi-quantitatively assess the coating toughness.

$$CPR_s = L_{c1}(L_{c2} - L_{c1}) \quad (2.14)$$

The parameter is higher, the more difficult it is to create cracks (larger L_{c1}) and the more capability the coating shows of retarding the crack propagation before fracture (larger $L_{c2} - L_{c1}$). Qualitatively, it means that greater resistance to cracking the coating possesses, *i.e.* toughness.

More recently, some numerical models of the scratch test were given. However, some ⁶⁰ were oversimplified in that they gave no consideration to the real state of stress in the groove ahead and right below the tip. Some models ⁵⁸ had difficulty in gaining practical application, as determining the required parameters was impossible. For example, no general expression for stress could be obtained through a three-dimensional finite element model.

Figure 2. 21 Typical scratch adhesion profile of nc-TiN/a-SiN_x coatings deposited on Si wafer with lower and higher critical load labeled ⁵¹

2.2.2. Quantitative evaluation

Quantitative evaluation methodologies include stress approaches and energy approaches for either coating/substrate system or a free-standing coating system. Free-standing coating means the coating is not being part of or affiliated with the substrate (*i.e.* no physically support from the substrate). Creating free-standing coating is much more difficult and usually involves specific MEMS (Micro-Electro-Mechanical System) fabrication process to remove the substrate.

However, it is advanced as the substrate effect in the toughness measurement can be eliminated.

2.2.2.1 Stress approach to the coating/substrate system

Among a number of quantitative evaluations of toughness through stress approach, an indentation test is the simplest and the most straightforward⁵¹. Quantitative toughness measurement is accomplished by the crack pattern induced by the applied force during the indentation. Different indent shapes are used, *e.g.* Vickers, Berkovich, or cubic corner. In the process of indenting, a crack is generated in the coating and driven by the tensile stress at the crack tip. The toughness is related to the crack length as measured from the center of impression as⁶¹:

$$K_{IC} = \delta \left(\frac{E}{H} \right)^{\frac{1}{2}} \left(\frac{P}{c^{3/2}} \right) \quad (2.15)$$

P is the applied indentation load

E is the Young's modulus of coating

H is the hardness of coating

δ is the empirical constant depending on the geometry of the indenter (Berkovich type, $\delta = 0.016$; Vickers type, $\delta = 0.016$; cubic-corner type, $\delta = 0.04$)

In this process, no pre-cracking is introduced. The application of this method is straightforward, as E and H could be directly deduced from the analysis of the indentation load-displacement data. However, the limitation is apparent, in that a cracking threshold of the indent force exists, below which no measureable crack appears⁶². Normally, the threshold to generate a well-defined crack is at the scale of a few hundred of mN. Depending on the different types of indenter, the

cracking threshold in most ceramic materials is about 100-150 mN, if Vickers indenter is used ⁶³. A sharper indenter, such as a cube-corner, can significantly reduce the crack threshold. Due to the large indentation force required, another problematic issue is the inevitable influence of the substrate on the determination of mechanical properties of coating being deposited on top (*i.e.* substrate effect). Under this circumstance, the indentation response of a thin film on a substrate is a complex function of the elastic and plastic properties of both the film and substrate.

According to the recommendations of U. K. National Physical laboratory, the indentation depth should not exceed one-tenth of the thickness of the region of the specimen that is being tested ⁶⁴. Buckle used an empirical model to show that if a coating has a thickness of 10 times the indentation depth, the contribution of the substrate can be negligible (<2%) ⁶⁵. However, it is difficult to keep the indent depth less than 1/10 of the coating thickness so that the elastic-plastic zone under contact region does not expand to the substrate when the coating is only a few hundred nanometers or a few microns at the most. Therefore, the measured value will be significantly affected by the substrate. An accepted way of correcting the substrate effect is conducting an extrapolation of the toughness calculated from different depths to the point of 1/10 of the coating thickness ⁶⁶. An indentation toughness of a thin nc-TiN/a-SiN_x coating was obtained in the scale of 1.15-2.60 MPa·m^{1/2}.

2.2.2.2 Energy approach to the coating/substrate system

To overcome the difficulties in evaluating toughness using the stress approach, indentation data can be analyzed in terms of the energy release rate, which is referred to the energy approach. The essence of this methodology is to determine the energy dissipation differences before and after crack occurrence. Malzbender *et al.* and Toonder *et al.* considered the dissipated energy in one indentation cycle with coating chipping as being consisted of two parts, if the thermal energy was ignored ⁶⁷:

$$W_{irr} = U_{fr} + U_{pl} \quad (2.16)$$

U_{pl} is the energy dissipated due to the plastic deformation

U_{fr} is the energy dissipated due to coating fracture or chipping

W_{irr} is the total dissipated energy

Here, W_{irr} could be calculated from the loading and unloading curves. A plot of W_{irr} as a function of the maximum indentation load is shown in Figure 2. 22. Then the fracture toughness (for plane stress state) is computed from the following expressions:

$$G = \frac{U_{fr}^c}{N\pi t' C_d} \quad (2.17)$$

$$K_{IC} = \sqrt{EG} \quad (2.18)$$

C_d is the diameter of the delamination crack that initiated the chip

N is the number of chipped areas

t' is the coating thickness

Figure 2.22 Irreversibly dissipated energy W_{irr} as a function of the applied load ⁶⁷

Li *et al.* on the other hand, described the energy dissipation with a three-stage chipping model as proposed in Ref. ⁶⁸ (Figure 2.23). The fracture of coating is classified into the following stages: (1) the first ring-like through-thickness crack is formed around the indenter by the tensile, (2) delamination and buckling take place around the contact area at the coating/substrate interface due to the high lateral pressure, and (3) a second ring-like through-thickness crack is formed and spalling is generated by the high bending stress at the edges of the buckled coatings.

Figure 2. 23 Schematic of three stages in nanoindentation fracture in a coating/substrate system ⁶⁸

Based on this model, the strain energy released because of the second ring-like crack and spallation is calculated from the corresponding step as in the load-displacement curve. Figure 2. 24 illustrates the schematic plot showing the step in the energy dissipation plot (*i.e.* the area of ABC) before and after the second ring-like cracking, which is responsible for the through-thickness crack. Then the toughness of the coating can be computed as:

$$K_{IC} = \left(\frac{E}{(1 - \nu_f^2) 2\pi C_R} \frac{\Delta U}{t} \right)^{1/2} \quad (2.19)$$

E is the Young's modulus of the coating

ν_f is the Poisson's ratio of the coating

$2\pi C_R$ is the crack length of the second circular crack

t is the coating thickness

ΔU is the strain energy difference before and after cracking

Figure 2. 24 Schematic of a load-displacement curve, showing a step during the loading cycle and associated energy release ⁶⁸

Toughness of amorphous carbon coatings has been evaluated using this method. However, errors could be introduced as a result of the measuring uncertainty in $2\pi C_R$ because of the irregular crack shape. In addition, accurate evaluation also depends on the area (extracted from the load-displacement curve) used to describe the energy differences. The debate on this issue is ongoing. The inconsistency leads to uncertainties in the estimating of dissipation energy, resulting in the errors in toughness evaluation. Chen *et al.* suggested the boundaries of the dissipation energy as shown in Figure 2. 25 ⁶⁹. The areas of OAB and ABFR correspond to the full elastic deformation and full plastic deformation of the coating/substrate system, respectively. However, Michel *et al.* ⁷⁰ thought that some energy should be consumed due to the deformation of Si substrate, so that the area ABH represents the energy of cracking (Figure 2. 26). More recently, Zhang *et al.* re-evaluated these methods and a serious doubt was cast on the role of this area-related “step” in determining energy dissipation. It

was asserted that the size of such a “step” had no logical relationship with the energy dissipation but only accounted for the free-fall of the indenter ⁷¹.

Figure 2. 25 Schematic illustration of the boundaries of dissipation energy at the plateau in the indentation curve ⁶⁹

Figure 2. 26 Schematic drawing representing load-unloading curve of nanoindentation in a film after chipping, the area of ABH represents for the dissipation energy due to the cracking

In addition to the indentation test, the tensile test has also been considered in quantitative determination of the coating toughness. Zhang *et al.* ⁷² utilized a two-step uniaxial tensile method to evaluate the toughness of ceramic coatings. A relatively thin and highly elastic substrate was coated and subjected to the

uniaxial tensile loading to coating was fractured. Afterwards, the coating/substrate system was unloaded and re-loaded again till the previous extension. The energy differences obtained from the load-displacement curve (Figure 2. 27) was used to determine the toughness of coating using the following equation:

$$K_{IC} = \left[\left(\frac{E}{2\omega\rho L} \right) \left(\frac{\Delta U}{h_f} \right) \right] \quad (2. 20)$$

E is the Young's modulus of coatings

h_f is the coating thickness

ΔU is the strain energy difference before and after cracking

ω is the substrate width

ρ is the crack density

Through this method, toughness of nc-TiN/a-SiN_x has been calculated as 2.6 MPa·m^{1/2}, which was comparable with the results from the indentation test. However, the disadvantage of this method is obvious. Firstly, there is a strict requirement of the elasticity on the substrate: the substrate must retain in the elastic deformation regime while the coating is undergoing a fracture. Secondly, perfect adhesion should be guaranteed between coating and substrate, otherwise significant uncertainty may be observed in the results.

Figure 2. 27 Schematic illustration of load-extension curve obtained using the two-step uniaxial tensile test (energy difference can be determined from the area differences $S_{OABCE} - S_{ODEO}$)⁷²

2.2.2.3 Stress approach to the free-standing coatings

With the aid of micro-machining techniques, free-standing coatings can be obtained by using photolithographic process, which is now frequently used in the semiconductor industry. This advance makes it possible to directly measure the toughness of coating without invoking the influence of the substrate. Notable progresses have been reported in the tensile test in micro- or nano-scale after the coatings were subjected to such pre-treatment. In a tensile test, a sharp pre-crack can be introduced by two methods 1) indenting the adjacent silicon substrate so that the resultant radial cracks can propagate to the freestanding coatings 2) using the focus ion beam. Afterwards, the well pre-existing crack was driven by a complicated apparatus with extra fine force (*i.e.* $\sim 10^{-4}$ N) and displacement resolution (*i.e.* ~ 4 nm). Jonnalagadda *et al.*⁷³ used this method and measured the fracture toughness of ta-C coatings with a thickness of 0.5 to 3 μm (from 3.06 to 4.25 $\text{MPa}\cdot\text{m}^{1/2}$). Espinosa *et al.*⁷⁴ performed the micro-tensile test in an

alternative way. A free-standing Si_3N_4 layer was fabricated on a Si wafer, as illustrated in Figure 2. 28. Then the coating to be tested was deposited on the Si_3N_4 layer. Coating became free-standing once the Si and Si_3N_4 were etched out, while the two ends remained tightly attached (Figure 2. 29). In this way, it avoided the problematic issue of clamping coatings and the reproduction of such coating bridge can be reliable without much geometrical error. An AFM induced normal force was used to create the deflection of coatings whose alignment was guaranteed using an interferometer. With the deflection angle and applied force as well as the dimensions of the coating, toughness could be precisely measured. Using this approach, they determined the toughness value of the diamond like carbon coatings with a thickness of 2.1 to 8.2 μm (from 4.1 to 4.8 $\text{MPa}\cdot\text{m}^{1/2}$).

Figure 2. 28 Schematic representation of the three general microfabrication steps used to process the specimens ⁷⁴

Figure 2. 29 An optical image of a freestanding coating with both ends attached to a wafer ⁷⁴

Enlightened by this progress, Zhang *et al.* prepared freestanding coatings and patterned them into strips as shown in Figure 2. 30 ⁷⁵. Pre-crack was made ahead of the coating strips with the aid of Vickers indenter in the adjacent region of the Si substrate. This crack was driven by a tensile force applied through the pin-holes. A force-displacement gauge controlled the extent of applied force manually. Coating bridge sustained the tensile force till breaking. During tensile testing, the strain of the striped coating was measured through the extension in the longitudinal direction. By assuming the elastic fracture in the ceramic coatings, critical stress can be calculated through the Hooke's law. Then the fracture toughness was obtained from the following expression.

$$K_{IC} = \sigma \sqrt{\pi a} f\left(\frac{a}{W}\right), \frac{a}{W} \leq 0.6 \quad (2.21)$$

a is the length of the pre-crack

W is the width of the crack mouth (*i.e.* displacement made by the crack opening)

$$f(a/W) = 1.12 - 0.23(a/W) + 10.55(a/W)^2 - 21.72(a/W)^3 + 30.41(a/W)^4$$

So far, this method has been utilized to measure the fracture toughness of CN_x (0.31 μm) and CuZr (1.10 μm) coatings. However, the most difficulty is maintaining the coatings intact after the etching process. It was admitted by the authors that all the measurement were carried out in the liquid (*i.e.* water) to overcome the tension force due to the weight of the coating itself. However, it is

obvious that the measured value will be influenced by the tension force from the liquid and thus degrades its accuracy if no post-correction is applied.

Figure 2. 30 Schematic representation of the testing configuration ⁷⁵

2.3 Toughening methodology

Toughness of the ceramic coatings can be increased by introducing toughening agents or tailoring coating architecture. Generally, using toughening agents such as metallic materials or ligaments components in terms of whisker/fiber or tube are the most straightforward. On the other hand, modifying the coating architecture (*i.e.* gradient or multilayers) is thought more effective in achieving desired features since varied specifications can be obtained by carefully manipulating the chemical concentrations or lamination arrangements through

the coating thickness. In the following, the most used toughening techniques as well as their mechanisms are summarized.

2.3.1 Incorporation of the toughening agent

Ductile phase toughening

To overcome the brittleness of the ceramic hard coatings, involving a phase with high toughness is the most straightforward. Normally, metals are promising candidates to be used due to their ductile nature. In general, the toughening effect is raised from two major mechanisms (Figure 2. 31): 1) the relaxation of the strain field around the crack tip through ductile phase yielding; 2) the bridging of cracks by ligaments of the ductile phase behind the advancing crack tip ⁷⁶. Hsieh *et al.* doped Cu into TaN films using reactive co-sputtering on tool steel substrates ⁷⁷. Nucleation and growth of Cu grains in the TaN matrix were realized by annealing at 400 °C for varied period of time. The coating with 1.4 at.% Cu was the best to resist crack propagation yet the best in hardness. Similar results were observed when 24 at.% Cu was doped in ZrO₂ nanocomposite ⁷⁸. To keep the strength of the nanocomposite with a soft metal at the same time, several requirements need to be satisfied (1) the metal content is low, (2) the matrix is strongly oriented with a dense columnar structure and (3) the columnar grains surrounded or separated by a very thin network-like layer of the soft metal phase ⁷⁹. Sam *et al.* studied the soft metal layer in terms of the varied Ni content in the nc-TiN/a-SiN_x nanocomposite ⁶⁶. They found that the density actually fluctuated at the place where Ni+a-SiN_x amorphous phases agglomerated, which gave rise to

a distribution of local stresses, hydrostatic as well as shear components. The Ni cluster was believed to reduce the stress fields by hampering the localization of shear bands. As a consequence, 0 to ~40 at.% Ni brought about a monotonic increase in the toughness from 1.15 to 2.6 MPa·m^{1/2}. However, the hardness dropped drastically from 30 to 14 GPa. It should be pointed out that, in the above studies, the toughening contribution of residual stress originated by the ion bombardment during deposition was comparably small due to the high sputtering temperature. However, when the deposition is operated at room temperature, the ion bombardment resultant large compressive stress cannot be ignored since toughness would be increased if the compressive stress existed. A proper compressive stress is beneficial to increase the toughness because cracking is generally initiated by the tensile stress. While a large compressive stress up to a few GPa always leads to an extreme brittleness. To solve this problem, Bui *et al.* doped Al in DLC (or a-C) coatings to eliminate the high compressive stress⁸⁰. The residual compressive stress decreased from 4.1 to 0.3 GPa when 19 at.% Al was added. To restore the hardness drop raised by the Al addition, Ti was introduced. In this way, the formed nc-TiC/a-C(Al) nanocomposite possessed hardness of 19.5 GPa with very a low residual stress of 0.5 GPa. A scratch test further confirmed that the nc-TiC/a-C(Al) nanocomposite was tough as shown in Figure 2. 32. nc-TiC/a-C basically failed in a brittle way at lower normal applied force (~359 mN, adhesion force), while TiC/a-C(Al) cracked however with no spallation and the scratch tip just ploughed into the coating⁸¹.

Figure 2. 31 Schematic diagram of ductile phase toughening: (1) ductile phase deformation, and (2) crack bridging ⁷⁶

Figure 2. 32 Optical image of scratch tracks on: (a) nc-TiC/a-C and (b) nc-TiC/a-C(Al) coatings ⁸¹

Carbon nanotube toughening

Carbon nanotubes (CNTs) are versatile and many researchers have utilized CNTs in reinforcing ceramics. This is attributed to their excellent mechanical properties due to the strong inter-atomic bonds. The carbon-carbon bond on the basal plane in graphite is one of the strongest in nature; therefore the CNTs have been predicted to be the stiffest and the most robust. A comparison of the mechanical

properties between the CNTs and the traditional engineering materials is presented in Table 2.1.

Table 2. 1 Mechanical properties of CNTs as compared to those of the tradition materials ⁸²

Material	Yield strength (GPa)	Elastic modulus (GPa)	Strength Weight Ratio
SWNT^a	65.0	542	462
MWNT^b	2.7	400	15
Titanium	0.9	103	2
Aluminum (2024)	0.5	69	2
Steel (1050)	0.8	207	1

SWNT^a: single-wall nanotube, one graphite basal plane rolled into a cylinder

MWNT^b: multi-wall nanotube, many graphite basal planes rolled into a series of closed coaxial cylinders

CNTs have been incorporated into bulk ceramics aiming at mechanical properties improvement. Ma *et al.* incorporated the CNTs into SiC via a hot-pressing process at 2273 K and 25 MPa in an argon atmosphere. Bending strength and fracture toughness were improved by ~10 % as compared to the monolithic SiC ⁸³. To obtain fully dense structure and avoid carbon nanotubes damage during sintering, Zhan *et al.* proposed a pressure-assisted fast sintering method (spark-plasma sintering) to fabricate SWNT/Al₂O₃ composite ⁸⁴. This technique utilized a high-temperature plasma to complete the sinter within a short period, *i.e.* 1150 °C for 3 min. Homogenous dispersion of SWNT in the matrix and effectively entanglement of carbon nanotubes over the alumina grains were confirmed as shown in Figure 2. 33. With a 10 vol.% of carbon nanotube, SWNT/Al₂O₃ exhibited three times the toughness of the pure nanocrystalline alumina.

However, these results were not always reproduced. Wang *et al.* reported that no significant improvement in the toughness was obtained as a result of the

involvement of SWNT (both were in the range of 3.22 to 3.32 MPa·m^{1/2})⁸⁵. But the greatly enhanced contact-damage-resistance of SWNT/Al₂O₃ composite suggested CNTs are still very attractive for applications where contact loading was prevalent (Figure 2. 34).

Figure 2. 33 SEM images of (a) SWNT network encompassing some of the alumina grains (SWNT 5.7 vol.%) (b) tangled rope network of SWNT⁸⁴

Figure 2. 34 Low- and high- magnification SEM micrographs showing top views of Vickers indentation sites: classical radial cracks can be seen in (a) the dense Al₂O₃ and (b) the porous Al₂O₃; no evidence of classical radial cracks in (c) the SWNT/Al₂O₃ composite or (d) the graphite/Al₂O₃ composite⁸⁵.

Researches concerned with carbon nanotube toughened ceramic coatings are less investigated, compared to those on bulk ceramics. This is largely due to the difficulty in homogeneously dispersing CNTs in coatings with the thickness of only a few tens of microns. Xia *et al.* fabricated highly oriented CNTs in the amorphous Al₂O₃ coatings with a thickness of 20-90 μm⁸⁶. In the proposed procedure, anodized amorphous aluminum with a hexagonal array of straight

pores (around 30-40 nm in diameter) was prepared at the first step. Then, Co or Ni catalyst particles were sputtered into the bottom of the deep-nanosized pores. Following sputtering, a low temperature (645 °C) CVD process was employed to grow MWNTs along the inside of the pore walls (Figure 2. 35). From the SEM investigation on the crack track introduced by the indentation, toughening mechanisms including crack deflection, crack bridging and tube pulling-out were observed. Using this in-situ synthesis, CNTs could homogeneously disperse in the Al_2O_3 matrix, and a fair enhancement in hardness (from ~ 8 to 9 GPa) and toughness (from 4.14 to 4.62 $\text{MPa}\cdot\text{m}^{1/2}$) were acquired accordingly. However, the key issue that has yet been explored in any detail is the control of the interface between the nanotubes and the matrix. At the same time, fabricating coatings with uniformly dispersed nanotubes remains a big challenge if the coating thickness is reduced to a few hundred nanometers.

Figure 2. 35 (a) SEM micrograph of as-fabricated CNT/ceramic composite viewed from the top, showing high degree of hexagonal order (b) Crack deflection around the CNTs along the interface (c) Crack bridging the gap between the crack surfaces (d) CNTs pulling out with longitudinal delamination and residual holes ⁸⁶

2.3.2 Toughening through architecture modification

Grading structure

In practical applications, requirements can be varied through the coating thickness. For example, good adhesion is required at the coating-substrate interface, while at the surface a very stable material is needed (more technical requirements can be referred to Figure 2. 36 ⁸⁷). However, in homogeneous single layer coatings, these desired properties are rarely reached simultaneously. Therefore, it is apt to apply graded coatings, consisting of a sequence of coating materials, to satisfy the requirements.

Figure 2. 36 Basic ideas for the development of gradient coatings ⁸⁷

By gradually changing the bias-voltage, Zhang *et al.* ⁵⁵ prepared a 1.5 μm thick a-C gradient coating on the tool steel with moderately high hardness (25 GPa) and high toughness (plasticity ratio approximately to 58%). As the negative bias voltage varied from 20 to 150 V, sp^3/sp^2 ratio of the carbon gradually increased from the bottom layer to the top surface. The lower sp^3/sp^2 ratio ensured the good adhesion at the coating-substrate interface, while the higher sp^3/sp^2 ratio

gave rise to the high hardness, as well as the coating of the improved tribological performance. The graded coatings became hard yet tough (Figure 2. 37).

Figure 2. 37 (a) Hardness of graded DLC coatings (b) scratch adhesion strength of the non-hydrogenated DLCs deposited under various constant bias voltage or bias-graded conditions ⁵⁵

In other gradient coating systems, such as commercial grading TiCN ^{88,89}, TiN-TiCN-TiC-DLC ⁹⁰ and Ti-TiC-DLC ⁹¹, high hardness with enhanced adhesion was also achieved. It was claimed that gradient structure was beneficial for the suppression of crack initiation due to the absence of sharp interface.

Multilayered structure

Koehler was the first (in 1970) to propose the concept of fabricating hard coatings through multilayering ⁹². The experimental prototype was validated by Lehoczkey in 1978. Koehler's theoretical explanation indicated that the dislocation motion was inhibited in a multilayered structure due to the image force on dislocations created by the different dislocation line energies in each layer ⁹³. Practically, the superior mechanical properties can be obtained by

alternating ultra-thin layers of materials with high and low elastic constant. This concept has led to the development of a variety of multilayers and superlattices of metal/metal, metal/ceramic, and ceramic/ceramic combinations ⁹⁴. The crack deflection at the layer interface, ductile interlayer ligament bridging and crack tip blunting due to the nanoplasticity at the interface were reported as the reasons accounting for the toughness improvement since more energy would be dissipated and consumed (Figure 2. 38) ⁹⁵.

Figure 2. 38 Toughening mechanism in ceramic multilayer materials ⁹⁵

These toughening mechanisms have been validated by a number of experimental observations. Suresha *et al.* ⁹⁶ demonstrated the cracking patterns in monolayer TiN and multilayered TiN/AlTiN at indentation load of 20 N. Severe edge cracking was observed in the monolayer while much less cracking was found in the multilayers (Figure 2. 39). In particular, TiN/AlTiN with bilayer thickness of 650

nm showed two edge cracks while that with bilayer thickness of 130 nm showed only one. Figure 2. 40 illustrates the cross-sectional images of the fracture region under the indentation with normal load of 5 N. Continuous shear cracks were evident in monolayer TiN. Multialyers of bilayer thickness of 650 nm displayed discontinuous shear cracks, while such cracks were absent in the multilayers of bilayer thickness of 130 nm. These results indicated the positive effects of the layered structure in preventing crack propagation.

Figure 2. 39 Surface view of the indentation with a load of 20 N showing dependence of edge cracking on layer spacing: (a) monolayer TiN (b) multilayer TiN/TiAlN with bilayer thickness of 650 nm (c) multilayer TiN/TiAlN with bilayer thickness of 130 nm ⁹⁶

Figure 2. 40 Cross-sectional images of the indentation under 5 N showing inclined shear cracks: (a) monolayer TiN (b) multilayer TiN/TiAlN with bilayer thickness of 650 nm (c) multilayer TiN/TiAlN with bilayer thickness of 130 nm ⁹⁶

For the same multilayer system, Lee *et al.* ⁹⁷ investigated the toughening effect using scratch test in addition to the nanoindentation. Multilayers presented great resistance to crack initiation and propagation, in great contrast with the monolayer, which exhibited extreme brittleness accompanied by severe coating

chipping off at the fringe of the groove track (Figure 2. 41). In parallel, nanoindentation tests further confirmed the advantage of the multilayers in fracture resistance. Only a few cracks spread out radially within the multilayers, whereas delamination was obvious in the monolayer, together with radial cracks.

Figure 2. 41 Scratch channels (a) and (b) and indent marks (c) and (d) of monolayer $(\text{Ti}_{0.5}\text{Al}_{0.5})\text{N}$ and $\text{TiN}/(\text{Ti}_{0.5}\text{Al}_{0.5})\text{N}$ multilayer coatings using ⁹⁷

Karimi *et al.* ⁹⁸ fabricated a variety of nanostructured $\text{TiAlN}(\text{Si}, \text{C})$. A summary of the results for several samples is given in Figure 2. 42, in which “M” stands for multilayers. It was shown that multilayers (4) exhibited the best performances, both in terms of hardness and toughness. A similar result was obtained when the CrN/AlN multilayer were subjected to the Rockwell C-Brale indentation test ⁹⁹.

Practically, the number of the interlayers, the thickness of each sub-layer, and the thickness ratio of different sub-layers all affect the toughness. The dependence of

the toughness on these factors is evaluated in coating systems such as TiC/TiB₂¹⁰⁰, TiC/TiB₂¹⁰¹, TiC/CrC¹⁰², CrN/AlN¹⁰³ and TiN/Ti¹⁰⁴. In general, increased number of the interface leads to the improved toughness. Besides the dimensional effect of the sublayers, studies have been carried out on the crystalline structure of the constituent layers. Yau *et al.*¹⁰⁵ investigated the multilayers with the bilayers of nanocrystalline/amorphous phases, such as nc-TiAlN/a-Si₃N₄. Maximum critical scratching load of the multilayers increased by 165% as compared to monolayer TiAlN. The improvement was attributed to the crack deflection at the layer interfaces (Figure 2. 43). In the more recent researches of TiN/SiN_x^{106, 107} and CrAlN/SiN_x multilayers^{108, 109}, the crystallite structure of the SiN_x layers were found to be dependent on the their thickness. At very small thickness, for example a few tens of angstrom, the SiN_x was in an epitaxial crystalline structure. However, when the thickness was larger than the threshold, the epitaxial crystalline structure can transform into an amorphous phase. The hardness was varied accordingly due to the phase change of the SiN_x but the trend of the toughness was not reported.

Figure 2. 42 Variation of hardness, critical load for cracking and fracture toughness for a number of coatings: 1. TiN; 2. TiCN, 3. TiAlN, 4. TiAlN(M), 5. TiAlSiN(M), 6. TiAlCN⁹⁸

Figure 2. 43 Cross-section TEM micrograph showed the propagation of nanocracks in nc-TiAlN/a-Si₃N₄ nanolaminate coatings with $\Lambda=20\text{nm}$ ¹⁰⁵

2.4 Comments on the reviewed literatures

Nanocomposites bring about a new era for the hard coatings. But this improvement of hardness has often been satisfied at the expense of toughness. To achieve hard yet tough coatings, architectural modification is more effective than just doping of a toughening agent. As reviewed, architectural modification through multilayering can utilize the layer interfaces since the barrier can stop the crack propagation and at the same time the hardness is enhanced if the layer thickness can be carefully optimized. Toughness evaluation remains a challenging problem. In an attempt to quantify toughness, stress approach using indentation is the most straightforward but should be used with great caution due to the possible substrate effect. In comparison, energy approaches are more advanced. But their accuracies rely on the proper estimation of the crack dissipation energy. So far, there is no common agreement on this issue. Although it will not be

influenced by the substrate when carrying out the measurement on the free-standing coatings, a complicated procedure and many uncertainties in sample preparation may decrease the reliability of the obtain data.

Chapter 3

Problem Statement and Proposal

In Chapter 2, different toughening methodologies and corresponding mechanisms reported in the literature have been reviewed. The current use of these methods can be further improved. For example, increasing toughness with the least or even no sacrifice of hardness is most desired. As shown in Chapter 2, proper control of the bilayer thickness and the interface of multilayers are able to yield great hardness as compared to the monolayer structure. At the same time, the numerous interfaces intrinsically form great barriers to crack propagation. Thus, multilayering has the potential to promote strength and toughness simultaneously.

To date, multilayers used for mechanical machining are limited to polycrystalline/polycrystalline, polycrystalline/amorphous, and amorphous/amorphous combinations. Due to the superb strength of nanocomposite, it is expected that multilayers with one of the sub-layer being a nanocomposite may lead to a new breakthrough. On the other hand, to realize a hard-yet-tough ceramic coating, the adjacent sub-layer should be a soft-tough layer to further impede the crack propagation. The use of soft sub-layer has been reported previously ¹¹⁰⁻¹¹². It is interesting to notice that the hardness did not suffer a great drop as a result of incorporation of such soft-tough layer. In view of this, a hard/soft multilayer is proposed (Figure 3. 1). To study the effect of this combination, CrAlN prepared at specific negative bias voltage (will be discussed

in Chapter 5) will be selected as the soft sub-layer, while nc-CrAlN/a-SiN_x nanocomposite will be the hard one. The hardness and toughness of nc-CrAlN/a-SiN_x will be modified by changing the Si content (discussed in Chapter 6). On the basis of thorough understanding of the monolayer CrAlN and nc-CrAlN/a-SiN_x, the multilayers consisting of these two layers are to be fabricated. In Chapter 8, the influence of the bilayer thickness on the mechanical properties of the multilayers will be studied.

Figure 3. 1 Schematic of the novel multilayers, where one layer is soft-tough nitride coating and one layer is the hard-brittle nanocomposite formed from the soft one

Chapter 4

Experimental Details

4.1 Overview

Hard ceramic coatings with improved toughness are much desired but difficult to come by. Based on the literature review, toughening can be realized through optimal design of microstructure and architecture. This project starts from the fabrication of CrAlN coatings and nc-CrAlN/a-SiN_x nanocomposite. Afterwards, two toughening strategies are evaluated, namely, the addition of a toughening agent and modifying the coating architecture. To elaborate, in synthesizing CrAlN coatings, the mechanical properties are tailored by changing the applied bias voltage, which is an essential factor in determining the hardness and toughness. Different amounts of Si are then doped to fabricate the nc-CrAlN/a-SiN_x nanocomposite and the role of Si on the microstructure and mechanical properties is studied in detail. Based on these two fundamental studies, the toughening effects of Ni, the influence of Si distribution and the multilayering structure of CrAlN and nc-CrAlN/a-SiN_x combination are investigated subsequently. An overview of the project is given in Figure 4. 1.

Figure 4. 1 Methodological overview

4.2 Experimental procedure

The coating fabrication and microstructure characterization are essential in this project. An introduction to the sputtering system, specific deposition parameters as well as the characterization instruments employed is given in the following paragraphs.

4.2.1 Coating preparation

In this section, the deposition system and parameters used in fabricating different kinds of coatings are presented.

4.2.1.1 Sputtering system

The overview of the magnetron sputtering system is shown in Figure 4. 2. Three targets (6 inch in diameter) are mounted on the high performance water-cooled magnetrons, so that complex layer stacks can be produced without breaking the vacuum. The distance between the target and substrate is 150 mm, ensuring the full reaction of working gas and sputtered target atoms. The substrate can be heated to a maximum temperature of 500 °C (temperature is calibrated at the surface of substrate). Two direct current (DC) and one radio frequency (RF) power supplies (maximum output: 1200 W) operated in the constant power mode are applied to the selected target. The DC power supply can be operated in pulse mode. Another individual RF power supply is applied to the substrate, functioning in the grounded, floated or powered mode. The vacuum system consists of one rotary dry pump and one high-efficiency turbo pump. Up to three mass flow controllers (MFC) are used to regulate the gas composition and the pressure during deposition. All of the process parameters, such as the target power density, deposition temperature, shutter opening period, substrate bias and gas ratio, can be controlled and displayed by a computer program.

Figure 4. 2 Overview of the sputtering system

4.2.1.2 Coating deposition

Si wafer squares and stainless steel 420C (SUS420C) discs were used as the substrates (Figure 4. 3). The $2.5 \times 2.5 \text{ cm}^2$ Si wafer square was 400 μm in thickness. SUS420C disc was 16 mm in diameter and 5 mm in thickness. These discs were all grounded by using the silicon carbide abrasive papers (#240, #400, #600, #800, #1000 and #2000 in sequence) and then polished by using an aluminum suspension (BUEHLER, 0.05 μm) to get the scratch-free mirror surface. Before deposition, substrates were ultrasonically cleaned for 20 min in the

acetone followed by 10 min in ethanol for 3 cycles, and finished up with ultrasonic cleaning for 5 min in the de-ionized water. All the samples are dried in the flowing gas using purified nitrogen. After loading, a 15 min plasma etching was conducted at the bias voltage of 160 V (*i.e.* RF $V_b=160$ V) to remove oxides (but may not be all) and contaminants that may still cling to the surface of substrates.

Figure 4. 3 SUS420C and Si wafer square used in experiments

The base pressure in the sputtering chamber was pumped better than 5×10^{-5} Pa and the processing pressure was maintained at 0.4 Pa with Ar flow rate of 40 sccm (standard cubic centimeter per minute) and N_2 flow rate of 20 sccm. The deposition temperature was set at 400 °C. To sputter the metal target (*i.e.* Cr, Al or CrAl alloy), the pulsed DC power supply was used, operated in the synchronous pulsed mode (voltage-time waveforms of the magnetrons were in

the same phase) with the frequency of 20 kHz and reverse time of 5 μ s. The use of pulsed DC power can eliminate arcing problems in the reactive sputter deposition, stabilize the discharge and reduce the formation of defects in the coatings³³. To sputter the non-metallic target (*i.e.* Si), RF power supply (radio frequency of 13.65 MHz) was adopted and operated at auto-matched mode. The purity of the targets are: Cr-99.95, Al-99.95, Cr_{0.7}Al_{0.3}-99.95 and Si-99.99 (all in at.%). To avoid unnecessary thermal stress, coated samples were cooled down to the room temperature (25 °C) in the vacuumed chamber without gas flowing before taking out. Specific deposition parameters are described in detail in the following.

(a) CrAlN coatings

Cr and Al targets were co-sputtered in Ar/N₂ atmosphere to synthesize CrAlN coatings. The power densities on the Cr and Al targets were set at 2.2 W/cm² and 3.3 W/cm², respectively. The negative RF bias voltage (V_b) was varied from 50 to 260 V. Specific deposition parameters are listed as follows in Table 4. 1.

Table 4. 1 Deposition parameters in fabricating CrAlN coatings

Coatings	CrAlN-50	CrAlN-160	CrAlN-210	CrAlN-260
Base pressure (Pa)	<1.3×10 ⁻⁵			
Working pressure (Pa)	0.4			
Ar: N ₂ gas ratio	2:1			
Total gas flow (sccm)	60			
Plasma etching	15 min Ar ⁺ bombardment at 0.4 Pa at V_b =160 V			
Substrate temperature (°C)	400			
Al Power density (W/cm ²)	3.3			
Cr Power density (W/cm ²)	2.2			
RF negative bias voltage (V)	50	160	210	260
Coatings thickness (nm)	~1000			
Substrate	Si wafer (100) and SUS420C			

(b) nc-CrAlN/a-SiN_x nanocomposite

Incorporation of Si into CrAlN was conducted via co-sputtering of Cr, Al and Si targets in Ar/N₂ atmosphere. Specific deposition parameters are summarized in Table 4. 2.

Table 4. 2 Deposition parameters in fabricating nc-CrAlN/a-SiN_x coatings

Coatings	CrAlSiN-1	CrAlSiN-2	CrAlSiN-3	CrAlSiN-4
Base pressure (Pa)	<5×10 ⁻⁵			
Working pressure (Pa)	0.4			
Ar:N ₂ gas ratio	2:1			
Total gas flow (sccm)	60			
Plasma etching	15 min Ar+ bombardment at 0.4 Pa at V _b =160 V			
Substrate temperature (°C)	400			
Al Power density (W/cm ²)	3.3	3.3	3.3	2.2
Cr Power density (W/cm ²)	2.2	2.2	2.2	1.5
Si Power density (W/cm ²)	1.4	2.7	4.1	4.1
RF negative bias voltage (V)	160			
Coating thickness (nm)	~1000			
Substrate	Si wafer (100) & SUS420C			

(c) CrAlSiN coatings with gradient Si distribution

Homogeneous grading of Si in the CrAlN was realized through gradual increase of the power on the Si target (Figure 4. 4(a)). Two series of graded coatings were prepared and identified by the concentration varied through the thickness. CrAlSiN-GL was made by changing the power density of Si target from 0 to 2.7 W/cm² (increase rate of 0.2 W/cm²/10 min). CrAlSiN-GH was made by changing the power density of Si target from 0 to 4.1 W/cm² (increase rate of 0.3 W/cm²/10 min). On the other hand, heterogeneous grading of Si (denoted as CrAlSiN-L) was achieved by changing the Si content in different layers of identical thickness (Figure 4. 4(b)). Specific deposition parameters are listed in Table 4. 3.

Figure 4. 4 Schematic of nc-CrAlN/a-SiN_x with gradient Si distributionTable 4. 3 Deposition parameters used in fabricating nc-CrAlN/a-SiN_x nanocomposite with gradient Si content

Coatings	CrAlSiN-GL	CrAlSiN-GH	CrAlSiN-L*
Base pressure (Pa)		$<5 \times 10^{-5}$	
Working pressure (Pa)		0.4	
Ar:N ₂ gas ratio		2:1	
Total gas flow (sccm)		60	
Plasma etching	15 min Ar+ bombardment at 0.4 Pa at V _b =160 V		
Substrate temperature (°C)		400	
Al Power density (W/cm ²)	2.2	2.2	B:3.3 I:2.2 U:2.2
Cr Power density (W/cm ²)	1.5	1.5	B:2.2 I:1.5 U:1.5
Si Power density (W/cm ²)	0-2.7	0-4.1	B:1.4 I:2.7 U:4.1
RF negative bias voltage (V)		160	
Coating thickness (nm)		~1000	
Substrate	Si wafer (100) & SUS420C		

*: B-Bottom Layer, I-Intermediate Layer, U-Upper Layer

(d) Ni doped nc-CrAlN/a-SiN_x nanocomposite

Doping Ni into nc-CrAlN/a-SiN_x was realized via co-sputtering of the Cr_{0.7}Al_{0.3}, Ni, and Si targets in the Ar/N₂ atomosphere. Specific deposition parameters are summarized in Table 4. 4.

Table 4. 4 Deposition parameters in fabricating Ni doped nc-CrAlN/a-SiN_x nanocomposite

Coatings	CrAlSiN	CrAlSiNiN-1	CrAlSiNiN-2	CrAlSiNiN-3	CrAlSiNiN-4	CrAlSiNiN-5
Base pressure (Pa)				$<5 \times 10^{-5}$		
Working pressure (Pa)				0.4		
Ar: N ₂ gas ratio				2:1		
Total gas flow (sccm)				60		
Plasma etching				15 min Ar ⁺ bombardment at 0.4 Pa at V _b =160 V		
Substrate temperature (°C)				400		
CrAl Power density (W/cm ²)	2.2	2.2	2.2	2.2	2.2	2.2
Ni Power density (W/cm ²)	0	0.2	0.3	0.6	1.1	2.2
RF negative bias voltage (V)				160		
Coatings thickness (nm)				~2000		
Substrate				Si wafer (100) & SUS420C		

(e) Multilayered [pc-CrAlN]/[nc-CrAlN/a-SiN_x]

The multilayer structure was realized by controlling the on-off state of the shutter on the Si target. The thickness of each sub-layer was controlled by varying the shutter-opening period. A schematic of the designed structure is shown in Figure 4. 5.

Figure 4. 5 Schematic of the multilayer structure

In this case, the bilayer thickness (*i.e.*, one layer of nanocomposite plus one layer of pc-CrAlN, denoted as Λ) of the multilayer was 10, 20, 40 or 60 nm. The

thickness ratio of the sub-layers is controlled at 1:1. Specific deposition parameters are listed as follows in Table 4. 5.

Table 4. 5 Deposition parameters in fabricating multilayers

Coatings	mt-10	mt-20	mt-40	mt-60
Base pressure (Pa)	<5×10 ⁻⁵			
Working pressure (Pa)	0.4			
Ar: N ₂ gas ratio	2:1			
Total gas flow (sccm)	60			
Plasma etching	15 min Ar ⁺ bombardment at 0.4 Pa at V _b =160 V			
Substrate temperature (°C)	400			
Bilayer period (nm)	10	20	40	60
Sub-layer thickness ratio	1:1	1:1	1:1	1:1
Al Power density (W/cm ²)	2.2	2.2	2.2	2.2
Cr Power density (W/cm ²)	1.4	1.4	1.4	1.4
Si Power density (W/cm ²)	4.1	4.1	4.1	4.1
RF negative bias voltage (V)	160			
Coatings thickness (nm)	~1000			
Substrate	Si wafer (100) & SUS420C			

4.2.2 Microstructure characterization

The chemical concentrations, chemical bonding states, morphology and crystalline structure of the coatings were evaluated using a spectrum of characterization instruments. In the following, characterization techniques used are described in detail.

4.2.2.1 Chemical concentrations

To evaluate the chemical concentrations of the homogeneous or monolayer coatings, Field Emission Electron Probe Micro-Analyzer (FE-EPMA, JEOL JXA-8500F) was employed. This technique utilizes a comparison of emitted x-ray intensity from a sample relative to a known standard (*e.g.* pure element) and converts the relation to the mass concentration by using the ZAF correction as

described in equations (4.1) and (4.2). The acronym “ZAF” describes a procedure in which corrections for atomic number effects (Z), absorption (A) and fluorescence (F) are calculated separately from suitable physical models.

$$k = \frac{I^{sample}}{I^{standard}} \quad (4.1)$$

$$C = k \times ZAF \quad (4.2)$$

C is the mass concentration of the detected element

Z is the factor of atomic number correction

A is the factor of absorption correction

F is the factor of fluorescence correction

Atomic number correction (Z) deals with the atomic number effect, which controls the amount of incident energy from the electron that is actually put into the sample. The atomic number effect consists of two components: backscattering factor (F_b) and electron-stopping power factor (F_s). Both are a function of the atomic number. The backscattering factor reflects the X-ray intensity lost due to backscattering. For materials of lower atomic number (*i.e.* less than 30), more electrons stay within the material and produce X-rays and thus the F_b is small (*i.e.* rarely exceeds 1.2). The electron-stopping power factor relates the amount of incident energy to the amount absorbed by atoms of specific atomic number. Normally, the electron-capture cross-section decreases with increasing atomic number. The net Z correction factor for both effects is: $F_b \times F_s$.

Since X-rays are generated below the surface of the sample, the emergent radiation suffers absorption prior to detection. The absorption correction (A) is a function of the take-off angle (or length of path traversed by the X-rays), the

distribution of X-ray, the wavelength of the emergent X-ray and the elements present. The fluorescence correction deals with the concentrations of fluorescing elements and elements fluoresced. In general, the correction for fluorescence is the least important factor in the *ZAF* correction.

In this project, the EPMA is equipped with wavelength-dispersive spectrometry (WDS) and energy-dispersive spectrometry (EDS) allowing the detection of five elements by WDS and 16 elements by EDS. The sensitivity of WDS was 100 ppm and that of EDS was 1000 ppm. The accelerating voltage was set at 12 kV to achieve a detection depth of around 1 μm . The *ZAF*-corrected program used was CITZAF as installed in the EPMA and the elemental concentrations were obtained from the sampling at least three points on the surface of the specimen.

For the coatings in which the elements are not uniformly distributed (*i.e.* homogeneously gradient CrAlSiN coatings), Glow Discharged Optical Electron Spectroscopy (GDOES, Horiba JOBIN YVON) was used. GDOES can provide a depth profiling analysis and thus is useful for exploring the tendency of elements on the dependence of the coating thickness. During the testing, Ar was used and the process was processed at the pressure of 1 kPa. The coated sample served as the cathode. When discharge was ignited, the Ar^+ ions formed in the plasma were accelerated toward the sample surface by means of electric fields. These energetic ions stroked the sample surface and ejected sample atoms out. In a very short period, the solid sample was atomized. Some fraction of the excited sputtered atoms relaxed to lower electronic energy levels (often the ground state) via photon emission. The wavelengths of these photons were characteristic

for the emitting species. By measuring the intensity of the plasma emission at specific wavelengths, the elemental constituents of the sample can be quantitatively estimated ¹¹³. The optical resolution of this GDOES is between 18 and 25 pm and the wavelength measurement range is from 180 to 800 nm. The sensitivity is in the range of 10^{17} atoms/cm² and the depth resolution is in the nm range.

4.2.2.2 Bonding state

To determine the elements presented and their chemical states, X-ray Photoelectron Spectroscopy (XPS, Kratos AXIS) was employed. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons that escape from the top 1 to 10 nm of the material being analyzed. With a monochromatic Al-K alpha (1486.71 eV) X-ray radiation, XPS was operated at 15 kV/10 mA in a high vacuum (10^{-9} Torr) condition. All the samples are subjected to an argon ion etching (4 kV and 15 mA) for 3 min to remove the possible surface contaminations.

For each sample, a wide scan from 1200 to 0 eV with a step size of 1.0 eV was carried out first to determine the elements presented. Then a narrow scan was carried out at a step size of 0.1 eV within the binding energy range covering the peak position of the detected elements. A charge neutralizer was employed to neutralize charge accumulation during the analysis. Thereafter, the results were referenced to C 1s line of the adventitious carbon set at 284.6 eV. The peak fitting

of the various bonding configurations was carried out with the aid of Casa 3.14 program using the Gaussian-Lorentzian distribution function.

4.2.2.3 Morphology

The coating morphology was observed using Field Emission Scanning Electron Microscopy (FESEM, JEOL JSM-6701F) operated at the accelerating voltage of 5 kV. Coating thickness as well as the deposition rate is determined from the cross-sectional observation. The surface topography was determined using Atomic Force Microscopy (AFM, Veeco Dimension 3000) operated under the tapping mode (resolution of 512 pixels $\times$ 512 pixels in 1 $\times$ 1 μm^2 area at scanning frequency of 1.0 Hz) The root mean square of surface roughness (R_q) was obtained from the scanning area of 10 $\times$ 10 μm^2 . The AFM tips used in this project were made of silicon nitride with a pyramidal geometry. The tip radius is 30 nm and the tip height is 3.5 μm .

The microstructure was analyzed in detail using High Resolution Transmission Electron Microscopy (HRTEM, JEOL JSM-2100F) operated at the accelerating voltage of 200 kV. In transmission electron microscopy, the sample thickness is electron transparent ranged in $\sim$ 100 to 150 nm. Preparation of samples in such a thickness needs the devising of suitable methods and utmost care since the specimens are extremely thin and hence prone to bending and breaking. In this project, more concerns are given to the cross-sectional microstructure since the through-thickness architecture (*i.e.* the crystallinity, thickness of sub-layers and nature of the interfaces) is modified. Cross-sectional TEM specimens can be

prepared by making a sandwich structure followed by slicing, dimpling and ion beam thinning, or straightforwardly by using Focused Ion Beam (FIB) milling. For the monolayer coatings with homogeneous elemental distribution, the specimens (coated on the Si wafers) were sliced into small rectangular pieces (10 mm in length and 2.5 mm in breadth) and were cleaned in ethanol. A sandwich structure was prepared by bonding two slices using a fast-curing epoxy (M-bond 610 kit, VISHAY). This epoxy was applied to the surface of the coatings. While the epoxy set, the sandwich structure was clipped with pressure to ensure good chemical bonding between the pieces. Thereafter, the bonded sandwich structure was sliced into small strips (2.5 mm in length and 1 mm in breadth) using a diamond saw. The strip was then bonded to a 3 mm diameter copper grid with a single hole of about 2 mm diameter. The above processes were shown in Figure 4. 6. Afterwards, the copper grid was wax-mounted to a disc grinder to gradually reduce the thickness by using sand papers (in steps of #1200, #4000) and diamond lapping films. Once the specimen thickness was below $\sim 100\ \mu\text{m}$, it was subjected to an ion-beam (Model 691, Gatan) thinning directly without the necessity of dimpling. The typical conditions of ion milling in a high purity argon ambient are: gun angles $\pm 4^\circ$, voltage 4.5 kV for the initial, and $\pm 2^\circ$, 2 kV for the final polishing. The use of low voltage was to avoid artifacts induced by the heat generated from the kinetic energy of incoming ions. The milling process was monitored using an optical microscope with a CCD attachment at a magnification of X200.

Figure 4. 6 TEM cross-sectional sample preparation

For coatings with specific structure, for example gradient or multilayering structure, FIB milling was applied to ensure the entire layout throughout thickness could be thoroughly investigated. In this project, Nova 200 NanoLab from FEI was employed. Dual-beam (*i.e.* electron and Ga ion beam) columns, gas-injection system and an Omniprobe (or micromanipulator) were attached for imaging, ion-beam sectioning of a thin lamella and transfer/welding to the Cu grid. The operation procedures follow the instruction described in reference elsewhere ¹¹⁴. The thickness of the prepared TEM sample was in the range of 50 to 100 nm.

4.2.2.4 Crystalline structure

Information such as the lattice structure, film orientation and grain size were obtained from the X-ray Diffractometry. In order to eliminate the interference from the substrate (*i.e.* Si wafer or SUS420C), a Glancing Angle X-ray

Diffraction (GAXRD, Panalytical X'Pert Pro) with a Cu-K α 40 kV/30 mA X-ray source (wavelength $\lambda=0.15406$ nm) was employed. The glancing incidence angle was set at 1° and the 2θ scanning range was from 20° to 90° at the step size of 0.02° and 0.5 seconds per step. Grain size was estimated from the Williamson-Hall (*W-H*) plot ¹¹⁵, from which the peak broadening due to the grain size variation and the micro-strain were taken into account. The Williamson-Hall relationship is expressed as:

$$\frac{\beta_i \cos \theta_i}{\lambda} = \frac{K}{D} + \varepsilon \frac{4 \sin \theta}{\lambda} \quad (4.3)$$

β_i is integral breath (in radians, 2θ) of the i th Bragg reflection

$K=0.89$

D is the average grain size

ε is the root mean square microstrain of the lattice

$\lambda=0.15406$ nm (wavelength of Cu X-ray source)

In the *W-H* plot, the reciprocal of the intercept with *y*-axis and the slope of the line give the grain size and microstrain, respectively. An example of the *W-H* plot is shown in Figure 4. 7. The raw data is from the Figure 5.3 ($V_b=160$ V). In this plot, the slope (ε) is 0.51% and the intercept is 0.0155 nm^{-1} , indicating that the average grain size in this material is $0.89/0.0155=57.4$ nm

Figure 4. 7 William-Hall plot of CrAlN coating prepared at bias voltage of 160 V

The lattice parameter of the face centered cubic structure (*e.g.* for CrAlN structure) was calculated according to peak positions and distance between the crystal planes through the Nelson-Riley function [15]:

$$a_{\text{exp}} = d_{hkl} (h^2 + k^2 + l^2) \quad (4.4)$$

$$a_{\text{exp}} = a_0 + K\Phi(\theta) \quad (4.5)$$

$$\Phi(\theta) = \frac{\cos^2 \theta}{\sin \theta} \quad (4.6)$$

a_{exp} is experimentally calculated lattice parameter

a_0 is the true value

d_{hkl} is the interplanar spacing and (hkl) are the crystal plane Miller indices.

θ is the Bragg angle

K is the slope of a_{exp} as a function of $\Phi(\theta)$

Plotting a_{exp} against $\Phi(\theta)$ and extrapolating the fitted line to $\Phi(\theta)=0$ give rise to the true lattice parameter.

4.2.3 Mechanical properties

Hardness, Young's modulus and toughness are the most concerned in this project. Tribological performance will be also assessed to evaluate the practical usage of the hard yet tough ceramic coatings.

4.2.3.1 Hardness & Young's modulus

A Hysitron TI-900 TriboIndenter was used to perform the depth-sensing nanoindentation testing, in order to obtain the values of Hardness (H) and Young's modulus (E). Here, Poisson's ratio is assumed to be 0.25 as it is a typical

value used for CrAlN coating system ¹¹⁶. In all cases, the experiments were performed using a Berkovich diamond indenter. To minimize the mechanical vibrations and the effects of thermal drift, the equipment was located on a vibration isolation table and was completely enclosed in a cabinet at the room temperature (25 °C). In an effort to minimize the substrate effect, the depth of indentation was limited at less than 10% of the coating thickness. The mean and standard deviation of H and E were determined from at least 8 (a 4×2 array) measurements separated by a distance of 30 μm in both x and y directions.

The hardness measurement is based on the well-established Oliver-Pharr method ¹¹⁷, which assumes that a downward elastic deflection (a sinking-in effect) is always on the material surface against the indentation (Figure 4. 8(a)). In this method, a complete cycle of loading and unloading is continuously recorded. A schematic representation of a typical load versus indent displacement for an indentation experiment is shown in Figure 4. 8(b). Prior to the analysis of the load-displacement curve, several assumptions are made:

- I Deformation upon unloading is purely elastic.
- II The compliances of the specimen and the indenter tip can be combined as springs in series.
- III The edge of the contact is vertically displaced with respect to the initial position of the surface so that the deformation manner can be modeled as indenting on an elastic-plastic half space by a rigid axisymmetric indenter.

In Figure 4. 8(b), P and h denote the applied force and the corresponding displacement, respectively. In the indent cycle, three measurable parameters can be obtained for H and E computation, in terms of the maximum load (P_{max}), the maximum displacement (h_{max}) and the contact stiffness ($S=dP/dh$). In particular, S is determined from the slope of the fitted unloading curve at the upper portion. With these measured parameters, contact depth (h_c) defined as the depth along the indenter axis to which the indenter is in contact with the specimen at the peak load, can be determined from the following relation.

$$h_c = h_{max} - \varepsilon \frac{P_{max}}{S} \quad (4. 7)$$

$\varepsilon = 0.75$ for a Berkovich indenter ¹¹⁸

The projected area of the contact (A), is then deduced from an geometry function at the contact depth h_c

$$A = F(h_c) \quad (4. 8)$$

This function correlates the cross-sectional area of the indenter to the distance h_c from the indenter tip. Particularly for the Berkovich indenter, this function takes the form as

$$F(h_c) = 24.56h_c^2 \quad (4. 9)$$

Then, the hardness can be determined according to the equation

$$H = \frac{P_{max}}{A} \quad (4. 10)$$

And the effective Young's modulus (E_{eff}) is evaluated from the equation

$$E_{eff} = \frac{1}{\beta} \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A}} \quad (4. 11)$$

$$\beta = 1.034 \text{ for the Berkovich indenter }^{119}$$

Then, the Young's modulus (E) of the specimen can be obtained from

$$\frac{1}{E_{eff}} = \frac{(1-\nu^2)}{E} + \frac{(1-\nu_i^2)}{E_i} \quad (4.12)$$

E is the Young's modulus of the specimen

E_i is Young's modulus of the indenter (1141 GPa)

ν is the Poisson's ratio of the specimen

ν_i is the Poisson's ratio of the indenter (0.07)

Before practical measurement, the load frame stiffness must be calibrated and the tip area shape function must be corrected due to the imperfect manufactory of the indenter. In this project, these calibration procedures were carried out by indenting on a bulk fused silica. The use of fused silica is due to its isotropic feature in the elastic modulus and hardness, which can be identified as a linear-elastic solid at the room temperature. The surface of the fused silica is smooth (roughness less than 2-3 nm) and is free of additional oxides. The material parameter S^2/P is recorded as a function of the displacement range of 50 to 200 nm, where the data are not affected by the tip rounding. S^2/P was found to be independent of depth and the average magnitude is 682 ± 5 GPa. This value is comparable with expected theoretical range of S^2/P for fused silica (656-770 GPa). In this regard, the load-displacement and the load frame stiffness are considered calibrated¹¹⁷. Afterwards, the indenter tip area function was corrected by evaluating the H and E of the fused silica. Over the displacement range of 50 to 200 nm, the average of H and E are 9.7 ± 0.1 GPa and 74.1 ± 0.5 GPa, respectively. This result indicates that the area function provided an accurate description of the physical geometry of the indenter tip when measuring range was at approximately 50 nm.

Figure 4. 8 (a) Schematic representation from a cross-section through an indentation, showing the maximum indentation depth $h_{\max}$, contact depth h_c , minimum indentation depth $h_{\min}$ and sinking-in condition (b) Schematic representation of a typical load versus indent displacement for an indentation experiment

4.2.3.2 Toughness

In this project, the toughness was evaluated from two approaches, using an indenter and a scratch tester. Indentation method relied on the analysis of cracks generated during elastic/plastic contact. These cracks emanate from the edge of the contact impression and are oriented normal to the specimen surface plane, as shown in Figure 4. 9. The toughness was then calculated using the equation (2.15). H and E are the average value directly measured from the indentation test and the crack length c is the average of the measured crack length in each indent mark.

Figure 4. 9 Characteristic radial traces of the cracks left on the specimen surface after unloading (a) Vickers indent impression (b) Cubic-corner or Berkovich indent impression

Micro-indenter (CSM Micro Indenter) with Berkovich tip was used to generate the indent mark with the radial cracks. As discussed in Chapter 2, a shallow indentation depth usually leads to difficulty in precisely measuring the radial crack length even using SEM. However, large indent force often introduces inevitable influence of the substrate. To minimize the substrate effect, a linear extrapolation to about 10% of the coating thickness was applied to the calculated toughness obtained at different indent depths⁶⁶. To ensure the testing reliability, an indentation array was made, including 16 indent marks (4×4) spaced by an interval of 30 μm in both x and y directions.

For those coatings whose toughness cannot be measured from indentation (*i.e.* which are too brittle), the scratch test was employed as an alternative. The scratch test involves a loaded diamond stylus (usually a Rockwell C profile) moving across the coated surface at ever-increasing loads until at some critical Load. The use of scratch test to evaluate the toughness is due to the fact that this

test does not only provide the information of the adhesion of thin films to substrates, but also the deformation behavior beneath and ahead the moving style. As mentioned in Section 2.2.1.2, the deformation resultant failure is associated to the critical load, which can be used to determine the scratch toughness. Burnett *et al.*¹²⁰ have systematically studied the common failure types, as illustrated in Figure 4. 10. As shown in Figure 4. 10 (a) and (b), the spalling and buckling coating failure modes occur as a result of the compressive stress field preceding the moving stylus. Spallation is the result of total delamination (adhesive failure) while bulking coating failure, at some characteristic distance ahead of the stylus, results in buckling and cracking in a roughly semicircular arc in front of the scratch. When this buckling or spalling is close to the leading edge of the stylus the chip may be ridden over and embedded in the bottom of the track, whereas beyond the edges of the scratch such regions will still be free to spall, resulting in a crack with regular chipping on either side (Figure 4. 10 (c)). The remaining failures, such as conformal cracking and tensile cracking (Figure 4. 10 (d) and (e)), occur when the coating remain fully adherent. Conformal failure mode consists of cracking belonging to the scratch only. The cracks follow semicircular trajectories parallel to the leading edge of the stylus. This phenomenon is due to the tensile bending moments within the coating as the stylus is pushed down underneath. Tensile cracking failure mode appears similar to the conformal cracking. The semicircular crack traces are now parallel to the trailing edge of the indenter, showing the mirror image of the conformal cracking. The formation of these cracks is due to the tensile frictional stresses present behind the trailing edge of the stylus. It is believed that these stresses balance the compressive frictional stresses ahead.

Figure 4. 10 Schematic representation of coating failure modes in the scratch test in profile and plan views: (a) spalling failure (b) buckling failure (c) chipping failure (d) conformal cracking (e) tensile cracking ¹²⁰

In this study, scratch toughness was evaluated through a micro-scratch test (J&L Tech. Scratch Tester). Tested coatings were deposited on the stainless steel substrates (SUS420C). A sketch of the system is illustrated in Figure 4. 11. Applied linear load was set to vary from 0 to 50 N. The scanning length was set at 5 mm with scanning speed of 0.08 mm/s. Figure 4. 12 shows the typical results

after scratch test. The load at which an acoustic signal first emitted was regarded as the lower critical load (L_{c1}) of the onset of cracking. The load associated with a sudden change of coefficient of friction was considered as the higher critical load (L_{c2}) corresponding to the coating spallation (total delamination between coatings and substrate) ^{121, 122}. To ensure the data reliability, visual verification of all the occurrences of cracking was carried out using a built-in optical microscope.

Figure 4. 11 (a) Schematic of the scratch test (b) experiment layout of the scratch tester

Figure 4. 12 A typical scratch profile with information of normal load, acoustic emission signal and friction force

4.2.3.3 Residual stress

The residual stress (σ) calculated by the Stoney's equation (4.13) ¹²³ was determined from the change in the radius of of the Si substrate before and after the deposition. The curvature change was measured using a surface profiler (Taylor Hobson, TALYSCAN 150).

$$\sigma = \frac{E_s}{6(1-\nu_s)} \frac{t_s^2}{t_c} \left(\frac{1}{R_2} - \frac{1}{R_1} \right) \quad (4.13)$$

$E_s/(1-\nu_s)$ is the substrate biaxial modulus (180.5 GPa for Si (100) wafers)

t_s is the substrate thickness (*i.e.* 400 μm)

t_c is the coating thickness

R_1 is the curvature radius of the substrate before deposition

R_2 is the curvature radius of the substrate after deposition

4.2.3.4 Tribology

The tribological performance was evaluated using a ball-on-disk micro-tribometer in a lubricant-free sliding condition. The equipment layout is shown in Figure 4. 13. In this study, a WC-6%Co ball of a diameter 6 mm was selected as the counterpart against the coated SUS420C discs. The applied normal force was set at 2 N and the initial Hertz pressure was around 0.7 GPa. The relative humidity (RH) was controlled in the range of 60–65 RH% at the temperature of 25 °C. The sliding speed, the radius of wear track and total sliding distance were fixed at values of 200 rpm, 4 mm and 1000 m, respectively.

Figure 4. 13 Equipment layout for a ball-on-disk tester, where F is the normal force applied to the ball, r is the ball diameter, R is the radius of the wear and w is the rotational speed of the disc

Chapter 5

Effect of Negative Bias Voltage on pc-CrAlN Coatings

The review of Section 2.1.1.1 showed that the mechanical properties of CrAlN can be manipulated via the deposition conditions, *i.e.* parameters such as working pressure ^{22, 23, 27-30} and bias voltage ^{19, 25, 37}. However, there are very limited studies concerning the influence of bias voltage on the toughness. The results of Xu *et al.* ³⁷ indicated that proper control of negative bias voltage can simultaneously improve toughness and hardness of the CrAlN coating. However in that study, no insight is provided from the microscopic viewpoint. Furthermore, the toughness obtained by Xu *et al.* is the mixture of the coating and the AISI H13 substrate. Therefore an overestimation of the coating toughness may occur, since the toughness of the AISI H13 substrate is at least one order of magnitude larger than that of the coating.

In light of these considerations, the following studies re-evaluate the essential role of the negative bias voltage in determining the hardness and toughness of CrAlN. The deposition procedure has been outlined in Table 4. 1. More specifically, only the negative bias voltage was varied (*i.e.* $V_b=50$ V, 160 V, 210 V, 260 V) while all the other deposition parameters were kept constant.

5.1 Deposition rate

The influence of bias voltage on the deposition rate of CrAlN is shown in Figure 5.

1. The deposition rate continuously decreased from 12.6 to 7.1 nm/min when the

negative bias voltage increased from 50 to 260 V. This decline in the deposition rate originates from the back-sputtering of the as-deposited coatings, *i.e.* kicking off the adatoms from the growing surface by the energetic incoming ions.

Figure 5. 1 Deposition rate of CrAlN at different value of the negative bias voltage

5.2 Chemical composition and bonding state

The average chemical composition determined by the EPMA is listed in Table 5.1. The results show that the N content for all the samples is around 55 at.%. The Al/(Al+Cr) content ratio ranges from 0.373 to 0.408. A similar trend was also reported previously in Ref. ³⁷. When bias voltage increases, the sputtered Al can be accelerated more than the Cr, since the mass of Al is smaller than that of Cr. As such, more Al can reach to the substrate. An inevitable oxygen contamination is observed, which is due to the residual gases in the deposition chamber or from impurities in the Ar or reactive N₂.

Table 5. 1 Summary of the chemical concentrations of as-deposited coatings determined by EPMA

Sample	Negative Bias Voltage (V)	Concentration (at. %)				Al/(Al+Cr)
		Cr	Al	N	O	
CrAlN-50	50	27.9	16.8	54.4	0.9	0.375
CrAlN-160	160	28.5	17.4	52.6	1.5	0.379
CrAlN-210	210	28.9	17.2	53.1	0.8	0.373
CrAlN-260	260	24.8	17.1	57.4	0.7	0.408

Figure 5. 2 plots the XPS narrow scan results of the CrAlN coatings at varied bias voltage. Cr $2p_{3/2}$ (binding energy 575.5 eV) and Cr $2p_{1/2}$ (binding energy 585.1 eV) lines are assigned to the CrN bonds ¹²⁴. No peaks of Cr₂N can be observed (Cr $2p_{3/2}$, binding energy 574.3 ± 0.4 eV ¹²⁴). The absence of the Cr₂N phase can be double confirmed from the scanning results of N 1s. As documented in Ref. ¹²⁵, the binding energy of N in Cr₂N is 397.4 eV, ~ 1 eV higher than that of CrN (binding energy 396.5 eV). From Figure 5. 2(b), only the peak assigned to CrN bond can be observed. As such, the existence of Cr₂N can be ruled out with confidence. In Figure 5. 2(c), the AlN bond is revealed from the peak centered at 74.1 eV. The asymmetric shoulder at higher binding energy is attributed to the overlap with Cr 3s line ^{24, 126}.

5.3 Crystalline structure

The dependence of XRD pattern on the negative bias voltage is illustrated in Figure 5. 3. Since the amount of Al is far less than the threshold beyond which the precipitation of hcp-AlN takes place, only solid solution CrAlN forms ²². This is verified by comparing with the referenced diffraction patterns of hcp-AlN (JCPDS 46-1200, Figure 5. 4(b)). No peaks of hcp-AlN can be observed in the XRD results.

On the other hand, typical diffraction peaks (111) at 37.7° , (200) at 43.8° , (220) at 63.7° and (311) at 76.5° confirm the fcc structure of CrAlN. Comparing with the referenced diffraction patterns of fcc-CrN (JCPDS 11-0065, Figure 5. 4(a)), the peaks of CrAlN solid solution are slightly shifted toward larger angle in peak position, indicating the lattice distortion due to the substitution of Cr by Al atoms.

Figure 5. 2 XPS core-level spectra of (a) Cr 2p (b) N 1s (c) Al 2p

Figure 5. 3 GAXRD results of CrAlN coatings at different bias voltage

Figure 5. 4 Referenced diffraction patterns of (a) fcc-CrN powder and (b) hcp-AlN powder

Owing to the increased bias voltage, peak broadening was also observed, indicating the reduced grain size. Using Williamson-Hall method, crystallite size and lattice strain are calculated and summarized in Figure 5. 5. With increased bias voltage, grain size of CrAlN drops from 52 to 13 nm and the micro-strain increases accordingly. Increase of the bias voltage can generate growing amount of defects due to the penetration of ions that leads to an increasing number of nucleation sites thus preventing the growth of the existent grains^{33, 127}.

Figure 5. 5 Calculated grain size and microstrain of CrAlN coatings at different bias voltage

In Figure 5. 3, the grain growth orientations of the as-deposited coatings are strongly related to the applied bias voltage. As V_b increased from 50 to 210 V, the I_{111}/I_{220} ratio decreased from 0.55 to 0.07. In general, the orientation evolution is determined by the minimization of free energy of the coatings, including surface and strain energies. In the normal condition, the vertical build-up of grains occurs on low energy surfaces. It has been proved that in the fcc structure,

the (111) type planes have the lowest surface energy ¹²⁸. However, the increased coating thickness and the additional kinetic or thermal energy incorporated in the deposition process would introduce higher strain energy, thus result in the change of coating orientation ³³. The dependence of kinetic energy of ions on the negative bias voltage is expressed as ⁶⁶:

$$E_i \propto \frac{D_w V_b}{P^{1/2}} \quad (5.1)$$

D_w is the power density of the target

E_i is the sputtered ion energy

V_b is the bias voltage

P is the process pressure

At increased V_b , moving ions can transfer more momentum to the coating surface. Fast diffusion takes place before the ions come to rest due to the extra energy. During this process, these adatoms collide with each other and result in a re-arrangement of the lattice atoms, thus will cause considerable increase of strain energy. To minimize the strain energy, adatoms arrange themselves into the less stressed plane. Taking into consideration the packing factor (PD) of the fcc structure (*i.e.* PD(111)>PD(200)>PD(220)), incoming adatoms tend to stay and form in the less dense (220) planes, since forcing an atom onto a denser plane would generate more strain than onto a more loosely packed plane. Here, the influence of the coating thickness on the strain energy can be ignored since all the coatings are of $\sim 1 \mu\text{m}$.

Therefore, the driving force to decrease the overall energy accounts for the dominant growth on the (220) planes and the suppressed growth on the (111) planes, when V_b increased from 50 to 210 V. When V_b further increases to 260 V,

random growth of crystallites occurs. It is believed that the re-arrangement of adatoms is caused by the enhanced thermal energy since the surface temperature increases rapidly when coatings are exposed to the intensive ion bombardment.

5.4 Microstructure

The dependence of cross-sectional morphology and surface roughness on the negative bias voltage will be discussed in the following paragraphs. The relationship between the coating morphologies and the deposition V_b are disclosed.

5.4.1 Cross-sectional morphology

As bias voltage increases, the coating morphology evolves from a columnar structure to a dense structure (Figure 5. 6). At $V_b=50$ V, the coating possesses the morphology that consists of columnar grains of large width. Increased bias voltage ($V_b=160$ V) results in the reduction of the width and the finer columns. When V_b exceeds 210 V, only dense glassy structure remains. This evolution can be explained by taking into consideration the SZD mode proposed by Barna ¹⁷. The Barna structure zone model illustrates the dependence of the morphology on the homologous temperature (T_s/T_m). Here, T_s is denoted as the substrate temperature and T_m is denoted as the melting temperature of the material. In this diagram (Figure 5. 7), Zone I is the columnar structure with pronounced pores and open columnar boundaries. At a higher T_s/T_m , Zone T shows dense array of

fibrous grains, since increased substrate temperature leads to the enhanced surface diffusion of adatoms.

Figure 5. 6 Cross-sectional morphology at different bias voltage (a) 50 V (b) 160 V (c) 210 V (d) 260 V

In this case, the melting temperature (T_m) of CrAlN is around 2445 K ¹²⁹ while the substrate temperature (T_s) is around 673 K assuming that temperature increase is small at lower bias voltage (*i.e.* $V_b=50$ or 160 V); this gives rise to T_s/T_m of 0.28 . When $0.2 < T_s/T_m < 0.4$, the surface diffusion of crystallites is remarkable while the grain boundary migration is strongly limited¹⁷. As a consequence, the coating structure is inhomogeneous along the coating thickness, resulting in V-shaped grains owing to the competitive growth of differently oriented neighboring crystals. At increased bias voltage (*i.e.* $V_b=210$ or 260 V), however, the ionized particles in the plasma are able to deliver high momentum to the substrate and create more chance of crystal re-nucleation. Hence, the grain boundary migration and restructuration become prevalent thus leading to the less textured and denser structure. Therefore, the morphology evolution is attributed to a sputter-induced redistribution of adatoms during growth process.

Figure 5. 7 Barna structure zone diagrams ¹⁷

Further investigation using TEM reveals that the width of the columnar grains in CrAlN coatings prepared at $V_b=50$ V is around 60 nm (Figure 5. 8(a)), while finer columnar grains with width of less than 30 nm at $V_b=160$ V (Figure 5. 8(b)). This trend is consistent with the calculated grain size from the XRD diffraction pattern. Several crevices are identified between the columnar grains as pointed by the arrows in Figure 5. 8(a). In comparison, no columnar structure is detected (Figure 5. 8(c)) in the coating prepared at $V_b=260$ V, but only a dense and compact structure. This variation of the microstructure produces the different mechanical properties, which will be discussed in section 5.5.

Figure 5. 8 TEM image of CrAlN coatings prepared at bias voltage of (a) 50 V (b) 160 V (c) 260 V

Figure 5. 9 demonstrates a typical selected area diffraction patterns of CrAlN coatings prepared at $V_b=160$ V. Crystalline rings in terms of (111), (200), (220) and (311) are clearly distinguished, confirming the fcc-structure. The dispersed spots arranged in the rings indicate larger crystallites (compared to crystal size of the nc-CrAlN/a-SiN_x nanocomposite and will discuss later in 6.1.4), as described in the similar study in Ref. ³⁸.

Figure 5. 9 SAD image of CrAlN coatings prepared at $V_b=160$ V

5.4.2 Surface topography

Surface morphology is another concern in optimizing the coating synthesis. Figure 5. 10 displays the surface roughness as a function of bias voltage. With increased bias voltage, the surface roughness declines from 17 to 5 nm. This decline can be interpreted from the viewpoint of ion kinetic energy. The

increased bias voltage results in the increase of the mobility of impinging atoms. Therefore, the higher degree of lateral diffusion of the incoming adatoms results in smoothing the roughness. However, extremely high bias voltage may lead to a rougher surface due to the considerable defects (*i.e.* edge dislocations inside column grains and distorted lattice) from the intensive ion bombardment¹³⁰, which is one reason of restricting the maximum negative bias voltage to no more than 260 V.

Figure 5. 10 Surface topography of CrAlN prepared at the different V_b

5.5 Mechanical properties

Hardness, Young's modulus and toughness are found to be in a close relation with the residual stress. This is the subject of the following discussion.

5.5.1 Residual stress

During sputtering, intensive ion bombardment usually leads to large internal stress in the as-deposited coatings (*e.g.* up to a few GPa as in diamond-like carbon coatings⁸⁰). This phenomenon is originated from the fact that the incoming atoms knock atoms out of their lattice position and bring about atom-collision cascades, if sufficient kinetic energy is provided to the atoms. As a consequence, the rearrangement of lattice atoms takes place and thus the resultant stress. As mentioned in the review paper by Sam *et al.*¹, proper level of stress would increase coating's hardness but too large stress is harmful since the coatings tend to be delaminated from the substrate. Given this reasoning, optimizing residual stress is crucial for the coating performance.

Figure 5. 11 illustrates the residual stress as a function of negative bias voltage. As expected, the residual stress increases from -0.7 to -1.4 GPa (where the minus sign indicates that the stress is “compressive”) as V_b increases from 50 V to 260 V. The increase of residual stress is attributed to the promoted ion peening effect due to the higher V_b , as observed in the case of TiC coatings synthesized by a filtered cathodic arc technique¹³¹ and in the cases of magnetron sputtered TiN¹³² and TiC¹²⁷ coatings. It is noted that the residual stress increases rapidly when the bias voltage ranges from 50 to 210 V. However, little increase can be observed with further increase of V_b .

Figure 5. 11 Residual stress of CrAlN coatings as a function of bias voltage

To understand this tendency, thermal stress is taken into consideration. As well-known, residual stress originates from the extrinsic stress (*i.e.* thermal stress) and the intrinsic stress (*i.e.* coating growth induced stress and structural mismatch induced stress) ¹³³:

$$\sigma = \sigma_T + \sigma_g + \sigma_m \quad (5.2)$$

σ is the residual stress

σ_T is the thermal stress

σ_g is the coating growth induced stress

σ_m is the structure mismatch induced stress

As only one phase exists in CrAlN, it can be assumed that the effect of structure-induced mismatch stress is not present. Therefore, residual stress is mainly contributed from σ_T and σ_g . Thermal stress can be estimated from the differences of the coefficient of thermal expansion (CTE) and the differences of temperature by following relation ¹³⁴:

$$\sigma_T = \frac{E_c}{1 - \nu_c} \int_{T_1}^{T_2} (\alpha_s(T) - \alpha_c(T)) dT \quad (5.3)$$

T_1 is the temperature at which depositing specimen

T_2 is the temperature at which taking out specimen

α_s is the coefficient of thermal expansion of substrate
 α_c is the coefficient of thermal expansion of coating
 E_c is the Young's modulus of coating
 ν_c is the Poisson's ratio of coating

Herein, α_c can be estimated according to the rule of mixture. Using $\alpha_{fcc-CrN}=2.3 \times 10^{-6} \text{ K}^{-1}$ and $\alpha_{fcc-AlN}=5 \times 10^{-6} \text{ K}^{-1}$ ¹²⁹, α_c is estimated as listed in Table 5. 2. Taking $T_1=673 \text{ K}$ and $T_2=298 \text{ K}$, $\alpha_s=2.6 \times 10^{-6} \text{ K}^{-1}$ and $\nu_c=0.25$ ¹³⁵, thermal stress can be calculated, as is also listed in Table 5. 2.

Table 5. 2 Calculated CTE and thermal stress

Specimen	fcc-AlN(%) ^a	fcc-CrN (%) ^a	CTE(10^{-6} K^{-1})	E(GPa) ^b	σ_T (GPa)
CrAlN-50	37.5	62.5	3.31	235	0.09
CrAlN-160	37.9	62.1	3.32	261	0.10
CrAlN-210	37.3	62.7	3.31	311	0.12
CrAlN-260	40.8	59.2	3.40	368	0.15

^a: calculated based on the data from

^b: data from Figure 5. 12

It should be noted that the thermal stresses has a positive value, indicating that the thermal mismatch results in a tensile stress in the coatings. This is understandable, since CTE of the Si substrate is smaller than that of the coatings. Upon cooling, coating shrinkage is greater than that of the substrate. Since no delamination occurs, coating should be in a stretched state to satisfy the continuity between the coating and substrate. As the overall residual stress shows a negative value, the thermal stress must play a role in offsetting the compressive stress induced during coating growth (*i.e.* σ_g). From the calculated values listed in Table 5.2, such offsetting effect becomes stronger (*i.e.* larger value

of σ_T) as bias voltage increases. Therefore, only a slight growth of residual stress is observed when V_b increases from 210 to 260 V.

5.5.2 Hardness and Young's modulus

Hardness and Young's modulus as a function of bias voltage are plotted in Figure 5. 12. Lowest hardness (10.4 GPa) and Young's modulus (235 GPa) are observed in coatings prepared at $V_b=50$ V. With increased V_b , the hardness gradually increases to 25.8 GPa, and so does the Young's modulus, to 368 GPa. The comparably lower hardness at lower V_b (*i.e.* 50 V and 160 V) is due to the large grains (*i.e.* around 52 nm) and less compact microstructure involved (Figure 5. 8 (a)). The dependence of hardness on the grain size is plotted in Figure 5. 13. The increase in hardness with higher V_b increase can be explained by the classical Hall-Petch effect, where the hardness is proportional to the $d^{-0.5}$. The decreased grain size can result in increased grain boundary fraction, thus providing additional hindrance to the dislocation mobility⁸⁻¹⁰. On the other hand, the increased residual stress also contributes to the strength improvement as a result of the stress hardening, which is another hardening mechanism often occurred in PVD process, as suggested in the Ref. ¹. Hence, the enhanced strength or hardness is the macroscopic manifestation of the synergistic effect of the decrease of crystallite size and compressive stress upon ion bombardment.

Figure 5. 12 Hardness and Young's modulus of CrAlN coatings at different negative bias voltage

Figure 5. 13 Hardness as a function of grain size

5.5.3 Toughness

Indentation toughness

As reviewed in Section 2.2.2.1, there always exists a cracking threshold of the applied force, below which the cracking would not occur. Figure 5. 14 shows the indent marks on the CrAlN coated onto a Si substrate. Subject to different levels of indent force, the coatings present different cracking patterns. At 700 mN, well-

defined radial cracks (*i.e.* $c > 2a$) can be easily observed. At 250 mN, no such cracks can be identified even at higher magnification with the aid of the SEM.

Figure 5. 14 Indent marks (Berkovich indenter) on the CrAlN fabricated at $V_b=160$ V under indent force of (a) 700 mN (b) 250 mN

The existence of the cracking threshold leads to the difficulty in clearly observing the crack length at lower indent force. Therefore, to generate measureable cracks, larger indent force is intentionally applied. However, the influence of the substrate when applying a large force is inevitable. Therefore, as the indent depth exceeds one tenth of the coating thickness, the elastic-plastic zone may extend to the substrate. In order to minimize the substrate effect, a first degree of estimation by using the linear extrapolation of toughness obtained at different indentation depth is thought to be an effective way to compensate. Figure 5. 15 shows the plot of the as-calculated toughness against the indentation depth, and the fitting parameters is summarized in Table 5. 3.

As seen from Figure 5. 15, when indentation depth decreases from 2.7 to 1.5 μm , the calculated toughness increases accordingly, indicating the significant substrate effect (toughness of Si substrate is around 0.9 GPa). The results of

interpolation toughness (shown by arrows in Figure 5. 15) indicate that the toughness increases from 1.7 to 2.0 $\text{MPa}\cdot\text{m}^{1/2}$ as V_b increases from 50 to 260 V. One reason for this improvement is the refining of the coating microstructure. With increased negative bias voltage, the occurrence of the defects (Figure 5. 8(a)) in between the columnar grains is prevented and thus there is less chance of through thickness cracking. In addition, the grain size drops drastically from 52 to 13 nm, giving rise to more extensive grain boundaries that may cause more crack bending or branching ¹³⁶. Moreover, the bias voltage induced growth of compressive stress also contributes. Normally, cracks initiate when tensile stress exceeds the critical value, hence, a higher level of compressive stress allows coatings to sustain more tensile strain before fracture ¹³⁷.

Figure 5. 15 Plot of calculated toughness of CrAlN coated onto a Si substrate prepared as a function of indent depth

Table 5. 3 Linear fitting of the toughness at different indentation depth

Samples	Fitting Curve	R ²
CrAlN-50	$y = -0.174x + 1.98$	0.85
CrAlN-160	$y = -0.100x + 2.02$	0.84
CrAlN-210	$y = -0.157x + 1.74$	0.94
CrAlN-260	$y = -0.107x + 1.67$	0.91

Scratch toughness

As reviewed in 2.2.1, the scratch test is an alternative method used to evaluate the toughness of coatings. As this project is not concentrating on the precise measurement of toughness, the scratch test can be employed to assess the toughening effect. Using linear-increasing-load mode in the scratch test, Ligot *et al.*¹³⁸ investigated the influence of intrinsic testing parameters on the value of the critical load. From their results, the effect of the loading rate (N/s) is much more significant than other parameters, such as scratching speed (mm/s). Therefore, the dependence of the average critical load on the loading rate was studied first at a given scratch length (5 mm) and maximum load (50 N) under linear-increasing-load mode. Figure 5. 16 shows the critical load versus the loading rate. With decreased loading rate, L_{c1} and L_{c2} (the characteristic forces described in section 4.2.3.2) increase accordingly, consistently with the results from Ligot *et al.*¹³⁸. At the loading rate of 0.8 N/s, the differences in the critical load are much more pronounced than at lower loading rates. Taking into consideration the practical conditions, in which higher contact force and rapid loading fluctuation may commonly take place, the loading rate of 0.8 N/s is preferred and corresponding data are adopted to interpret the toughness variation in this project. It should be pointed out that loading rates higher than 0.8 N/s easily

wear or even break the diamond tip of the stylus, which would result in tremendous measurement errors.

Figure 5. 16 (a) Lower and (b) higher critical load of CrAlN coatings as a function of the loading rate

Figure 5. 17 illustrates the scratch tracks. It is obvious that the CrAlN coating prepared at $V_b = -160$ V presents the lowest L_{c1} and L_{c2} . The plot of CPR_s (i.e. $L_{c1} \times (L_{c2} - L_{c1})$) versus the negative bias voltage is shown in Figure 5. 18. The indentation toughness is also inserted for comparison. When negative bias

voltage increases from 50 to 210 V, the tendency of scratch toughness is consistent with that determined by the indentation. At $V_b=260$ V, however, the scratch toughness drops drastically. This might be due to the fact that the adhesion degrades at higher bias voltage, thus causing in the interfacial fracture at a small critical load ($L_{c1}=6.4$ N and $L_{c2}=24.8$ N). This observation is supported by the results obtained by Wang *et al.*¹²⁷. In their study of TiC coatings, adhesion declined greatly when V_b exceeded 100 V.

Figure 5. 17 Scratch tracks of CrAlN with different negative bias voltage (black arrow: L_{c1} ; white arrow: L_{c2})

Figure 5. 18 Crack propagation resistance and indentation toughness as a function of negative bias voltage

Chapter 6

Influence of Si on nc-CrAlN/a-SiN_x nanocomposites

In this section, the influence of the Si content and its distribution in the nc-CrAlN/a-SiN_x nanocomposite will be discussed. Corresponding investigations will be given on the microstructure evolution and the mechanical property variation.

6.1 Effect of Si content on the nc-CrAlN/a-SiN_x nanocomposite

As reviewed in Chapter 2, the amount of Si is essential for the mechanical properties of nc-MeN/a-SiN_x nanocomposite. Therefore, in this section, Si is used to doped CrAlN to different extents. The influence of Si concentration on the microstructure and the mechanical properties on the will be investigated in the following paragraphs.

6.1.1 Deposition rate

Different Si contents are realized by varying the power density applied on the Si target during deposition (Table 4. 2). The variation in power density tends to alter the sputtering yield and thus changing the deposition rate. Figure 6. 1 presents the deposition rate as a function of power density on the Si target. With fixed power density on the Cr and Al targets, the deposition rate gradually increases with the increasing target power density on the Si target. According to

the elastic-collision theory, maximum possible energy transferred in the first collision, T_m , is given by

$$T_m = \frac{4M_1M_2}{(M_1 + M_2)} E \quad (6.1)$$

M_1 is the masses of the incident ions

M_2 is the masses of the target atoms

E is the energy of incident ions

The sputtering yield, S , is related to the T_m by the following equation.

$$S = k \frac{1}{\lambda(E) \cos \theta} \frac{M_1 M_2}{(M_1 + M_2)^2} E = k \frac{1}{\lambda(E) \cos \theta} T_m \quad (6.2)$$

k is the constant with respect to different target material

$\lambda(E)$ is the mean free path of elastic collisions near the target surface

θ is the incident angle of ions with respect to the normal of the target surface

In a first-order estimation, the sputtering yield is proportional to T_m . As power density increases, the energy of incident ions increases accordingly, resulting in the increase of T_m thus increasing the sputtering yield. As a consequence, the deposition rate grows.

Figure 6. 1 Deposition rate as a function of power density on the Si target

6.1.2 Chemical concentration and bonding state

Chemical composition of Si doped CrAlN measured by EPMA is summarized in Table 6. 1. As a result of Si addition, the Al/(Al+Cr) ratio experiences a slight increase from 0.38 to 0.4. Inevitable residual oxygen is also detected for the entire specimen.

Table 6. 1 Summary of chemical concentration of as-deposited coatings

Samples	Concentration (at.%)					Al/(Al+Cr)
	Cr	Al	Si	N	O	
CrAlN	28.5	17.4	-	52.6	1.5	0.380
CrAlSiN-1	28.6	17.6	0.4	51.9	1.5	0.381
CrAlSiN-2	26.7	16.8	1.8	53.6	1.2	0.386
CrAlSiN-3	23.4	15.6	5.9	53.8	1.3	0.400
CrAlSiN-4	21.4	13.5	8.5	55.2	1.4	0.387

Typical analysis of the bonding states is shown in Figure 6. 2. With 8.5 at.% Si, the major chemical bonds of CrAlSiN are confirmed. Cr 2p_{3/2} and Cr 2p_{1/2} are observed at 575.6 eV and 584.8 eV, respectively, corresponding to the Cr-N bond. The N 1s peak reveals two different chemical features: the one centered at 396.5 eV is for the Cr-N bond and the one at 397.7 eV is for the Si-N bond ¹³⁹. In the Si spectrum, no peaks can be observed at the bonding energy 99.0 eV, which is possibly related to Si⁰ ⁴⁴, Si-Cr bond or K_{α5,6} Al(2s) ⁴³. Also, no SiO₂ bond (binding energy 103.0 eV ⁴²) but only the Si-N bond at 101.8 eV is detected ⁴³. Since no stoichiometric determination is applied, only the presence of the phase of SiN_x is confirmed. Analysis of Si 2p spectrum corroborates the common tenor in the literature that Si prefers to form Si-N bonds due to its larger Gibbs free energy (ΔG , Si₃N₄= -642.1 kJ/mol ⁴³). However, no clear statement regarding the substitutional incorporation of Si into CrAlN can be made based on the XPS

results due to the comparable bonding structure presented for CrAl(Si)N and CrAlN/SiN environments. Dependence of the Si-N bond on the Si content is illustrated in Figure 6. 3. The signal is too weak to be detected when the Si content is 0.4 at.%. At higher Si content, an increased intensity of Si-N bond is observed without a chemical shift. The characteristic peak at 74.2 eV in the Al 2p spectrum (Figure 6. 2 (d)) indicates the formation of the Al-N bond ¹³⁹.

Figure 6. 2 XPS core level of (a) Cr 2p (b) N 1s (c) Si 2p and (d) Al 2p in CrAlSiN-4

Figure 6. 3 Evaluation of the Si narrow scan as a function of Si content

6.1.3 Crystalline structure

The X-ray diffraction patterns are found to be strongly dependent on the Si content, as illustrated in Figure 6. 4. From the XRD results, the variation of the preferred orientation is observed, manifested in the growth competition between (111), (200) and (220). The coating with Si content less than 1.8 at.% presents a similar XRD pattern to that of the CrAlN prepared at $V_b=160$ V (CrAlN-160), that is, only diffraction peaks (111) and (220) are observed. When Si content exceeds 1.8 at.%, the (200) peak emerges. This tendency is consistent with the results reported by Chen *et al.* ^{40, 132}, and the minimization of system energy is considered to account for this change. With increasing Si, the peaks become broader, indicating the refinement of the grain size. Using the Williamson-Hall method, the calculated grain size as a function of Si content is plotted in Figure 6. 5. As Si content increases, the grain size decreases from 52 to 8 nm.

It has been reported that the incorporation of Si may lead to the segregation of hcp-AlN⁴³. However, in this case, only peaks associated with fcc CrAlN are observed. This is attributed to the lower Al content involved that it does not exceed the critical point at which hcp-AlN precipitates²². In parallel, no peaks corresponding to crystalline silicon nitride can be identified. This is understandable, since sputtered silicon nitride retains the amorphous structure even at 1100 °C², which is much more larger than the temperature (400 °C) used in the current fabrication process. In conjunction with the results of XPS, it is inferred that Si leads to the formation of a-SiN_x and the amount of a-SiN_x should be proportional to the doped Si content.

Figure 6. 5 illustrates the grain size as a function of Si content. The decline of CrAlN grain size is due to the continuous interruption of grain growth by segregated a-SiN_x (this phenomenon will be discussed later in section 6.1.4). During this process, the segregated a-SiN_x serves as a surface cover layer that partially or completely limits the grain growth periodically, leading to a repeated re-nucleation and resulting in smaller grains¹⁷. With the growth of power density on the Si target, this process can be further promoted, since Si ion mobility or the reactivity in forming SiN_x is largely increased. It should be pointed out that with decreased size of CrAlN grains, the mean grain separation could become wider, which will exert a strong influence on the mechanical performance¹. A detailed discussed on this issue will be presented in section 6.1.5.

Figure 6. 4 GAXRD pattern of CrAlSiN with varied Si content

Figure 6. 5 Grain size of Si doped CrAlN as function of Si content

The lattice parameter as a function of Si addition is shown in Figure 6. 6. In the absence of Si, the lattice parameter is around 0.4143 nm, smaller than that of fcc-CrN powder ($a=0.415$ nm from JCPDS 65-2899). This is due to the substitution of Cr by the Al atoms, since the radius of Al (125 pm) is smaller than that of Cr (140 pm). With the increase of Si content up to 1.8 at.%, the lattice parameter undergoes a slight drop from 0.4143 to 0.4137 nm. This is caused by the enhanced substitution of Cr by the smaller Al atoms since the Al/(Al+Cr) ratio continuously increases (Table 6.1). However, further increased Si content (5.9 at.% and 8.5 at.%) leads to the increase of the lattice parameter to 0.4153 nm. The increase is caused by the decrease of residual stress. As shown in Figure 6. 6, compressive residual stress decreases by 44% when Si increases from 0 to 8.5 at.%. An increased amount of a-SiN_x is believed to account for the stress decline, since internal strain can be prevented due to the continuous interruption by the a-SiN_x during the grain growth ^{46, 140}. As once reported previously, 5 at.% addition of Si resulted in decrease of compressive stress by 50% as compared to that of pure CrAlN ⁴³. Therefore, the variation of lattice parameter is a synergetic contribution of the atom substitution and stress variation.

Figure 6. 6 Lattice parameter and residual stress as a function of Si content

6.1.4 Microscopic morphology

Figure 6. 7 reveals the evolution of the film growth. Increasing the Si content converts the rough columnar structure to less texture and denser structure. Refined grains caused by the increased amount of a-SiN_x phase accounts for the morphology evolution.

Figure 6. 7 Cross-sectional images of CrAlN (a) and CrAlSiN with different Si content (b) 0.4 at.% (c) 1.8 at.% (d) 5.9 at.% (e) 8.5 at.%

Direct observation of the nano-sized grains surrounded by a-SiN_x is illustrated in Figure 6. 8. CrAlN nano-crystallites of the size less than 10 nm are observed in Figure 6. 8(a). In parallel, analysis of the SAD pattern (Figure 6. 8(b)) proves that these crystallites are polycrystalline with fcc structure. Crystallographic rings are clearly seen and assigned to the (111), (200), (220) and (311) peaks, respectively, in agreement with the results of XRD. The effect of Si on the microstructure change in the CrAlN and CrAlSiN can be revealed by comparing Figure 5.9 and Figure 6. 8. Without Si, SAD patterns consist of discrete spots arranged in crystalline rings with clear fringes. With Si addition, the rings become

blurred with broader halo in the center and dispersed spots merge to form completed circles, indicating the co-existence of nano-crystallites and amorphous phase³⁸. Based on the analysis of XPS, XRD and TEM results, this combination of nano-crystalline and amorphous phase is confirmed as nc-CrAlN/a-SiN_x nanocomposite.

Figure 6. 8 High-resolution TEM image of CrAlSiN coatings with Si content of 8.5 at.%, inset is the corresponding SAD pattern

In addition to the orientation, grain size and vertical morphology, the surface roughness is also associated with the Si content. Figure 6. 9(a) to (d) illustrate the gradual reduction of roughness from 14.1 to 1.1 nm as Si content increases. Lateral diffusion of the incoming ions governed by the kinetic energy of the arriving ions is one possible reason for the change. As shown in Table 4. 2, the power density on Si the target increases from 1.4 to 4.1 W/cm², while keeping that on Cr and Al constant in synthesizing CrAlSiN-1 to CrAlSiN-3. At lower target power density, ions have low mobility and coalescence takes place at where they arrive. As a result, rougher surface is more common. When the Si target power

density is increased, the kinetic energy of Si ions is increased, allowing lateral diffusion that leads to a smaller surface roughness. For CrAlSiN-4, the power density on Si target remains at 4.1 W/cm² while that on the Cr and Al is decreased by 30 %, which leads to the increased amount of Si. More Si means more a-SiN_x. It has been proved that the amorphous structure can result in ions impact-induced “downhill” flow of atoms, efficiently dampening the fluctuation of surface height and erasing the surface asperities. The increase of amorphous phase is thus essential to achieve ultra-smoothness¹⁴¹. Therefore, the dependence of surface roughness on the Si content originates from the enhanced ion mobility and the increased amorphous phase content.

Figure 6. 9 Evaluation of the surface topography of CrAlSiN for different Si content (at.%) (a) 0.4 (b) 1.8 (c) 5.9 and (d) 8.5

6.1.5 Hardness and toughness

Hardness as a function of Si content is plotted in Figure 6. 10. To compare, the hardness of pure CrAlN (*i.e.* CrAlN-160) is also shown. At 0.4 and 1.8 at.% Si, the hardness is almost the same as that of the coating without Si addition, *i.e.* at around 11 GPa. Comparatively low value of hardness comes from the loose microstructure and larger grain size, as shown in sections of 6.1.3 and 6.1.4. The hardness gradually increases with the increase of Si and reaches the maximum value of 29.5 GPa at Si 8.5 at.%. To understand this tendency, it is helpful to consider the dependence of the deformation mechanisms upon the grain size. In polycrystals with coarse grains (grain size large than 30 nm), the volume fraction occupied by grain boundaries is small. In this condition, the grain boundaries prevent lattice dislocation slip thus determining the level of the yield stress (Hall-Petch relation) ¹⁴². With the further continuous decrease of the grain size to below 10 nm, however, the volume fraction of grain boundaries can increase rapidly and becomes comparable with that of the crystallites. Under this condition, the lattice dislocation slip is suppressed by the alternative deformation mechanisms involving grain boundary sliding and grain boundary diffusional creep, so the strength of the material decreases as the grain size reduces further. This abnormal behavior (*i.e.* inverse Hall-Petch effect) was first reported by Chokshi *et al.* ¹⁴³ and was observed in many successive studies ¹⁴⁴⁻¹⁴⁷. In this regard, grain boundary sliding or creep must be inhibited to stop the strength degradation and achieve further hardening ².

With this notion, the tendency of hardness as a function of Si can be explained. From Figure 6. 10, when Si content increases from 0.4 to 1.8 at.%, the grain size decreases from 43 to 38 nm. The hardness improvement is from the obstacles due to the increased amount of grain boundaries. However, when Si content increases up to 8.5 at.%, the grain size rapidly decreases to a few nm. The further strengthening effect is therefore attributed to the segregated a-SiN_x, effectively preventing the grain boundary sliding and creep^{5, 148-150}.

Figure 6. 10 Hardness and Young's modulus as a function of Si content

The emphasis and commercial interest in the development of coatings with superb hardness is driven by practical demands on the mechanical performance such as the wear resistance of the industrial components. Although hardness has long been regarded as the primary property in determining the wear resistance, increasing evidences have suggested that the elastic strain to failure (related to the ratio of H/E) is a more suitable parameter in predicting the wear behavior in the practical applications¹⁵¹. Tsui *et al.* have also illustrated that other important near-surface material properties (*i.e.* resistance to plastic deformation) can be described in terms of H and E . For example, the resistance to plastic deformation

in a rigid-ball on elastic-plastic plate contact is proportional to $(H^3/E^2)^{1/2}$. Thus, H^3/E^2 is a strong indicator of a coating's resistance to plastic deformation for wear application. Figure 6. 11 shows the ratio of H^3/E^2 as a function of the Si content. In this case, the obtained tendency is in a good agreement with that of hardness.

Figure 6. 11 H^3/E^2 ratio as a function of Si content

To evaluate the toughness of the nc-CrAlN/SiN_x coatings, microindentation is employed first. However, extreme brittleness of the hard coating (CrAlSiN-4) prevents using this methodology. As shown in the indent array (Figure 6. 12(a)), even at 200 mN (crack threshold, indent depth around 1 μ m), most of the indent marks do not remain intact but show a severe buckling and delamination. Close up of the indent neighborhood reveals that the coating fails to resist the crack, leading to catastrophic fracture once the crack appears. Under this condition, no measureable radial crack length can be obtained. Therefore, the calculation of toughness from the indentation is not possible.

Figure 6. 12 Brittle fracture of CrAlSiN-4 at indent force of 400 mN (a) fracture of the intent array (b) close up of the intent neighborhood

Using the scratch method, the trend of toughness can be revealed. Figure 6. 13 shows the fracture development under the moving stylus. Increasing Si content causes the decline of L_{c1} (showed by black arrows in Figure 6. 13), indicating increasing brittleness. Particularly, with 8.5 at.% Si (*i.e.* CrAlSiN-4), a severe chipping and buckling occur at the lowest load (L_{c1} = 3.69 N). Figure 6. 14 illustrates the fracture pattern at the emergence of spallation (L_{c2}). The decreased value of L_{c2} confirms that coatings become less durable under sliding/scratch contact.

Figure 6. 13 Optical observation of micro-scratch test of CrAlSiN coating with different Si contents on SUS420 substrates (black arrow: L_{c1} , white arrow: L_{c2})

Figure 6. 14 Fracture behavior at the emergence of spallation of CrAlSiN with different Si content

Values of L_{c1} and L_{c2} from the scratch tests can be used to plot the coating hardness versus the CRP_s (Figure 6. 15). As a comparison, CPR_s of CrAlN-160 is added. Generally, the increasing hardness results in a rapid decrease of toughness. CrAlSiN-4 possesses the highest value of hardness (29.5 GPa) while having the least toughness. On the other hand, coatings with zero (CrAlN-160) or lower Si content (CrAlSiN-1) are much tougher (*i.e.* almost 10 times as much as that of CrAlSiN-4) but are also rather soft (~ 11 GPa).

Figure 6. 15 Plot of hardness versus CPR_s depending on Si content in CrAlSiN coatings

6.2 Influence of gradient distribution of Si on nc-CrAlN/a-SiN_x nanocomposite

As shown above, the increasing hardness leads to the rapid decrease of toughness. To overcome it, homogeneously and heterogeneously graded Si structures are proposed. Experimental details of the coating fabrication can be found in Table 4. 3. In the following paragraphs, the effect of gradient incorporation of Si will be investigated and discussed in detail.

6.2.1 Chemical composition and microstructure

By increasing the target power on the Si target at fixed or variable rate, coatings of homogeneously (*i.e.* CrAlSiN-GL and CrAlSiN-GH) and heterogeneously (*i.e.*

CrAlSiN-L) gradient Si are achieved. Morphological differences are evident as shown in Figure 6. 16. Columnar grains dominate the CrAlSiN-GL and CrAlSiN-GH microstructure, while CrAlSiN-L exhibits a clear laminated structure. At the bottom, columnar structure dominates, but in the intermediate and top layers, the coating becomes much more dense. These observations indicate that heterogeneous doping of Si leads to architectural modification. The sketch on the right margin of Figure 6. 16 illustrates the architectural evolution, which will be verified later in this section. The chemical concentrations of each layer in CrAlSiN-L are determined from EDS and the value is labeled accordingly in Figure 6. 16(c). However, the chemical concentrations labeled in homogeneously graded coatings (Figure 6. 16(a) and Figure 6. 16(b)) are the average value throughout the coating thickness. To determine the Si distribution in CrAlSiN-GL and CrAlSiN-GH, GDOES is employed and corresponding results are shown in Figure 6. 17. The increased concentration of Si and the decrease of other elements indicate that the detection region approaches to the interface between coating and Si substrate. From the spectra, Si increases from almost 0 at the substrate to ~5 at. % at the top surface of CrAlSiN-GL and to ~8 at. % at the top surface of CrAlSiN-GH.

Further examination of the columnar structure in CrAlSiN-GL (Figure 6. 18) reveals that CrAlN nano-grains around 10 nm exist near the top surface. The occurrence of nano-grains is due to the fact that only with higher Si content almost at the end of deposition, the complete interruption of columnar structure could be accomplished owing to the increased amount of a-SiN_x. In addition, the domination of columnar structure is believed to correlate with the small step

wise nature of the grading. By increasing the Si in a larger grading step-wise as in CrAlSiN-L, columnar structure occurs only at the bottom where the Si content is low (Figure 6. 19 (a)). Thereafter, dense structure with reduced grain size is observed along the coating thickness. In the intermediate layer (Figure 6. 20(a)), CrAlN nanograins with the size of ~ 10 nm are seen. Even smaller grains of ~ 5 nm are found at the top (Figure 6. 21(a)). SAD patterns also confirm the transition. Due to the increased amount of Si, an amorphous ring becomes more evident and the crystalline ring becomes more continuous and diffused (Figure 6. 19(b) to Figure 6. 21(b)), indicating the formation of finer grains as growth proceeding from the bottom to the top. Based on these results, it is believed that both the Si amount and the Si grading rate determine the gradient structure.

Figure 6. 16 Cross-sectional morphology of CrAlSiN with (a) homogeneously and (b) Heterogeneously gradient Si

Figure 6. 17 GDOES results of CrAlSiN with gradient Si distribution (a) CrAlSiN-GL (b) CrAlSiN-GH

Figure 6. 18 High-resolution TEM image of the upper part in CrAlSiN-GL

Figure 6. 19 TEM image (a) and selected area diffraction patterns (b) of the bottom layer

Figure 6. 20 TEM image (a) and selected area diffraction patterns (b) of the intermediate layer

Figure 6. 21 TEM image (a) and selected area diffraction patterns (b) of the top layer

6.2.2 Mechanical properties

Hardness and scratch toughness of graded coatings are plotted in Figure 6. 22. Results of CrAlN-160 and CrAlSiN with different Si contents are also inserted. With homogeneously gradient structure, CPR_s of CrAlSiN-GH becomes nearly 3

times as high as that of CrAlSiN-4, whilst at the same time maintaining high hardness of 25.9 GPa. The hardness drops only 12% as compared to that of CrAlSiN-4. The toughening effect is more pronounced in the heterogeneously gradient structure; compared to CrAlSiN-4, CrAlSiN-L presents scratch toughness increase by as much as 6 times at the expense of only 10% hardness drop. These results demonstrate the advantage of the gradient structure, in which the inner low-Si partition is softer but tougher thus serving as a cushion with more tolerance to the crack propagation while the outer high-Si partition is much harder, and thus maintaining the resistance to plastic deformation.

Figure 6. 22 Hardness versus CPR_s of homogeneous CrAlSiN coatings with different Si and graded CrAlSiN coatings

Chapter 7

Toughening Effect of Ni on nc-CrAlN/a-SiN_x

Nanocomposite

As mentioned in Chapter 2, the incorporation of metallic elements can improve the toughness of ceramic coatings. In the next paragraphs, the toughening effect of Ni on the nc-CrAlN/a-SiN_x nanocomposite will be discussed.

7.1 Chemical concentration

The chemical concentration of the Ni in the doped CrAlSiN nanocomposite is listed in Table 7. 1. In the as-deposited coatings, Ni content varies from 1.4 to 39.8 at.%. The composition of the pure nc-CrAlN/a-SiN_x nanocomposite is also listed for comparison.

Table 7. 1 Chemical concentration of Ni-doped CrAlSiN nanocomposite

Specimen	Concentration (at. %)					
	Cr	Al	Si	N	Ni	O
CrAlSiN	22.9	11.1	10.3	54.8	0	0.9
CrAlSiNiN-1	21.5	10.5	10.5	54.9	1.4	1.2
CrAlSiNiN-2	20.9	10.4	10.5	52.9	4.2	1.1
CrAlSiNiN-3	18.5	9.2	10.9	48.1	12.0	1.3
CrAlSiNiN-4	16.3	8.2	10.0	40.5	23.4	1.6
CrAlSiNiN-5	13.1	6.4	8.3	29.8	39.8	1.9

Figure 7. 1 illustrates the Al/Cr ratio as a function of Ni content. The increase of Ni causes no variation of the Al/Cr atomic ratio in the as-deposited coatings. It is

noted that the Al/Cr ratio is slightly larger than that in the Cr_{0.7}Al_{0.3} alloy target used (Al/Cr=0.43). This is due to the higher sputtering yield of Al than that of Cr. In parallel, Si remains at around 10 at.%, as Ni content varies from 0 to 23.4 at.%, but undergoes a slight decrease to 8.5 at.% when Ni is at 39.8 at.%. The calculated Si/(Cr+Al) ratio increases monotonically with the increase of Ni (Figure 7. 2). This is due to the smaller enthalpy of formation of Si-N bonds (-642.1 kJ/mol) as compared to that of Al-N (-297 kJ/mol) and Cr-N (-117 kJ/mol)^{153, 154}. The oxygen which come from the residual gas in the chamber remains at around 1 at.% but increases to around 2 at.% when Ni content increases to 39.8 at.%.

Figure 7. 1 Al/Cr ratio of Ni-doped nanocomposite nc-CrAlN/a-SiN_x

Figure 7. 2 Si/(Cr+Al) ratio of Ni-doped nanocomposite CrAlSiN as a function of Ni content

7.2 Microstructure

Figure 7. 3 demonstrates the dependence of XRD patterns on the Ni content. Without Ni, the coatings have nc-CrAlN/a-SiN_x fcc structure. As Ni increases from 1.4 to 23.4 at.%, the diffraction peaks shift toward higher position with peak broadening. The peak shifting comes from the lattice distortion since Ni atoms have chance to disperse in the CrAlN lattice, and also from the formation of solid-solution CrAl(Ni)N, where Ni could possibly bonds with Al to form AlNi or AlNi₃. The standard diffraction patterns of NiAl and Ni₃Al are referenced in the figure as well. However, the Al atoms prefer to bond with N atoms since the enthalpy of formation of NiAl is in the range between -59.8 and -72 kJ/mol and that of Ni₃Al is from -37.6 to -47.0 kJ/mol^{155, 156}, which are smaller than that of AlN (-297 kJ/mol). In addition to the peak shifting, the peak broadening is also noticeable. This broadening is attributed to the reduced grain size. Studies of Ni-doped TiN¹⁵⁷ and Ni-doped nc-TiN/a-SiN_x⁶⁶ have revealed that Ni adatoms tend to form together with the a-SiN_x as an amorphous layer to block the grain growth. The calculated grain size decreases from ~7 to ~2 nm when the Ni content increases to 23.4 at.%, as seen in Figure 7. 4.

Figure 7. 3 GAXRD pattern of Ni-doped nc-CrAlN/a-SiN_x as a function of Ni content

Figure 7. 4 Average grain size of Ni-doped nc-CrAlN/a-SiN_x as a function of Ni content

With the aid of XPS, the bonding states in the nanocomposite with 12.0 at.% Ni are revealed. Cr bonds with the N as seen from the peaks centered at 584.2 and 574.8 eV (Figure 7. 5(a)). The bonding of Cr-N and Al-N are observed from the N 1s narrow scan, in which the N is also partially bonded with Si (Figure 7. 5(b)). Si-N bonding is confirmed from the Si 2p peak (Figure 7. 5(c)) centered at 101.9 eV. No pure Si (99.0 eV) or Si-O (103.9 eV) bonds can be observed, indicating that the Si entirely bond with N. In the Ni 2p spectrum (Figure 7. 5(d)), binding energy of 852.8 eV (Ni 2p_{3/2}) and 870.7 eV (Ni 2p_{1/2}) are assigned to the Ni⁰ state^{66, 158}. No other bonding state of Si such as Ni²⁺ (854.6 eV) or Ni³⁺ (856.1 eV) can be observed. However, it is difficult to differentiate Ni-Al bonds due to the overlapped binding energy. Al 2p (Figure 7. 5(d)) centered at 73.6 eV indicates that Al is bonded with N. The peak at the lower binding energy (67.9 eV) is attributed to the Ni 3p. Herein, Ni 3p peak is considered the synergetic contribution of the pure Ni and Ni-Al bonds. However, it is also unable to deconvolute this peak due to the binding energy overlapping. Figure 7. 6 exhibits the tendency of Ni 3p as a function of the Ni content. With increased Ni, the peak

intensity of Ni 3p and the intensity ratio of Ni/Al increase accordingly. When the Ni content increases from 1.4 to 23.4 at.%, no significant deviation in peak position can be observed. However when Ni is at 39.8 at.%, the Ni 3p peak shifts to a higher position which is due to the formation of Ni-O, since a higher content of oxygen is involved (1.9 at.%).

Figure 7. 5 XPS narrow scan of CrAlSiN with 12.0 at.% Ni: (a) Cr 2p (b) N 1s (c) Si 2p (d) Ni 2p and (e) Al 2p

Figure 7. 6 Tendency of the Al 2p and Ni 3p intensities as a function of the Ni content

Figure 7. 7(a) illustrates the high-resolution TEM image of nc-CrAlN/a-SiN_x with 12.0 at.% Ni. CrAlN nanocrystallites (as circled) is observed in the scale of around 3 nm, in a good agreement with the calculated value. These nanograins embed in the amorphous phase, as reflected from the crystalline rings and the amorphous halos in the SAD pattern (Figure 7. 7(b)). The rings of (111) and (200) are evidentially observed, in correspondence with the results of XRD. The morphology evolution is revealed in Figure 7. 8. A dense glassy texture is

observed when Ni content is less than 12.0 at.%. However, with Ni content larger than 23.4 at.%, columns perpendicular to the substrate emerge. This evolution is attributed to the fact that with increased content, Ni agglomerates and grows into large grains.

Microstructural change is also observed from the changes in the surface topography variation (Figure 7. 9). The surface roughness (R_q) increases monotonically when the Ni content increases up to 39.8 at.%. The increase of roughness is much more rapid when Ni content exceeds 12.0 at.%. This trend is also attributed to the formation and the agglomeration of crystallized metallic Ni when its content is sufficiently large.

Figure 7. 7 TEM image of Ni-doped nanocomposite CrAlSiN (Ni-12.2 at.%) (a) grain size around 3 nm imbedded in amorphous phase (b) selected area diffraction pattern

Figure 7. 8 SEM cross-sectional image of Ni-doped nanocomposite CrAlSiN as a function of Ni content

Figure 7. 9 Surface morphology of Ni-doped nanocomposite CrAlSiN coatings with varying Ni addition

7.3 Mechanical properties

Hardness (H) and Young's modulus (E) as a function of Ni content are presented in Figure 7. 10. H and E decrease monotonically from 27 to 12 GPa when Ni content increases from 0 to 23.4 at.%. Normally for the nanocomposites, a threshold amorphous fraction exists, beyond which drastic degradation takes place ¹. For the nc-CrAlN/a-SiN_x nanocomposite, 10 at.% Si have led this critical point being reached, therefore any addition of Ni may cause excessive amorphous phase and hence the hardness decrease. However, the hardness decline to 10 GPa (at 39.8 at.% Ni) independently of the amorphous phase, but comes from the occurrence of large amount of soft crystallized metallic Ni. The larger error in the measurement is due to the rough surface.

Figure 7. 10 Hardeness and Young's modulus of Ni doped nanocomposite CrAlSiN coatings with varying Ni addition

The scratch toughness versus the hardness is plotted in Figure 7. 11. Owing to the presence of the ductile Ni, the scratch toughness increases continuously. The fracture behavior at the higher critical load (L_{c2}) indicates the same trend: severe chipping or buckling no longer presents because of the increased Ni content. It is believed that this improvement originates from the ductile phase deformation that causes blunting of the crack tip, so that more work is required for the crack propagation. Considering the practical usage where hardness should be no less than 20 GPa, the nc-CrAlN/a-SiN_x with 4.2 at.% Ni appears optimized. With this composition, the scratch toughness increases by around 200% at the expense of 18% hardness drop, as compared to the hard nc-CrAlN/a-SiN_x nanocomposite with the hardness of 28 GPa.

Figure 7. 11 Hardness versus “toughness” (scratch crack propagation resistance) of the nanocomposites

Chapter 8

Influence of Bilayer Thickness on [pc-CrAlN]/[nc-CrAlN/a-SiN_x] Multilayers

In previous studies, the hardness and toughness of monolayer CrAlN and monoalayer CrAlSiN were tailored by changing the bias voltage and the Si content, respectively. As mentioned in Chapter 3, the multilayering structure has potential to maintain high hardness and toughness simultaneously. In this section, alternative stacking of soft-tough CrAlN (*i.e.* denoted as pc-CrAlN) and hard-brittle nc-CrAlN/a-SiN_x on top of each other is achieved. The experimental details can be found in section 4.2.1.2. The influence of the bilayer thickness on the multilayering structure and the mechanical property is explored.

8.1 Chemical composition

The chemical compositions of the multilayers are summarized in Table 8. 1. The chemical composition of the monolayers CrAlN and nc-CrAlN/a-SiN_x which are the constituents of the multilayers are also listed for comparing. To ensure no other crystalline phases except fcc-CrAlN are present, the Al/(Al+Cr) content ratio is controlled at around 0.4. The detected Si content is an average throughout the coatings since the electron penetration depth of EPMA is at 1 μm . By considering the designed sub-layer thickness ratio ($t_{\text{pc-CrAlN}}:t_{\text{nanocomposite}}=1:1$), the Si content in the nanocomposite sub-layer is around 8 at.%.

Table 8. 1 Summary of chemical concentration of monolayers and multilayers

Code	Period Thickness (nm)	Concentration (at. %)				
		Cr	Al	Si*	N	O
pc-CrAlN	-	28.5	17.4	-	52.7	1.4
nanocomposite	-	21.4	13.5	8.5	55.3	1.3
mt-10	10	26.1	15.4	4.1	54.2	0.2
mt-20	20	26.5	15.0	4.2	54.1	0.2
mt-40	40	26.3	15.1	4.2	54.1	0.3
mt-60	60	26.3	15.5	4.1	53.9	0.2

*: Average value through coating thickness

8.2 Crystalline structure

Figure 8. 1 shows the GAXRD spectra of the monolayer and multilayers. Face-centered cubic crystalline structure can be identified from the presence of (111), (200) and (220) peaks. As compared with pc-CrAlN monolayer, the (111) peak in nanocomposite monolayer shifts toward lower diffraction angles. In contrast, the (111) peak of multilayers sits in between that of pc-CrAlN and nanocomposite monolayer, but shifts toward higher angles when the bilayer thickness increases. It is believed that the stress fluctuation resultant lattice distortion accounts for the peak position variation. As seen from Figure 8. 2, the addition of Si leads to the lattice expansion from 0.4143 (pc-CrAlN monolayer) to 0.4153 nm (nc-CrAlN/a-SiN_x monolayer). The reason for the lattice expansion as a result of Si addition has been discussed in detail in section 6.1.3. Moreover, Figure 8. 2 demonstrates the dependence of lattice parameter on the bilayer thickness. Compared to the lattice parameter of the monolayer, that of multialyers is smaller. The lattice parameter expands from 0.413 to 0.414 nm as Λ decreases from 60 to 10 nm, signaling that the accumulated internal stress is gradually

released. The assumed tendency of stress is confirmed as shown in Figure 8. 3. For the monolayers, the addition of Si leads to the stress decrease from -0.9 to -0.5 GPa (“-” means the stress is compressive). For the multilayers, the stress decreases from -1.7 to -1.0 GPa as Λ decreases from 60 to 10 nm. Bilayer thickness resultant stress decline is attributed to the fact that the interfaces in multilayers are the sites for the strain energy dissipation ⁹⁵. As demonstrated in WC/DLC multilayers with constant coating thickness, the compressive stress is proportionally diminished as the bilayer thickness decreased ¹⁵⁹. In particular, as bilayer thickness varies from 100 to 10 nm, stress is decreased from -2.5 to -0.8 GPa. In this case, the total coating thickness is controlled at 1 μ m. Therefore, decreased bilayer thickness leads to the increased number of interfaces, and thus the enhanced capability of dissipating the strain energy. Consequently, the decrease of compressive stress and expansion of lattice parameter are observed.

Figure 8. 1 XRD patterns of monolayers and multilayers with different bilayer thickness

Figure 8. 2 Lattice parameter of multilayers as a function of period thickness

Figure 8. 3 The dependence of residual stress on the bilayer thickness of multilayers

The grain size of multilayers is also strongly dependent on the bilayer thickness. As shown in Figure 8. 4, the grain size in the multilayers reduces continuously from ~21 to ~7 nm as λ decreases. The constraint of grains is attributed to the periodically interruption of the growth of pc-CrAlN layer. This observation is in good

correspondence with the former study (*e.g.* CrAlN/SiN multilayers), in which the grain size could be effectively manipulated by varying bilayer thickness ¹⁰⁸.

Figure 8. 4 Grain size of multilayers as a function of the period thickness

8.3 Morphology and microstructure

Cross-sectional observation of the multilayers was carried out by using FESEM in the backscattered electrons imaging (BEI) mode. The use of BEI mode is to better identify the period thickness in the small scale. The observation is close to the designed value, as shown in Figure 8. 5. The darker strip is pc-CrAlN and the lighter one is nc-CrAlN/a-SiN_x. The contrast in the color is due to the average atomic mass of individual layers with different constituents. The thickness ratio is approximate to 1:1, indicating the accurate control of the dwell time during the deposition.

Figure 8. 6 illustrates the TEM image of the cross-section of the multilayer coating with the period thickness of 20 nm. The coating is confirmed dense and multilayered within the 1 μm thickness.

Figure 8. 5 Cross-sectional images (BEI mode) of the multilayer coatings with varying period thickness: (a) 10 nm (b) 20 nm (c) 40 nm and (d) 60 nm

Figure 8. 6 TEM image of the cross-section of the multilayer coating with period thickness of 20 nm

Figure 8. 7(a) through (c) illustrate the close up of the multilayers with $\Lambda=20$ nm. The interfaces shown by the white arrows in Figure 8. 7(a) are enlarged in Figure 8. 7(b). The continuing growth of the columnar pc-CrAlN grains is periodically interrupted due to the insertion of the nanocomposite layer, which is similar as observed in Ref. ¹⁶⁰. No epitaxial relation is found to take place within the adjacent layers. However, owing to the nanocomposite layer, the interface is not ideally sharp. At the interface, pc-CrAlN layer with large grains (around 10 nm) is observed. These layers conjunct with the nanocomposite layer (with nanocrystallites around 5 nm as seen in Figure 8. 7(c)), leading to a complex atoms match, analogous to gears in mesh (Figure 8. 7(d)). In this observation, only a few nano-crystallites, whose lattice planes orient parallel to the electron beam, appear in the lattice resolution due to random orientation.

Figure 8. 7 (a) HRTEM image of the multilayer coating with period thickness of 20 nm, (b) an enlarged interface at the white arrows in (a), (c) HRTEM image of the

nanocomposite (*i.e.* nc-CrAlN in a-SiN_x) sub-layer and (d) the schematic representative of the sandwich structure

The dependence of the surface topography on the bilayer thickness and monoalyers is shown in Figure 8. 8. The nanocomposite monolayer has a much smoother surface ($R_q=1.1$ nm) than the pc-CrAlN monolayer ($R_q=16.2$ nm). The reason for the drastic decrease has been discussed in 6.1.4. For the multilayers, as bilayer thickness increases from 10 to 60 nm, surface roughness increases from 2.5 to around 6 nm accordingly. The increase of roughness is due to the accumulated asperity in pc-CrAlN sub-layer ¹⁶¹. In this case, the coating becomes rougher when the layer of pc-CrAlN is thicker.

Figure 8. 8 Surface morphology of pc-CrAlN monolayer, nanocomposite monolayer and multilayers with varying period thickness

8.4 Mechanical properties

Figure 8. 9 shows the hardness (H) and Young's modulus (E) of the multilayered coating as a function of the period thickness. As a comparison, hardness and Young's modulus of the pc-CrAlN and the nanocomposite monolayers are also shown. At $\Lambda=20$ nm, a maximum H and E are reached at 33 GPa and 364 GPa, respectively. The degradation of hardness and Young's modulus are observed when the period thickness increases to 40 nm ($H=27.9$ GPa, $E=305$ GPa) and 60 nm ($H=23.6$ GPa, $E=287$ GPa).

Figure 8. 9 (a) Hardeness and (b) Young's modulus of the pc-CrAlN monolayer, nanocomposite monolayer and multilayers with varying period thickness

Currently known hardening mechanisms for nano-multilayers include image force effect, multilayering Hall-Petch strengthening and strain effect at the layer interfaces ⁹³. Among them, contribution of strain effects is relatively small. And the other two models are not expected to apply on the non-isostructural multilayers since the component layers have different dislocation glide systems ¹⁶². To date, there is a lack of a proper model to describe the strengthening behavior in multilayers of non-isostructural structure. This insufficiency is attributed to the complexity of the interfaces, which is influenced by the properties of the component layers. As reported in the case of TiN/SiN multilayers, amorphous SiN of thickness in 0.5-0.7 nm can become crystalline and epitaxial with its adjacent TiN. This observation was then verified in the research of Kong *et al.* ¹⁰⁷, Hultman *et al.* ¹⁰⁶ and Lin *et al.* ¹⁰⁸. In addition to the layer thickness-dependent phase evolution of SiN, Lin *et al.* ¹⁰⁸ and Tsai *et al.* ¹⁰⁹ also noticed that the strength of CrAlN/SiN_x non-isostructural multilayers was strongly related to the bilayer thickness as it governed the grain size of the crystallites.

In this view, the trend of hardness is plotted against the inverse of square root of grain size (Figure 8. 10). The results reveal that the hardness is well fitted by the Hall-Petch relation ⁸⁻¹⁰. However, the multilayers of $\Lambda=10$ nm deviates from this relation and show a value of the same level as a monolayer nanocomposite. Under this condition, the individual sub-layer is only 5 nm for each; therefore the grain size of CrAlN in pc-CrAlN would be limited at around 5 nm. Since the grain size of the nanocomposite sub-layer is around 5 nm (Figure 8. 7(c)), multilayer coating at this small period thickness is effectively reduced to a quasi-nanocomposite

coating if considering the possible interlayer diffusion. Hence, no significant difference in hardness is observed. Given the above analyses, hardness increment of the non-isostructural multilayers relies on the variation of grain size due to the tailored bilayer thickness.

Figure 8. 11 and Figure 8. 12 show the overview of the scratch tracks and a close investigation of the crack behavior at L_{c2} , respectively. It is obvious that the multilayer coatings reveal a tougher behavior with more localized chipping or cracking as compared to the nanocomposite monolayer.

Figure 8. 10 Hardness as a function of grain size

Figure 8. 11 Optical observation of the micro-scratched morphology of the coatings on SUS420C substrates (black arrow: L_{c1} , white arrow: L_{c2})

Figure 8. 12 Optical observation at the emergence of spallation (at onset of L_{c2})

To demonstrate whether the hard yet tough coatings are achieved, the hardness versus scratch toughness is plotted. As seen in Figure 8. 13, the pc-CrAlN monolayer is tough but soft (the star at the lower right corner), whereas the nanocomposite monolayer is hard but very brittle (the open triangle at top left).

Ideally, top right corner is the best, *i.e.* hard yet tough. The multilayer coatings (the open circles), do appear to move toward that direction to a varying extent at with changing period thickness: at $\Lambda=10$ nm, the hardness of the multilayer coating matches that of the nanocomposite monolayer, meanwhile, its toughness is better (moving towards right in the Hardness vs Toughness space). At even larger period thickness, $\Lambda=60$ nm, the multilayer's hardness drops with increased toughness; at $\Lambda=40$ nm, hardness returns with much improved toughness (7 times as much as that of nanocomposite monolayer); at $\Lambda=20$ nm, the hardness further improves, and even surpasses that of the nanocomposite (from less than 30 to 33 GPa) with a slight drop in toughness from that at $\Lambda=40$ nm. With this architecture ($\Lambda=20$ nm), the multilayer coating's toughness is increased 5-fold from that of the hard nanocomposite (the open triangle).

Figure 8. 13 Plot of hardness versus scratch toughness

For the monolayer nanocomposite, the nc-CrAlN grains are enveloped by a thin layer of a-SiN_x phase, leading to the loss of ductility and the sacrifice of toughness.

However, in the nanocomposite sandwiched with the softer but tougher polycrystalline CrAlN, more chance of deflection and branching of the cracks at the interface is expected. Moreover, since the total coating thickness is controlled at 1 μm , large period thickness means decreased number of interfaces; small period thickness means more interface with each layer being thinner. Due to the complicated atomic configuration at the interface, the number of interface and thickness of each layer synergetically govern the toughening effect. As a consequence, at $\Lambda=20$ nm, a good combination of both hardness and toughness is achieved.

8.5 Tribological performance

The multilayers have exhibited improved toughness in addition to the high hardness and it is also desired to investigate the tribological performances. The complete understanding of the tribological process in a contact in which two surfaces are in relative motion is very complex because it involves simultaneously friction, wear and deformation mechanisms. In this project, concerns are focused on the micro-scale mechanical effect with expect to the effect of the number of the layers, although tribochemical effects and the material transfer may also take place. The micromechanical tribological mechanisms are related to the stress and strain, crack generation and propagation and material liberation.

As described in 4.2.3.4, the wear test was carried out on coated SUS420C discs. Figure 8. 14 displays the wear track of the multilayers coatings against the loading at 2 N. The images in the top row (Figure 8. 14(a)-(d)) are the wear tracks

from the Secondary Electron Imaging (SEI) observation, while those in the bottom row (Figure 8. 14(e)-(h)) are from the Backscattered Electron Imaging (BEI) observation at the same place. Within the sliding distance of 1000 m, no obvious wear can be observed for the entire specimen, except some debris along the tracksides. It should be pointed out that the wear rate is not evaluated due to a very shallow wear depth.

Figure 8. 14 SEI (a)-(d) and BEI (e)-(h) observation of the wear tracks in multilayers

Figure 8. 15 shows the average coefficient of friction (COF) of the monolayer and multilayer coatings. The multilayer coatings outperform the monolayer counterparts to different extent. At $\lambda=10$ and 20 nm, the best lubricant performance is obtained with the lowest COF, 0.37 and 0.38 respectively. Further increased bilayer thickness results in a slight increase of COF, 0.44 at $\lambda=40$ nm and 0.51 at $\lambda=60$ nm. As compared to the monolayer coatings, the decreased COF of the multilayers coatings is believed to be associated with the interface, which can increase crack propagation resistance and provide opportunities for energy dissipation. In particular, the stress and strain fields periodically changed in the multilayers may play an important role in strengthening the layered surface and

changing the amount of the emitted debris. Due to the numerous obstacles at the layer interface, deviation of cracks may easily take place. As shown in Figure 8. 16, cracks tend to penetrate deeper into the monolayer coating and lead to large size of the coating liberation. The liberated debris agglomerate at the wear contact region, resulting in increased abrasive wear. At the same time, these agglomerated debris can generate increased shear stress at the contact interface, which largely increases the COF. For the multilayers, small size of liberated coating is expected. This is attributed to the fact that the cracks can be deflected when encountering the layer interface and close up when propagate along the interface ¹⁶³. It is expected that more barriers in the multilayers (*i.e.* thinner bilayer thickness in this case) result in even smaller emitted debris. These small debris can hide in the valley of the coating surface due to the surface roughness, and thus interposing small effect on the surface shear stress. Therefore, the COF drops rapidly (from 0.51 to 0.37) at the decreased period thickness (from $\Lambda=60$ nm to $\Lambda=10$ nm).

Figure 8. 15 Coefficient of friction of pc-CrAlN, nanocomposite monolayer and multilayer

Figure 8. 16 Schematic illustration of proposed wear model of monolayered (left) and nanometer scale multilayered (right) coatings ¹⁶³.

Chapter 9

Conclusions and Suggestions for Further Work

9.1 Conclusions

In the previous chapters, the crucial influences of the negative bias voltage and the Si content on the microstructure and mechanical properties of CrAlN are revealed. As shown in the obtained results, the hardness and toughness are increased simultaneously at a proper level of the negative bias voltage. The addition of the Si leads to the formation of nc-CrAlN/a-SiN_x nanocomposite. The increase of Si content leads to the continuous increase of the hardness, but at a large expense of the toughness.

To overcome the brittleness of the hard nc-CrAlN/a-SiN_x nanocomposite, toughening methods are evaluated by doping the ductile phase such as Ni, changing the Si distribution through the coating thickness and fabricating the multilayers consisting of one layer soft-tough CrAlN and one layer hard-brittle [nc-CrAlN/a-SiN_x]. In the Ni-doped nc-CrAlN/a-SiN_x, the influence of the Ni addition is revealed with respects to the microstructure and mechanical properties. Increased toughness due to the ductile phase deformation is observed and an optimal value of the doped content is achieved in balancing the toughness and the hardness. On the other hand, the study of the nc-CrAlN/a-SiN_x nanocomposite with a grading structure shows that the heterogeneous grading is efficient in toughening than the homogeneous grading, since the heterogeneous

grading results in a laminated structure with the clear interfaces. This observation leads to the initiative of the fabrication of the multilayers. The obtained results suggest that the multilayering structure is the most promising way out. The microscopic studies show that the complex interfaces can enhance the toughening effect, while at the same time remaining the hardness to the largest extent. The major findings in this project are summarized in the following.

1. In depositing the CrAlN coatings, the negative bias voltage (V_b) is an essential factor in governing microstructure and mechanical properties. With the increased V_b from 50 to 260 V, the coatings become dense and compact with fewer defects. In parallel, the compressive stress is increased from -0.7 to -1.4 GPa. Owing to the synergetic contributions of the refined structure with fewer defects and the increased compressive stress, the hardness increases from 10 to 26 GPa and the toughness improves from 1.67 to 2.02 MPa·m^{1/2}. This indicates that the simultaneous increment of hardness and toughness is achievable if the negative bias voltage is properly controlled.
2. Incorporation of the Si (from 0.4 to 8.5 at.%) into CrAlN results in the formation of the nc-CrAlN/a-SiN_x nanocomposite. The morphology change is observed as the columnar texture evolving into a dense structure with refined grains (from ~50 to ~8 nm). The hardness increases sharply from 11 to 29.5 GPa due to the a-SiN_x phase segregated. However, this increment is at a large expense of toughness, which makes it less durable under the contact force.

3. Grading Si in the nc-CrAlN/a-SiN_x can restore the toughness of hard nanocomposite. The heterogeneous grading is more effective in balancing the hardness and toughness than homogeneous grading. The heterogeneous grading leads to the lamination throughout the thickness. The outer layer with a higher fraction of Si provides the great resistance to the plastic deformation. The inner layer with a lower fraction of Si offers the good tolerance to the crack propagation. As a consequence, the scratch toughness of the nc-CrAlN/a-SiN_x with a heterogeneous grading is 6 times the value of the pure nc-CrAlN/a-SiN_x nanocomposite, while the hardness is dropped by only 10%.
4. The incorporation of Ni (from 0 to 39.8 at.%) into nc-CrAlN/a-SiN_x leads to the morphology evolving from dense to coarse columnar. As Ni content increases up to 23.4 at.%, the grain size decreases from 7 to 2 nm due to the blocking effect from the amorphous layer, formed by both the Ni and the SiN_x. The increase of the Ni content leads to a continuous decrease of the hardness but a large increase in the toughness. With the addition of 4.2 at.% Ni, the toughness of nc-CrAlN/a-SiN_x nanocomposite (~28 GPa) is improved by around 200% at an expense of only 18% hardness drop.
5. Non-isostructural multilayering of [pc-CrAlN]/[nc-CrAlN/a-SiN_x] leads to the ceramic coatings with the hard-yet-tough properties. Owing to the decreased grain size and the complex configuration of atomic planes at the layer interfaces, a high hardness (33 GPa) is achieved with a greatly improved toughness (5 times as compared to the nanocomposite monolayer). In addition, the hard-yet-tough multilayer coating with the

period thickness of 20 nm presents a relatively low coefficient of friction (0.38), indicating a promising potential for the practical applications.

9.2 Suggestions for further work

1. The optimum condition of the nanocomposite for the super hardness remains unclear. The concept of fabricating coatings with super hardness has suggested that the ideal coating structure consist of nanocrystallites encapsulated by 1-2 monolayer amorphous phase. However, recent studies discovered that this 1-2 monolayer might not be necessarily in the form of amorphous state. As in the case of Ti-Si-N coating system, the state of the SiN_x can vary from the epitaxial crystalline structure to the amorphous structure, depending on the thickness¹⁰⁶⁻¹⁰⁹. This observation may lead to a new hardening mechanism by precisely controlling the thickness of the second phase. It is recommended to take a further investigation at the atomic level by using the molecular dynamics. The use of the multilayering structure can provide the proper way in validating the new hardening mechanism, and in turn optimize the bilayer thickness to obtain the best combination of the hardness and toughness.
2. In this project, the nitride coating with hardness of only 10 GPa was observed. It is believed that lower quality of the plasma flux is the reason for this inferior strength. Therefore, the precise monitor and control of the plasma density or ion flux by using the real-time surveillance technique is necessary. It is necessary to understand the direct causal relationship

between plasma and the resultant mechanical properties in sputtering by using the technique such as optical emission spectroscopy.

3. Expanding the application of the non-isostructural multilayering proposed in this project to other coating systems is also desirable, for example the combination of the carbide and the carbide-based nanocomposite. Moreover, the mechanical properties of these multilayers at the elevated temperature are also worth evaluating.

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