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ZrN based Nanostructured Hard Coatings

Structure-Property Relationship

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NANOSTRUCTURED MATERIALS

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Abstract

Ever since the hard coatings have been introduced, there has been a constant push for better mechanical properties, which motivates for deeper understanding of the microstructure-mechanical properties correlation. The aim of this thesis is to extend the knowledge on how microstructural variation influences the deformation, fracture and wear behavior of ZrN based nanostructured coatings.

Few microns thick, monolithic Zr-Si-N and multilayered Zr-Al-N coatings were deposited by reactive arc deposition and unbalanced reactive magnetron sputtering techniques respectively. The microstructures of the coatings were studied using x-ray diffraction, transmission electron microscopy and scanning electron microscopy. Indentation induced plastic deformation and fracture behavior was visualized by extracting the lamellae under the indent using focused ion beam milling technique combined with transmission electron microscopy. Wear behavior of the coatings were characterized by reciprocating sliding wear test following microscopic observations of the wear track.

Monolithic Zr-Si-N coating shows a systematic variation of microstructure, hardness and fracture resistance as a function of Si content. Si forms a substitutional solid solution in the cubic ZrN lattice up to 1.8 at. % exhibiting a fine columnar structure. Further Si additions result in precipitation of an amorphous SiN_x phase in the form of a nanocomposite structure (*nc* ZrN- *a* SiN_x) that is fully developed at 6.3 at. % Si. Dislocation based homogeneous deformation is the dominating plastic deformation mode in the columnar structure, while grain

boundary sliding mediated plastic deformation causing localized heterogeneous shear bands dominates in the nanocomposite structure.

Indentation induced cracking shows the higher fracture resistance for columnar structure compared to the nanocomposite coatings. Crack branching and deflection were observed to be the key toughening mechanisms operating in the columnar structured coating. Reciprocating wear tests on these coatings show a bi-layer wear mode dominated by tribo-oxidation. Nanocomposite coatings offer superior resistance to both static and tribo-oxidation, resulting in higher wear resistance even though they are soft and brittle.

Monolithic and multilayers of $\text{Zr}_{0.63}\text{Al}_{0.37}\text{N}$ coatings were grown at a deposition temperature of 700 °C. Monolithic $\text{Zr}_{0.63}\text{Al}_{0.37}\text{N}$ coating shows a chemically segregated nanostructure consisting of wurtzite-AlN and cubic-ZrN rich domains with incoherent interfaces. When the same composition is sandwiched between ZrN nanolaminates, $\text{Zr}_{0.63}\text{Al}_{0.37}\text{N}$ shows a layer thickness dependent structure, which results in systematic variation of hardness and fracture resistance of the coatings. Maximum hardness is achieved when the $\text{Zr}_{0.63}\text{Al}_{0.37}\text{N}$ layer shows semi-coherent wurtzite-AlN rich domains. While the maximum toughness is achieved when AlN- rich domains are pseudomorphically stabilized into cubic phase. Stress induced transformation of metastable cubic-AlN to thermodynamically stable wurtzite-AlN was suggested to be the likely toughening mechanism.

Preface

This is a summary of my work between March 2012 to April 2014. During these two years the main focus has been to study the correlation between microstructure and mechanical properties of the ZrN based hard coatings. The key results are presented in the appended papers. The work has been performed in the group of Nanostructured Materials at the Department of Physics, Biology and Chemistry (IFM) at Linköping University, Sweden and at the Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica, Universitat Politècnica de Catalunya, Spain. The work has been supported by The EU's Erasmus Mundus graduate school in Material Science and Engineering (DocMASE), the Swedish foundation for strategic research (SSF) through the grant Designed Multicomponent Coatings (MultiFilms).

Included papers

Paper I

Structure, deformation and fracture of arc evaporated Zr-Si-N ternary hard films

K. Yalamanchili, R. Forsén, E. Jiménez-Piqué, M. P. Johansson Jöesaar, J.J. Roa, N. Ghafoor and M. Odén

Submitted for publication

Paper II

Influence of microstructure and mechanical properties on the wear behavior of reactive arc deposited Zr-Si-N coatings

K. Yalamanchili, J.J. Roa, E. Jiménez-Piqué, M.P. Johansson Jöesaar, N. Ghafoor and M. Odén

In manuscript (on going work)

Paper III

Growth and Mechanical Behavior of Nanoscale Structures in $ZrN/Zr_{0.63}Al_{0.37}N$ Multilayers

K. Yalamanchili, I.C. Schramm, E. Jiménez-Piqué, L. Rogström, F. Mücklich, M. Odén, and N. Ghafoor

In manuscript

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Table of contents

1. Introduction

1.1 Background to hard coatings	1
1.2 Structure –property relation of the coatings, motivating questions.....	6
1.3 Aim and Outline of the thesis	8

2. Mechanical properties of hard coatings

2.1 Hardness	11
2.2 Fracture toughness.....	14
2.3 Hot hardness	18

3. Growth of hard coatings

3.1 Sputter deposition	22
3.2 Magnetron sputtering	25
3.3 Cathodic arc deposition	28
3.4 Reactive vapor deposition	31
3.5 Growth of PVD coatings	32

4. Material systems

4.1 Zr-N	37
4.2 Si-N	38
4.3 Zr-Si-N	39
4.4 Al-N	40
4.5 Zr-Al-N	41

5. Characterization

5.1 Hardness	45
5.2 Fracture toughness	47
5.3 Focused ion beam	49

5.4 Electron microscope 51

5.5 Atomic force microscope 55

5.6 X-ray diffraction 57

6. Summary of the included papers and proposed future work 59

7. Paper I 66

8. Paper II (On going work)..... 93

9. Paper III 115

1. Introduction

1.1 Background to hard coatings

Coatings are often an integral part of engineering components. They can be applied as an anti-reflective coating on an eyeglass lens, as a thermal barrier coating in a gas turbine engine to protect the components at 1200 °C or as a wear resistant coating on a cutting tool insert for the machining of a Ni based super alloy.

Hard coating acts like a hard skin protecting the materials against all the forms of wear with the principle driving force of economic benefits, environmental friendly operations and improved sustainability of the components. Within the scope of this thesis, the word hard coating implies to monolithic and multilayers of transition metal nitride (TMN) coating with a hardness of 20-40 GPa. These coatings were grown by physical vapor deposition techniques (PVD) such as reactive arc deposition and magnetron sputtering up to a thickness of 1- 4 μm .

The evolution of the hard coating material system was strongly motivated by the continuous demands from the cutting tool industry. One of the primary requirements for the application is hardness. Figure.1.1 shows the hardness of various engineering materials ranging from the low carbon steel with a hardness value of 6 GPa to the hardest material known to the mankind, diamond with a hardness of 95 GPa.

However, the room temperature hardness may not be sufficient for the cutting application, a real time cutting operation accelerates the contact temperature up to 900 °C [1], and the temperature softens both the tool material and feed material. But, nonmetallic inclusions such as carbides and oxides in the feed stock retain high hardness comparable to the level of the tool insert even at elevated

1. Introduction

temperature and acts as abrasive particles to the cutting tool. The cutting tool also suffers from oxidation and material build up due to the harsh conditions prevailing during metal cutting operation.

Figure 1.1. Comparison of hardness, low carbon steel [2], WC-10 wt. % Co cermet [3], ZrN, ZrN/Zr-Al-N [Paper-3], Ti-Al-N [4] and Diamond [5].

To handle this problem Sandvik Coromont, (Sweden) and Krupp Wedia, (Germany) independently came up with a solution in 1969 to apply few micron thick TiC coating by chemical vapor deposition (CVD) on cutting tools [6]. Soon it was realized that the coating of transition metal carbide and nitride can handle the chemical and abrasive wear better than bare carbide tool and this was translated into higher productivity in the machine shop with higher cutting speeds. With increased cutting speeds, again chemical wear of the coating has become the bottle neck, and then the solution was offered by Al_2O_3 coating which is more inert to oxidation. By the year 1975, a bi-layer coating of inner TiC and outer Al_2O_3 has

1. Introduction

almost become the industrial standard coating. These coatings complement each other in protecting the cutting edges from the harsh conditions [6]. However, the industry was aware of the some of the serious drawbacks associated with CVD technique such as high depositing temperatures (900 °C) causing decarburization of tungsten carbide substrate, leading to poor transverse rupture strength and toughness. The coatings also suffered from undesirable tensile residual stresses and microcracks [7].

Physical vapor deposition technology has evolved to handle the issues in CVD. The first industrial scale PVD TiN High Speed Steel (HSS) drill bits were introduced in 1982 by Sandvik Coromant [6]. The techniques allowed to grow crack free coating over sharp edges with favorable compressive stress at much less deposition temperatures ~ 500 °C. PVD technology gradually gained popularity and became the standard for the applications requiring interrupted cutting and sharp edges e.g. threading and end milling. The success of PVD TiN has led to the development of second generation Ti-C-N coatings with higher hardness, but the oxidation resistance was not satisfactory [8]. The metallurgical community was already aware of the benefits of Al addition, to protect against oxidative damage, so there was an obvious interest in Ti-Al-N system. The first PVD Ti-Al-N coatings were reported in 1986 [8] with improved oxidation resistance and superior cutting performance compared to both TiN and Ti-C-N. After 20 years, a new scientific perspective was discovered for the superior cutting performance of Ti-Al-N coatings known as age hardening phenomenon [9,10], which is very similar to the first patented metallurgical age-hardenable Al-Cu alloy about 100 years ago. The phenomenon of age hardening at elevated temperature is triggered by self-organized nanostructure as a result of spinodal decomposition pathway from the metastable cubic (*c*) Ti-Al-N to thermodynamically stable phases of cubic (*c*) TiN and wurtzite (*w*) AlN [9].

1. Introduction

This knowledge was applied in the industry to optimize the Al content of Ti-Al-N coating.

Since the early 90's, there has been an upsurge of ternary and multinary nanostructured coatings, following the success of Ti-Si-N as a super hard coating material [11,12], with hardness higher than 40 GPa. The extreme hardness is a result of handicapping the dislocation motion by scaling down the grain size to few nanometers and architecting the interfaces to suppress grain boundary sliding [13,14].

Compositionally modulated structures are a relatively new class of materials with impressive properties. These coatings were proved to have superior hardness and fracture toughness over the monolithic coatings [15–17]. Nanoscale multilayers provide the unique opportunity to tune the crystal structure and hence the mechanical properties, simply by changing layer thickness [18–20].

Today, there are at least more than 100 different coatings (figure 1.2) available [21], which are tailor-made to suit the specific needs and proven to improve the component life time up to ten times. The applications of hard coatings are also getting diversified as shown in figure 1.3, from the original cutting tool application to the more complex engineering application such as automotive engine components [22].

1. Introduction

Figure 1.2. PVD coatings available in the market, [21].

The current technological challenges are quite different from the traditional simple hardness based coating development. The cutting tool industry constantly seeks higher cutting speeds which translate to higher hot hardness and better oxidation resistance of the coatings and the substrate. In addition, the engineering components demand for toughness improvement of coatings. Probably, these three factors will be the prime drivers of the materials science community of the hard coating industry for a while.

1. Introduction

Figure 1.3. Typical market share of PVD coatings between 2005 and 2011, showing significant fraction of coated engineering components [21].

In spite of extensive research from both industrial and academic fronts in the past three decades, the structure-property relation of hard coatings is still an area with several open questions. Some of the most relevant questions to the current thesis are highlighted in the next section. Today with the sophisticated computational and experimental facilities at hand, structure-property understanding will be the central idea of the knowledge based design of next generation hard coatings in place of traditional empirical development methods and this motivates the title of the thesis.

1.2 Structure-property relation of hard coatings, motivating questions

Understanding the relationship between microstructure and mechanical properties has always been the central idea of material development. The structure-property relation essentially describes how the microstructural variation influences mechanical properties such as hardness, ductility and fracture toughness. This understanding is exploited in tuning the mechanical properties of the hard coatings. Some of the questions which motivated this thesis are summarized as following.

The principle deformation mechanism of hard coatings has been heavily debated between interface driven deformation such as columnar boundary sliding or cracking and atomic scale mechanisms such as dislocations [23–25]. The motivating question is: can we gain more understanding of the dominant deformation mode of hard coatings?

For bulk ceramic materials it has been shown that material becomes softer and an inverse hall-petch relation is seen, when the grain size is sufficiently low (30-50 nm) [26]. However, such a transition between columnar and nanostructured hard coatings was never visualized.

The brittleness of hard coatings restricts their application scope, hence tuning the toughness without sacrificing the hardness is a key challenge. In spite of many theoretical considerations such as increasing the valence electron concentrations, transformation toughening [27–29]; there is a shortage of candidate materials or approaches that can enhance the toughness of the hard coatings on industrial scale. The microstructure of the coating is an important factor which influences the fracture behavior. However, this phenomenon is not adequately studied for hard coatings. Determining the optimal grain size, morphology and microstructural

details for the improved fracture toughness is an important technical need, which motivates for deeper fracture studies of these coatings.

Ultimately, these coatings have to demonstrate better wear resistance under a sliding contact. Higher hardness of the coating does not guarantee better wear resistance. Wear is a complex interaction of surface forces, contact mechanics, deformation behavior, contact geometries and environmental parameters [30]. Under such complex interaction, the influence of microstructure and mechanical properties on the wear behavior of the hard coatings is not conclusive.

1.3 Aim and Outline of the thesis

The aim of this thesis is to provide a deeper understanding of the complex relationship between microstructure and mechanical properties of a few micron thick ZrN based hard coatings deposited by plasma based physical vapor deposition techniques.

This thesis includes chapters with a comprehensive overview of the techniques, materials used and finally the results are presented in the papers.

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2. Mechanical properties of hard coatings

Considering the generic proportionality between hardness and abrasive wear resistance, hardness is the most important mechanical property. But often these coatings are to operate at elevated temperature and the contact temperature in a typical cutting operation may reach up to 900 °C with a peak normal stress up to 2 GPa [1]. Hence the hardness of these coatings measured at room temperature may not be relevant at elevated temperatures. New deformation mechanism such as grain boundary sliding may become activated at elevated temperatures, and this defines the additional requirement called *hot hardness*. The stresses are never monotonic in real situation and the coatings should then handle fluctuating stresses which highlights need for fatigue resistance. If there is a defect or crack, the crack should not run through the coating at unpredictable rates to ensure reasonable sustainability of the coating, hence the need for fracture toughness, K_{Ic} . An additional factor that is unique to PVD hard coatings is the presence of higher growth stress. Compressive residual stress about 2-5 GPa is routinely reported [2,3] in PVD coatings and these stresses are beneficial for room temperature mechanical properties.

2.1 Hardness

The conventional definition of hardness is the resistance to plastic deformation [4], but this definition may not be applicable to a typical hard coating, when the hardness is measured by nanoindentation technique. Almost all the super hard coatings ($H > 40$ GPa) also have relatively high elastic modulus [5–7]. The hard coating with a high E/H ratio subjected to a Berkovich indentation under fully

2. Mechanical properties of hard coatings

developed plastic zone consists about 60% ($\pm 10\%$)¹ elastic deformation and 40% ($\pm 10\%$) plastic deformation. Hence, the hardness extracted from the mean contact pressure is a measure of resistance to both elastic and plastic deformation [8]. The hardness of the coating can be improved either by increasing elastic modulus or by constraining the plastic flow. This suggestion also explains the similar trends between hardness and elastic modulus of the nanoindentation measurements on these coatings [9].

For a single crystal material, the elastic modulus is mostly determined by the electronic structure and bonding characteristic. However, for a polycrystalline and nanocrystalline material, the elastic modulus is influenced by the interfaces, especially the grain boundary free volumes contribute to reduced elastic modulus, hence the microstructural dependency of the contact elastic modulus [10].

Figure 2.1. Strengthening mechanisms of coating (a) grain boundary strengthening, (b) coherency strengthening and (c) solid solution strengthening.

¹ values obtained from ZrN based coatings, paper 1 and 3

Plastic flow of a material is closely related to dislocation motion. Dislocation motion can be handicapped by carefully architecting the interfaces and phase constituents of the coating [11]. Following are the dominant hardening mechanisms aimed in the advanced ternary and quaternary coatings.

a) Hall-Petch strengthening: Grain boundaries are the effective barriers to dislocation motion (figure 2.1a). Strengthening of the coating is achieved by reducing the grain size. An inverse square root relation between the yield stress and the grain size was proposed by Hall [12] and Petch [13] independently around 1950. This is the primary strengthening mechanism for nanocomposite of Ti-Si-N, Al-Si-N and W-Si-N hard coatings [14–16]. However, when the grain size is sufficiently low ($\sim 30\text{-}50\text{ nm}$) the Hall-Petch relation is not valid, instead the material softens by so called inverse Hall-Petch effect (IHPE) [17]. This transition is observed around 50 nm for TiN coatings [18]. Grain boundary sliding was suggested to be one of the principle mechanism for IHPE effect, similar to what has been observed in the nanocomposite of Zr-Si-N (paper 1).

b) Coherency strengthening: lattice misfit between iso-structural and non iso-structural phase constituents across the coherent interfaces generates coherency stresses. These stresses interact with the elastic stress fields of dislocations and hinders the dislocation motion (figure 2.1 b) [19]. The well-known examples are age hardening in monolithic Ti-Al-N coating [20], hardness enhancement in the multilayers of TiN/VN [21].

c) Solid solution strengthening: Solid solution induced lattice distortion stress fields interact with the elastic stress field of dislocation, which results in strengthening (figure 2.1 b) [22]. Si addition about 1.8 at. % in ZrN lattice has resulted in a hardness increment of 4 GPa (Paper 1). The strengthening can be further magnified by having non-symmetrical tetragonal distortions in ZrN lattice.

d) Koehler strengthening: Spatially fluctuating elastic properties results in strengthening of a material [23]. The difference in dislocation line energy between the regions of low and high shear modulus offers hindrance to dislocation motion. Koehler strengthening was reported to be a likely strengthening mechanism responsible for the hardness increment in the multilayers of TiN/VNbN in spite of absence of coherency stresses [24,25].

Most often, the above described strengthening mechanisms operate simultaneously, it may be difficult to quantify the individual contribution. Multilayers of ZrN/Zr_{0.63}Al_{0.37}N has shown hardness increment about 10 GPa over the rule of mixture (paper 3), which is a result of simultaneous operation of coherency and Koehler strengthening mechanisms.

2.2 Fracture toughness

Toughness is the ability of a material to resist both crack initiation and propagation, while the fracture toughness (K_{IC}) is the ability to resist the crack propagation. Improving the fracture toughness without sacrificing the hardness is an obvious need to make the coatings more effective in handling the ever growing demands of mechanical and thermal stresses of the operations. The coating development program on the fracture toughness front has been relatively slow, one of the reasons perhaps is the difficulty in getting the reliable K_{IC} of the few micron thick coating. Several techniques were proposed to measure the K_{IC} of the coatings, further description is presented in chapter 5.2. Fracture toughness of conventional binary hard coatings such as TiN and CrN were reported between 1.2 and 3.3 MPa $\sqrt{m}$ [26,27], the variation is a result of differences in the measurement techniques and growth condition. Fracture toughness of inherently brittle, hard coatings were suggested to be enhanced by the following ideas.

a) Intrinsic toughening: The toughness is enhanced by tuning the composition of the coating to have favorable electronic structure, such as higher valence electron concentration (VEC) and increased fraction of metallic bonding [28]. Theoretical studies suggest that the fracture resistance of TiN can be improved by alloying with Ta, Mo and W [28] without significant loss in hardness. Similarly, fracture resistance of CrN coatings may be improved by alloying with V, Nb, Ta, Mo and W to CrN [29].

b) Extrinsic toughening

In contrast to intrinsic toughening, extrinsic toughening mechanisms operate along the crack front, based on their principle toughening mechanism they can be classified as following.

1) Ductile phase toughening: A ductile phase is included in the hard coating, to relax the strain field in the vicinity of the crack tip. It was shown that the Ni addition to nano crystalline TiN/amorphous-SiN_x coating was reported to increase K_{IC} from 1.15 MPa $\sqrt{m}$ to 2.6 MPa $\sqrt{m}$ but with a significant drop in hardness [30].

2) Crack deflection: The stress intensity at the crack tip can be reduced up to 50% [31] by deflecting the crack away from the maximum tensile stress direction. Crack deflection is achieved by having a preferential weak plane. Multilayers offer crack deflection and crack blunting (figure 2.2 a) at the interface. In case of monolithic coatings, grain boundaries may cause such a crack deflection. Similar deflection and branching also observed in ZrN columnar coatings (figure 2.2 b), which are likely caused by columnar grain boundaries. Reducing the grain size makes the crack propagation more difficult, and finer grain size enhances the fracture toughness. Theoretical calculations show that the maximum fracture toughness is achieved when the grain size is about 100 μm for bulk ceramic materials [32].

Reducing the grain size less than the critical value has a negative effect on fracture toughness. When the grain size is down to the nanoscale, the effective length of the fracture process zone tends to be larger than the characteristic length scales of the microstructure. Then the microstructure is unable to influence the crack propagation path, which results in an uninterrupted crack growth similar to what has been observed for the nanocomposite coating of Zr-Si-N (figure 2.2 b) (Paper 1).

Figure 2.2. Crack deflection mechanism (a) schematic illustration in multilayers (b) SEM oblique angle image after FIB cut of the indent showing crack deflection and branching (black arrow) in columnar ZrN but not in nanocomposite Zr-Si-N coating. Indentations were made at a penetration depth of 3000 nm.

3) Zone shielding: The stress concentration at the crack tip is reduced by the volume dilatation around the crack by stress induced phase transformation of the unstable phase constituents of the coating. Figure 2.3 (c, e) shows the comparison of indentation induced fracture of 15nm ZrN/2nm $Zr_{0.63}Al_{0.37}N$ and 15nm ZrN/30nm $Zr_{0.63}Al_{0.37}N$ coatings (Paper 3). Metastable cubic-Al(Zr)N is pseudomorphically stabilized in 2nm $Zr_{0.63}Al_{0.37}N$ multilayer structure. The higher fracture resistance of multilayer of 2 nm $Zr_{0.63}Al_{0.37}N$ is likely an effect of the above suggested zone shielding mechanism. The likely indentation induced transformation of metastable cubic-Al(Zr)N crystals to thermodynamically stable

wurtzite-Al(Zr)N crystals causes molar volume expansion about 20% [33], which relieves the tensile strains around the indent.

Figure 2.3. Zone shielding toughening mechanisms of coating (a) schematic illustration of zone shielding, (b) proposed transformation induced toughening of metastable cubic AlN to wurtzite AlN. Contact induced fracture at a force of 200 mN and corresponding SAED pattern of (c, d) 15nm ZrN/2nm $\text{Zr}_{0.63}\text{Al}_{0.37}\text{N}$ multilayer, (e, f) 15nm ZrN/30 nm $\text{Zr}_{0.63}\text{Al}_{0.37}\text{N}$ multilayer coatings.

4) Contact shielding: Fiber reinforcement was proven to improve the fracture toughness of a bulk ceramic by the additional energy dissipative mechanisms such as crack deflection, crack bridging and fiber pull out (figure 2.4).

Figure 2.4. Schematic illustration of contact shielding mechanism.

2.3 Hot hardness

Hot hardness is a measure of material resistance to deformation at elevated temperatures. Elevated temperature softens most of the materials due to increased bond length and the relative ease of dislocation motion.

Thermally assisted dislocation motion, such as dislocation climb may become active and trigger new slip systems, even creep deformation mechanisms may become operative above homologous temperature $T_h(T/T_{mp})$, of 0.4-0.5 [34].

High temperature micro hardness measurement shows a significant hardness drop for PVD TiN coating as a result of relaxation of growth induced stresses and grain growth of the fine columnar microstructure. The hardness of TiN was reported to reduce from 23 GPa at room temperature to 10 GPa at 800 °C and 5 GPa at 1000 °C [35]. Ti-Al-N coating has higher hardness compared to TiN up to 800 °C, but lost its advantage at 1000 °C [35]. However the inherent deformation behavior of these coatings at elevated temperatures was never studied adequately. For a typical hard coating with grain size varying between sub-micron and nanosize length scales, the cutting temperature of 900 °C corresponds to a homologous temperature of 0.35. This temperature may be sufficiently high to invoke grain boundary dominated deformation mechanisms.

When grain boundary sliding is the active deformation mechanism, larger grain size (even single crystal) is beneficial, though it is a trade-off for the room temperature hardness. Deformation studies of the coatings at elevated temperatures is relatively less explored area with several open questions, detailed knowledge may lead to a paradigm shift in the microstructural design of hard coatings with emphasis on preventing migration and sliding of grain boundaries to achieve high temperature hardness.

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3. Growth of hard coatings

There are wide range of techniques available for the deposition of thin coatings, such as chemical deposition (plating, solution and vapor deposition) and physical deposition (thermal spray, mechanical and vapor deposition). In this thesis coatings were grown by plasma based physical vapor deposition (PVD) techniques such as unbalanced magnetron reactive sputtering and reactive arc deposition techniques. Plasma based PVD coatings have favorable residual stresses, higher density and better adhesion compared to other techniques. The most striking advantage of the plasma based PVD technique is the ability to grow metastable and unstable phases with superior mechanical properties.

Reactive arc deposition technique was used to deposit relatively thicker Zr-Si-N coatings in paper 1 and paper 2. Unbalanced magnetron sputtering technique was used to deposit epitaxial multilayer coatings of ZrN/ZrAlN in paper 3. An overview of both processes are described in the following sections.

3.1 Sputter deposition

Sputtering is simply the process of surface erosion by energetic particles, a kind of atomistic scale sandblasting. Sputter deposition involves condensing the eroded particles on the substrate. The process is driven by momentum exchange between the incident projectiles and the target atoms. The incident particle initiates a collision cascade in the target, when the cascade recoil and reaches the target surface with an energy higher than the surface binding energy (U_s) of the target, the atom will be ejected as shown in figure 3.1 [1].

3. Growth of hard coatings

Figure 3.1. Schematic illustration of sputtering mechanism.

Besides sputtering, several other effects take place at the particle bombardment surface, such as adsorption or reflection, chemical reaction, backscattering and implantation etc. The efficiency of sputtering process can be quantified as sputtering yield (Y), defined as the number of target atoms ejected per incident particle. The sputter yield depends on the target atoms, bombarding species, energy and the incidence angle of the projectiles [2]. The sputter yield above the threshold energy is given by the following equation [3].

$$Y = \frac{3}{4\pi^2} \alpha \frac{4 M_1 M_2}{(M_1 + M_2)^2} \frac{E}{U_s} \quad (3.1)$$

Where E is the energy of the incident atom, M_1 and M_2 are the masses of the incident and target atoms, U_s is the surface binding energy and α is a dimensionless parameter, which is typically about 0.2 (depending on mass ratio and the ion energy). From the equation 3.1 it can be interpreted that maximum momentum transfer occurs when $M_1 \sim M_2$, the sputter yield varies inversely proportional to

3. Growth of hard coatings

surface binding energy of the target atoms and the maximum yield is achieved when the particles strikes the target at an incident angle about $60\text{-}70^\circ$ [4].

The surface binding energies of the most metals are around $3\text{-}7\text{ eV}$ [5], the collision cascade should provide an energy higher than this value to the surface or near surface atoms, if an atom to be sputtered out. Ions serve as the best incident projectiles considering the high energy requirement of the sputtering process and the energy of the ions can be manipulated by using electric fields. The incident ions are generated by so called *glow discharge* process, by applying a high voltage (couple of hundred volts) and low current (typically few amps) between the target (cathode) and the target shield (anode) in a low pressure inert gas environment.

Figure 3.2. Schematic illustration of sputtering process.

The sputtering process is schematically shown in figure 3.2. When a potential difference is applied between the electrodes, free electrons (generated by background radiation) in the sputtering gas accelerate towards the anode by the

electric field. The accelerated electrons will gain energy and collide with neutral gas atoms and eventually ionize the gas. The ionized gas (typically Ar^+) is accelerated by the electric field towards the target and ejects the target atoms

(figure 3.2). Besides sputtering, secondary electrons are also ejected from the target as a result of ion-surface interactions [6]. Secondary electrons further give rise to new ionization collisions, creating new ions and electrons. This process of secondary electron emission at the cathode and further ionization of carrier gas eventually leads to self-sustaining plasma with sufficient ions and charge carriers.

3.2 Magnetron sputtering

The ionization processes of the sputtering are enhanced by using magnetic field close to the target surface [7], the process is known as magnetron sputtering. A magnetron generates static magnetic field, and the magnet is located parallel to the target surface (figure 3.3). The crossed electric and magnetic field ($\mathbf{E} \times \mathbf{B}$) confines the electrons close to the target with long trajectories, shown schematically in figure 3.3. Such electron confinement increases the electron-atom collision, yielding a high ionization probability. Increased ionization results in dense plasma close to the target which translates into an increased ion bombardment of the target, resulting higher sputter rate and hence a higher deposition rate. The strength of the magnetic field is the key operational parameter, higher the strength of the magnetic field better the ionization efficiency, but deeper the race track and less utilization of the target. However the efficiency saturates at higher field strength, typically about 500-700 G ($B_{\text{Tangential}}$) [8].

3. Growth of hard coatings

Figure 3.3. Cutaway view of magnetron

Based on the configuration of the magnetic field, magnetrons are classified as balanced and unbalanced magnetrons (Type I and II) as shown in figure 3.4. In case of balanced magnetron, the strength of the inner and outer poles are balanced. Unbalanced type 1 configuration consists stronger inner pole relative to the outer pole leading to much reduced ion fraction near the substrate, such an effect was exploited to produce porous and chemically reactive films [9]. In type II unbalanced magnetron sputtering, the outer pole is relatively strengthened to the center pole. Not all the field lines are closed at the center pole, some of the outer field lines are directed towards the substrate and secondary electrons are able to follow these lines. Secondary electrons near the substrate cause ionization of the sputtering gas (typically Ar) and increase the ion to atom arrival ratio ($J_{\text{ion}}/J_{\text{met}}$) at the substrate.

3. Growth of hard coatings

During the deposition of monolithic and multilayer coatings of ZrN and ZrN/Zr_{0.63}Al_{0.37}N, an additional tunable solenoid surrounding the substrate was synchronized with the individual unbalanced type II magnetrons to guide the secondary electrons from the target to the substrate there by increasing the ion to metal atom flux ratio $J_{\text{ion}}/J_{\text{met}}$. Such an arrangement was reported to boost the $J_{\text{ion}}/J_{\text{met}}$ by about 100 times (from 0.5 to more than 50) [10,11]. A higher ion fraction of the metal species with moderate energy (20-30 KeV) at the growth front promotes better adhesion, dense and uniform coatings with improved mechanical properties [12].

Figure 3.4. Plasma confinement of balanced and unbalanced magnetron sputtering [7].

3.3 Cathodic arc deposition

Cathodic arc technology is the workhorse for depositing industrial scale hard and wear resistant coatings. The primary motivation is the process ability to generate highest ion fraction of the target metal vapor (> 90%) compared to any other PVD

3. Growth of hard coatings

techniques [13], facilitating greater surface mobility which in turn results in a better adhesion, higher density and better uniformity of the coating.

Figure. 3.5 (a) arc evaporation process at cathode (b) industrial scale arc deposition chamber used for the deposition of Zr-Si-N coating.

The electric arc is characterized by a low-voltage, high-current discharge between the electrodes. An industrial scale arc evaporation chamber used for the deposition of coatings in paper 1 is shown in figure 3.5 b. The process begins with striking an arc (figure 3.5a) on the cathode (target) surface that gives rise to a few micrometers (1-10 microns) energetic emitting area known as cathode spot. The power density at the spot is extremely high and reaches up to 10^9 Wm^{-2} [14]. Such high power densities can transform the cathode materials from a solid phase to plasma phase in extremely short time period of 10-100 ns, known as explosive phase transformation [15]. Electrons are emitted by so called “explosive electron emission process” [13] which is a combined effect of high temperature, high electric field strength at the cathode spot. The localized temperature of the cathode spot is extremely high ($\sim 5000\text{-}10000 \text{ }^\circ\text{C}$) [16], which results in a high velocity jet of vaporized

3. Growth of hard coatings

cathode material, leaving a crater on the cathode surface. After a cathode spot is generated it expands laterally, resulting in reduced power density. This lowers the peak temperature of cathode spot and further reduces the electron emission, which results in a transition of the cathode spot from explosive phase to evaporative phase and finally the discharge ceases. The whole cycle takes place between 10 ns to 1 μ s [13], then it self-extinguishes and re-ignites in a new area close to the previous crater and it moves either randomly or steered in the presence of external magnetic field [17]. This behavior is responsible for the apparent motion of the arc. The plasma pressure within a cathode spot is high, and the strong pressure gradient causes the plasma generated there to accelerate away from the surface. The plasma also supports the current flow between the electrodes and make the arc process self-sustaining. There is a lower limit to arc current, called the chopping current below which the spot will not persist [18], an upper limit is determined by source cooling requirements. The typical arc discharge current for Zr cathode is 100 A resulting in a burning voltage of 30 V in the pure N₂ atmosphere (paper 1).

The single most important challenge to cathodic arc deposition is the control of macroparticles (SEM image is shown in figure 3.6). Macroparticles are formed by the ejected molten droplets from the hot cathode spot by higher plasma pressure within the cathode spot. Stoichiometry of these particles being completely different [19] from the rest of the coatings, these particles also offer the local source of variation in physical and mechanical properties. The voids surrounding the macroparticle are caused by the shadowing effect of the incident ion flux and such voids are expected to act as stress concentrators that facilitate crack initiation. Previous studies [20] have shown that both flank wear and rake wear of the tool gets accelerated in the presence of macroparticles.

3. Growth of hard coatings

Some strategies are followed to reduce the density or to avoid the macro particles. The traditional way is to filter the macroparticles using curved magnetic filters [21], but without much success in the hard coating industry due to poor economics of the process as a result of reduced deposition rates. Magnetic fields are used to steer the arc, thereby controlling the lifetime of cathode spot and to reduce the density of macro particles [17,22]. Other option which is also an active research idea exploring in the same research group is to restrict the size of the active cathode spot thereby the size of the molten pool by reducing the mean grain size of preferentially eroding phase in a composite powder metallurgy cathode as observed in Ti-Si-N coatings [23].

Figure 3.6. SEM image of macro particle in arc evaporated ZrN coating.

3.4 Reactive vapor deposition

The nitride coatings in this thesis were grown by condensing the metallic vapor flux in a nitrogen atmosphere. Process gas (N_2) interacts with the metal plasma and the molecular nitrogen dissociates and gets activated by electron impact ionization and charge exchange coupling. The chemical bonds between the metallic and gas species are established on the growth front of the coating, while the substrate offers

the conservation of momentum and energy resulting from the compound formation. The stoichiometry of the coating can be varied by changing the partial pressure of nitrogen [24]. The reactive gas also forms a compound layer on the target surface leading to so called poisoning effect. The compound layer being electrically resistive interrupts the charge transport between the cathode and anode and this has consequences. In a reactive sputtering process the poisoning is generally not desirable, as this causes reduced deposition rate [2]. The same is true in case of arc deposition also, but with an advantage of reduced macroparticle density by having a compound layer on the cathode surface, which has been demonstrated for the TiN coatings [25].

3.5 Growth of PVD coatings

Coating growth by the PVD process essentially consists of condensation of hyperthermal particles on to a substrate at a cooling rate close to 10^{10} K /s [12], resulting in a dense and continues coating. The incident hyperthermal particles make a random walk on the substrate looking for thermodynamically more stable positions, in this process individual atom gather to make clusters. If the clusters acquire the critical radius they becomes stable nuclei [26] and the impinging atoms are drawn to these clusters, these clusters grow in size and gets coalesced to form a dense coating. Because of very high cooling rates involved in the growth process, the resultant microstructure is essentially controlled by the mobility of the ad-atom species.

A comprehensive overview of the influence of the various deposition parameters and the resultant microstructure are represented by so called *Structure Zone model (SZM)*. The first model dates back to 1969 developed by Movchan and Demchishin (MD) in 1969 based on the evaporation studies on various metals [27].

3. Growth of hard coatings

In the current work, coatings were grown by plasma based vapor deposition techniques, the kinetic and potential energy of the arriving species is significantly high to cause local atomic scale heating, to amplify the mobility of the ad-atom species and altering the resultant microstructure. The earliest model for hyperthermal particles was developed by Thornton et al., [28] and then it was extended by Anders [29] with three axes as shown in the figure.3.7.

Figure 3.7 (a) structure Zone diagram for plasma based thin coating growth from Anders [29], (b) cross sectional view of the structure zone diagram.

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T^* , consisting of deposition temperature (T_h) and the local atomic scale heating caused by the potential energy of the ad-atoms species. Potential energy (mainly contributed by ionization energy) of the arriving ad-atom can vary between 5 eV to 15 eV per ion [30]. E^* consisting of the kinetic energy of the arriving flux which depends on the bias voltage and the charge state of the metal ions, the velocity of the arriving atom /ion. Finally t^* , thickness of the coating to illustrate ion etching effects at higher energies of the ad-atom species.

3. Growth of hard coatings

The cross sectional view of the microstructure model presented in the figure. 3.7 b for better understanding. Zone 1 corresponds to low deposition energies and temperatures, with limited ad-atom diffusivities resulting in a fine porous columnar structure. Zone T represents the transition region, where surface diffusion is active but not the grain boundary diffusion. Zone T represents a characteristic microstructural variation across the thickness of the coating, the competitive growth mechanism between a low diffusivity plane and high diffusivity planes, resulting in a V shaped faceted dense columnar structure. Zone 2 represents coating growth, where both surface diffusion and grain boundary diffusion are active, resulting in a homogenous columnar microstructure. Further increase in temperature or mean energy of the arriving atoms result in the Zone 3 equiaxed structure, likely a combination of re-crystallization and co-deposition of residual elements from the chamber [31].

Figure 3.8 TEM micrograph of (a) epitaxial ZrN coating deposited by magnetron sputtering (dark contrast revealing threading dislocations), (b) polycrystalline ZrN deposited by arc deposition.

The deposition parameters used for the coating growth in Paper 1 and 2 are close to Zone T. But this is still a simplified approximation of the real growth conditions which includes the influence of co-deposited species and the substrate template effects etc. Comparison of ZrN coating microstructure deposited by two different techniques are shown in figure 3.8.

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4. Material systems

Transition metal nitrides (TMN) such as TiN and ZrN have several common interesting physical and mechanical properties. High hardness, high melting point, high thermal stability, impressive aesthetic properties and reasonable oxidation resistance of these nitrides make them as an important candidate material for wear resistant applications [1]. Three decades of extensive studies on TiN based coatings have resulted in several successful ternary and multinary nitrides such as Ti-Al-N [2,3], Ti-Cr-Al-N [4], Ti-Al-Si-N, Ti-Zr-Al-N [5–7] with improved functional properties.

ZrN based coatings are relatively new and less studied. Recent theoretical and experimental investigations have shown several interesting facts about ZrN based coatings. Zr-Al-N has higher enthalpy of mixing compared to Ti-Al-N [8] and hence a higher driving force for the decomposition of the metastable solid solution, which is an enabling criteria for the evolution of self-organized nanostructures. Other interesting phenomena observed in Zr-Al-N is that *w*-AlN can be grown semi-coherently with *c*-ZrN that gives higher hardness [9], which is normally incoherent in Ti-Al-N with significant loss of hardness. These interesting facts have motivated the choice of ZrN based coatings.

4.1 Zr-N

Zirconium Nitride (ZrN) with mixed metallic, ionic and covalent bonding characteristics [10], has NaCl - type (B1) crystal structure. Crystal structure and mechanical properties of ZrN closely resemble TiN, but has a larger lattice parameter (ZrN, $a = 4.58 \text{ \AA}$ [11] and TiN, $a = 4.24 \text{ \AA}$ [12]). Hardness and contact

elastic modulus of the ZrN coating was measured to be around 25 and 420 GPa respectively [13–15]. ZrN coating outperforms TiN coating in the cutting application of titanium alloys [16]. ZrN has an aesthetic advantage over TiN with pleasing light gold color similar to elemental gold, which is a good selling argument for the industry. Figure 4.1 shows B1 crystal structure of ZrN, each Zr atom is coordinating six N atoms and vice versa.

Figure 4.1. Crystal structure of ZrN.

4.2 Si-N

Silicon nitride (Si_3N_4) is the only line compound in the phase diagram of Si-N system [17] with predominantly covalent bond (70 %). Si_3N_4 can exist in α phase with trigonal symmetry and β phase with hexagonal symmetry. While γ phase with cubic structure can be synthesized at high pressures (15 GPa and 2000 K) with a hardness of 30 GPa [18]. For sintered Si_3N_4 components, M-Si-O-N glassy phase surrounding the long elongated in-situ grown β phase grains provides the energy dissipative mechanism by crack deflection, which results in high fracture toughness (7- 10 $\text{MPa}\sqrt{\text{m}}$) [19]. Better thermal shock resistance, and high strength over a wide

range of temperatures makes this a candidate material for cutting inserts, automotive and gas turbine applications [20].

Si_3N_4 coatings deposited by reactive sputter deposition shows an amorphous dominated structure, even at a growth temperature of 800 °C with a hardness of 23 GPa and elastic modulus of 220 GPa [21]. α phase was only observed above 1300 °C, which indicates the sluggish nature of Si_3N_4 crystallization. Figure 4.2 shows the trigonal structure of Si_3N_4 , Si atoms are at the center of SiN_4 tetrahedra, every Si atom coordinates four nitrogen atoms and every N atom coordinates three Si atoms.

Figure 4.2. Crystal structure of α Si_3N_4 .

4.3 Zr-Si-N

Zr-Si-N material system was inspired from Ti-Si-N [22–24] to synthesize superhard nanocomposite coating. Vepreck et al., proposed a generic concept [25] for the design of self-organized nanocomposite structure in an immiscible Metal-Si-N systems. The columnar growth of TiN was suggested to be interrupted by surface segregated SiN_x phase, which leads to the evolution of a nanocomposite structure when the Si concentration is around 6-8 at. % Si [26–28]. The

nanocomposite consists of TiN nanocrystals (~5-10 nm) wrapped by few monolayers of amorphous (*a*)-SiN_x phase. The super-hardness ($H > 40$ GPa) of such a nanocomposite was suggested to be a combined result of a) inability of dislocation nucleation and operation and b) prevention of grain boundary sliding by strong interfaces between TiN and *a*-SiN_x phase [29,30].

The observed growth model of Zr-Si-N follows very similar to Ti-Si-N, resulting in a nanocomposite of Zr-Si-N [15,31–33] around 3-6 at. % Si, however the super hardness is missing, instead the nanocomposite coating is softer than binary ZrN and this question is addressed in paper 1.

4.4 Al-N

Aluminum nitride (AlN), with predominantly covalent bonding between Al and N has many impressive properties and one of the primary alloying nitride in the state of the art ternary coatings. Thermodynamically stable crystal structure of AlN is wurtzite, with lattice parameters a , $b = 3.78$ Å and $c = 4.98$ Å [34]. Wurtzite structure of AlN is shown in figure 4.3. The structure consists of each aluminum atom being surrounded by 4 nitrogen atoms (vice- versa).

Figure 4.3. Crystal structure of wurtzite-AlN.

4. Material systems

The hardness and elastic modulus of *w*-AlN coatings deposited by sputtering was reported to be 17 GPa and 190 GPa respectively [35]. The lower hardness of AlN restricts its application as a binary compound, but the superior oxidation resistance above 700 °C [36] make this as technically very important alloying nitride for the ternary coatings such as Al-Ti-N and Al-Cr-N. A metastable cubic (*c*)- AlN phase can be grown epitaxially up to 2 nm layer thickness by nanolaminate coatings, such as AlN/(CrN or TiN) [37], which results in increased hardness and fracture toughness [38]. The *c*-AlN metastable phase also evolves during the iso-structural decomposition of metastable cubic Ti-Al-N, which is responsible for the observed age hardening of Ti-Al-N coatings.

4.5 Zr-Al-N

ZrN and AlN are immiscible material systems with the enthalpy of mixing even higher than TiN and AlN [8]. Rogstrom et al., [39], have reported pseudo binary phase diagram under metastable growth conditions of the reactive arc deposition process. Results show that metastable solid solution of cubic Zr-Al-N can be grown up to 36 at. % Al, mixed cubic and wurtzite structure between 36 and 70 at. % Al and (*w*) Al-Zr-N above 70 at. % Al. Recently it was shown that Zr-Al-N coatings with 36 at. % Al can form self-organized semi-coherent nanostructures with epitaxial relation of $(10\bar{1}0)_{\text{AlN}} / (100)_{\text{ZrN}}$ at a growth temperature of 900 °C [9]. The close lattice parameter between *c* of *w*-AlN and *a* of *c*-ZrN is likely responsible for the semi-coherent interface. There are several interesting questions related to this self-organized structure, such as the effect of growth temperature, influence of Al concentration and the multi layering effect. Paper 3 deal with answering some of these questions.

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5. Characterization

Different characterization techniques were used to analyze the coatings in the current work. Comprehensive overview of the important techniques used in this thesis are described in this chapter.

5.1 Hardness

Indentation technique has been a very traditional way of measuring the hardness of the materials at least for 100 years, the hardness value is obtained by measuring the area of the residual imprint of the indentation.

The distinguishing feature of the nanoindentation technique (also known as instrumented indentation) is the ability to measure the penetration depth of the indenter down to few nm without any microscopy [1]. The advances in instrumentation and deeper understanding of contact mechanics allows for a continuous estimate of the contact depth as a function of penetration depth. This ability makes the nanoindentation very apt for the hardness measurement of thin coatings. The other advantage with nanoindentation technique is the ability to extract the contact elastic modulus which is not possible with conventional indentation techniques like Brinell, Vickers and Rockwell hardness test. In a typical nanoindentation test, the hardness, H is the contact pressure, equal to

$$H = \frac{P}{A} \quad (5.1)$$

Where P is the applied load and A is the projected contact area. The projected contact area of a Berkovich indenter with an included angle of 142.35° is given by

$$A = 24.49 h_c^2 \quad (5.2)$$

5. Characterization

$$h_c = h_t - \varepsilon \frac{P}{dP/dh} \quad (5.3)$$

Where ε is a geometric function with a value of 0.75 for the Berkovich indenter [2]. The test comprises, continuous recording of force (P) and depth of penetration (h) as the force is increased from zero to the set value and again back to zero. Figure 5.1 schematically explains the indentation process, the loading cycle of an indentation consists of elastic and plastic deformation (h_t). Part of the elastic deformation recovers during the unloading cycle (h_c) and the plastic deformation generates a residual imprint. The analysis of the unloading curve gives an estimate of the indentation elastic modulus. The reduced modulus E_r is given by

$$E_r = \frac{1}{2} \sqrt{\frac{\pi}{A}} \left(\frac{dP}{dh} \right) \quad (5.4)$$

Where, dp/dh is the contact stiffness determined from the slope of the unloading curve at maximum force. The elastic modulus of the specimen is calculated from the following relationship.

$$\frac{1}{E_r} = \left(\frac{1-\nu^2}{E} \right) + \left(\frac{1-\nu_i^2}{E_i} \right) \quad (5.5)$$

E_r is the contact modulus, E and ν are the elastic modulus and Poisson's ratio of the specimen and E_i and ν_i are the elastic modulus and Poisson's ratio of the diamond indenter.

Figure 5.1. Displacement process under a Berkovich indenter.

5. Characterization

A typical load-depth curve of Zr-Si-N coating is shown in figure 5.2, coating with 6.3 at. % Si shows higher penetration depth and lower contact stiffness (dp/dh) indicating lower hardness and elastic modulus compared to other coatings.

Figure 5.2. Measured P-h curves for Zr-Si-N coatings for different Si concentration.

Substrate effects are inevitable while measuring the hardness of the coating. As a rule of thumb, the maximum penetration depth is restricted to 10 % of the total coating thickness to reduce the substrate effects. However, this number is only empirical and does not have any validation of the physical laws, 10% rule can differ based on the stiffness of a specific combination of the coating and substrate together. Though Berkovich tip is a standard indenter for hardness measurement, other indenter geometries were also used in the current work. Cube corner indenter was used to generate well defined cracks and spherical indenter was used for probing the elastic-plastic transition of the indent induced deformation.

5.2 Fracture toughness

Fracture toughness (K_{IC}), defined as the ability of a material to resist the growth of a pre-existing crack. Fracture toughness of bulk materials is measured by Charpy impact test, three point and four point bend test. The size limitations of the thin coatings make them very difficult to apply the conventional measurement techniques. Various techniques have been developed for K_{IC} measurement of thin coatings such as straining the free standing coatings [3], in situ micropillar compression [4], scratch test [5] and indentation techniques [6]. Fracture studies in the current thesis are primarily based on indentation technique. The technique essentially consists of indenting the coatings with sharp indenter and relating the length of the radial cracks (c) emanating from the edge of the impression, to the K_C of the coatings using the equation formulated by Lawns, Evans and Marshall [7].

$$K_C = \alpha \left(\frac{E}{H} \right)^{1/2} \left(\frac{P}{c^{3/2}} \right) \quad (5.6)$$

α is an empirical constant based on the geometry of the indenter ($\alpha = 0.040$ for cube corner indenter), P is the maximum applied load, E is the elastic modulus of the coating and H is the hardness of the coating. Several modifications were suggested to the above equation with different exponents of (E/H) [8]. Even though the above equation is originally developed for Vickers indent, later it was confirmed that this is equally valid for Cube Corner indenter with modified α [9]. Radial cracks developed in a Zr-Si-N nanocomposite coating under cube corner indent with a penetration depth of 3000 nm are shown in figure 5.3. The fracture toughness (K_c) of the Zr-Si-N nanocomposite coatings using eq. 5.6 was estimated to be 7.5 MPa $\sqrt{m}$.

Figure 5.3. SEM image of indentation induced cracking at a force of 250 mN (a) plan view and (b) X-View.

There are some serious challenges to this technique, cracking phenomena is extremely material dependent [10] and radial cracks do not readily generate in all the material systems. The cracking threshold strain cannot be induced within 10% penetration depth of the coating thickness, hence the substrate effect is inevitable in most of the cases. Therefore the technique should be considered more a qualitative method to compare between different coatings.

5.3 Focused ion beam

Focused ion beam (FIB) is a well-established technique for extracting the site specific samples. TEM lamellae under the indent (paper 1), from the wear track (paper 2) were not possible by conventional TEM sample preparation techniques and FIB is a good choice in such cases. The FIB is essentially very similar to scanning electron microscope with an additional ion column having the capabilities of site specific cross sectioning and nanofabrication. A typical dual beam workstation is equipped with ion beam and electron beam column, beam activated Pt deposition system and micro manipulator to facilitate the lamellae lift out. Gallium

5. Characterization

is the preferred ion source due to low melting point, low volatility and heavy enough for ion milling. During the operation, a focused (Ga^+) primary ion beam hits the surface with an energy about 30 KeV. This energy is sufficient to knockout the atoms of the target by sputtering process, which results in site specific milling. Figure 5.4 shows various steps involved in a TEM lamellae preparation, which includes trenching, liftout, grid attachment and polishing. Typical milling parameters used in the current work are 30 kV 2 nA beam for coarse milling, and 30 kV 50 pA for fine polishing. The strong incident ion beam also causes localized sample damage and heating. To avoid the sample damage from the ion beam, thin platinum layer is deposited by electron beam prior to ion milling.

Figure 5.4. Sequential procedure of TEM lamellae preparation from the wear track of Zr-Si-N coatings using FIB, (a) trenching (b) lift out and transfer (c) grid attachment and (d) polishing.

5.4 Electron microscope

Rayleigh criterion suggests the smallest distance that can be resolved in an imaging system is proportional to the wavelength of the probing radiation. A modern optical microscope illuminated by a beam of light with a wavelength about 500 nm results in a theoretical resolution about 250 nm. This is at least two orders of magnitude lower than the microstructural features of Zr-Si-N nanocomposite coating in the current study. The resolution of the microscope increases phenomenally if the beam of light is replaced by a beam of electrons. When the electrons are accelerated through a potential difference of 200 kV in a transmission electron microscope (TEM), the wave length of the probing radiation is about 0.03 Å and a theoretical resolution limit of 0.015 Å is achieved. Even though the theoretical resolution is not achieved due to aberrations of electromagnetic lenses in reality, spatial resolution up to sub-nanometer length scales are readily achieved.

5.4.1 Transmission electron microscope

In a typical transmission electron microscope (TEM) operated at 200 kV, the electrons are accelerated at a velocity equal to half the speed of the light ($\sim 0.5c$), and then penetrates through an electron transparent specimen (< 100 nm). Objective lens collects all the electrons after interacting with the sample and form diffraction patterns (DP) in the back focal plane of the lens, and an image in the image plane. The image is magnified by the intermediate and the projection lens onto the screen.

TEM can be operated in either imaging mode or diffraction mode, a schematic ray diagram shown in figure 5.5. In the imaging mode, the image formed in the image plane of the objective lens is transferred to the view screen (5.5 d). In diffraction

5. Characterization

mode, the diffraction pattern formed in the back focal plane of the objective lens is projected onto the viewing screen (5.5 c).

Figure 5.5. Ray diagram of (a) diffraction, (b) imaging modes of TEM, (c) SAED, (d) BF-TEM image of $Zr_{0.63}Al_{0.37}N$ monolithic coating.

An aperture can also be inserted to select the area that contributes to diffraction, known as selected area diffraction pattern (SADP). The transition between imaging mode and diffraction mode can be performed by changing the strength of intermediate lens which is executed by just pressing a button in the state of the art microscope.

5.4.2 Contrast mechanism

The specimen is illuminated by parallel or near parallel beam in TEM. When the electrons reach the sample they can either be transmitted (without interacting), absorbed, elastically scattered (deviated from the original path, but no loss of energy), inelastically scattered (deviated from the original path with loss of energy). The electron sample interaction in combination with appropriate apertures and detectors provides the contrast in a gray scale TEM image. If a transmitted beam is used to generate an image it is known as bright field TEM (BF-TEM) (Fig.5.5a). On the other hand, if the image is formed by scattered electrons, it is called as dark field TEM image (DF-TEM). Using these techniques, grain size, morphology, orientation distribution, defects and grain boundaries can be visualized. Lattice imaging is obtained in high resolution TEM (HR-TEM) mode by the interference of the diffracted beams with the direct beam (phase contrast). While TEM offers the unique opportunity to investigate both real and reciprocal space information down to the atomic scale, there are some serious limitations as well. Extensive sample preparation to obtain electron transparent regions may induce several artifacts which could lead to misinterpretation. The small area of investigation is considered as a representative for the complete coating, which may not be true in some cases. Most importantly, the projection of three dimensional features of a typical nanocomposite structure into a two dimensional image causes overlapping of the details leading to inaccurate conclusions.

5.4.3 Scanning transmission electron microscope

In a scanning transmission electron microscope (STEM) imaging, a converged beam is scanned across the specimen and the image is formed by collecting the scattered electron flux as a function of probe position (Figure 5.6). High angle annular dark field (HAADF) has been used (paper 1 and 2) for acquiring the Z-contrast imaging of the specimen, the detector collects the electrons scattered to higher angles and a Z contrast image is generated. The in-coherent elastic scattered electrons at higher angles mostly originate from the interaction of the incident electrons with the nucleus of the atom in the specimen, heavy atoms scatter more strongly to higher angles and appear brighter in the Z-contrast image. The intensity of the image approximately varies Z^2 of the specimen and thus amplifies the chemical differences of the specimen.

Figure 5.6. (a) schematic line diagram of STEM mode, (b) STEM (HAADF) image of $Zr_{0.63}Al_{0.37}N$ coating showing ZrN rich (bright regions) and AlN rich (dark regions).

5.4.4 Scanning electron microscope

Scanning electron microscope (SEM) image is generated by scanning the focused beam of electron on the sample surface. An accelerating voltage of 3-5 kV and 15-20 kV was used for imaging and spectroscopy respectively. The electron beam and specimen interactions generate secondary electrons (SE), backscattered electron (BSE) and X-ray radiation among others. SE (sensitive to topographical contrast) and BSE (sensitive to atomic number contrast) signals are used for imaging while the X-ray radiation is used for spectroscopy.

5.4.5 Energy dispersive X-ray spectroscopy

Energy dispersive X-ray spectroscopic technique (EDS) was used to acquire semi quantitative elemental information of the Zr-Si-N coating wear tracks (Paper 2). The basic principle of this technique is that, if the incident electron beam knocks out an electron from the inner shell of the atom in the specimen, the electron hole is filled by an electron from the higher energy shell. The difference in the energy may be released as an X-ray photon with a characteristic wavelength corresponding to the excited element. The flux and energy of the emitted X-rays are detected by energy dispersive spectrometer, allowing the estimation of the composition. However the quantification of lighter elements ($Z < 11$) are not reliable due to low fluorescence yield, absorption of low energy X-rays and overlap of characteristic peaks with heavier elements.

5.5 Atomic force microscope

Atomic force microscope (AFM) technique was used to study the topographical details of the indentation induced deformation of Zr-Si-N coatings (Paper 1). The working principle of AFM, in its most basic form is very similar to stylus profilometer, it consists of a cantilever with a sharp tip. The tip is brought into the

proximity of the sample surface and raster scanned across the surface. While the tip follows the surface profile, either the vertical deflection of the cantilever or the feedback control to maintain the tip at constant height is used to generate the topographical image. AFM has three main modes of operation.

(1) Contact mode: The cantilever tip is in contact with the surface, dragged across the surface and the cantilever deflection is used to generate the contour of the surface. A rough surface can damage both the sample and tip.

(2) Tapping mode: The cantilever is driven at resonant frequency, the interaction forces (van der Waals forces and electrostatic forces) between the tip and surface cause the amplitude of the oscillation to decrease as the tip approaches the surface. The feedback control, adjust the height of the cantilever to maintain a constant amplitude and this vertical movement generates a topographical image. Figure 5.7 shows the AFM tapping mode image of the indentation induced shear bands in Zr-Si-N nanocomposite coating.

Figure 5.7. AFM-tapping mode image of the residual imprint (a) ZrN (b) Zr-Si-N nanocomposite coating revealing shear bands.

(3) Non contact mode: The operation is very similar to tapping mode, except the distance between the sample and the tip is relatively higher so that only long range forces such as van der Waals forces can influence the amplitude of the oscillation.

5.6 X-ray diffraction (XRD)

X-ray diffraction is the most powerful technique to characterize the structural details of the coatings without any detailed sample preparation. When X-rays are directed at the crystalline sample they are scattered by the atoms. Usually scattered X-rays are out of phase except at specific angles known as Bragg angle, where the scattered rays are in phase giving rise to strong diffraction intensity. The relation between the distance of atomic planes d , diffraction angle 2θ and wavelength λ of the probing radiation is given by Bragg's law.

$$n\lambda = 2d \sin \theta \quad (5.7)$$

Where n is an integer. Bragg's law is only a necessary condition for diffraction, the sufficient condition is met by fulfilling the structure factor considerations. The net result is the absence of diffraction intensity of the atomic planes satisfying eq.5.7. Diffraction occurs when $h+k+l$ is even for BCC crystal structure, whereas h , k and l must all be either odd or even for FCC structure.

The XRD line scans in this thesis were performed in θ - 2θ scanning mode where the incident angle θ and diffracted angle 2θ are scanned simultaneously. In this mode only the lattice planes parallel to the sample surface contribute to the diffraction intensity. The diffracted peak position and profile can be used to extract the structural details such as lattice parameter, residual stress measurement and grain size approximation among others.

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6. Summary of the included papers and proposed future work

6. Summary of the papers and proposed future work

This chapter presents the summary of the papers, some ideas and further open questions.

6.1 Paper 1

This paper provides deeper understanding of the influence of the microstructure on the hardness and fracture resistance of the Zr-Si-N coatings.

Previous work shows that a three dimensional nanocomposite consisting of nanosized metal nitride crystals encapsulated with few atomic layer thick SiN_x phase shows a hardness maximum in Ti-Si-N, Al-Si-N and W-Si-N. Si addition to ZrN also induces similar structural changes; however the nanocomposite of Zr-Si-N is softer than that of binary ZrN and we have answered the question by exploring the structure-property relationship of these composites. In this paper, Zr-Si-N coatings were grown over WC-Co substrate using an industrial scale reactive arc deposition technique. The Si content of the coatings changed between 0.2 and 6.3 at. % Si forms a substitutional solid solution with ZrN up to 1.8 at. % in a columnar structure, further Si addition causes precipitation of amorphous- SiN_x phase on the growth front causing the break-down of columnar structure and evolves a nanocomposite structure at 6.3 at. % Si. Indentation induced deformation was visualized by the artificial layering of the coating. Both atomic force microscopy and electron microscopy studies reveal a homogeneous dislocation based

deformation mechanism for the columnar structured coating, whereas the deformation of the nanocomposite coatings are dominated by heterogeneous grain boundary sliding. The observed grain boundary sliding mechanism explains why the nanocomposite of Zr-Si-N is softer than the binary ZrN, however the softness did not translate as higher fracture resistance for the nanocomposite coatings.

Fracture studies reveal that a fine columnar structure is more resistant to radial cracks compared to a nanocomposite structure. The observed crack pattern suggests a crack deflection and branching to be the active toughening mechanism in the columnar structure. Such crack deflection mechanism is not evident in the nanocomposite structure. The grain size about 5 nm of a nanocomposite structure is much lower than the size of fracture process zone (~ 30 nm), hence the nanostructure could not able to offer any local hindrances for the crack growth.

6.2 Paper 2

The deeper understanding of the structure-hardness-fracture correlation of Zr-Si-N coatings in paper 1 has motivated us to investigate the intricate influence of microstructure and mechanical properties variation on the tribology behavior of the coatings under a sliding contact.

Results show a systematic variation of wear rate as a function of Si content of the coatings, but did not follow the expected trend of either the hardness or the fracture resistance. The wear rate has increased with Si content of the coating with a maximum wear rate of $1.37 \times 10^{-5} \text{ mm}^3/\text{Nm}$ at 1.8 at. % Si (columnar microstructure) and then decreases gradually to $6.39 \times 10^{-6} \text{ mm}^3/\text{Nm}$ at 6.3 at. % Si (nanocomposite structure). Electron microscopy of the wear track shows tribo-oxidation as the dominating wear mode. The growth rate of the tribo-oxide layer is the wear rate determining mechanism. Higher growth rate of tribo-oxide layer in the columnar

structured coating leads to layer delamination and high wear rate. While the lower growth rate of tribo-oxide layer in the nanocomposite coating results in reduced wear rate of the coatings. The oxidation of ZrN coating is driven by the inward diffusion of oxygen. The oxide layer of the nanocomposite coatings (6.3 at. % Si) has a higher resistance to oxygen penetration, which offers superior resistance to both static and tribo-oxidation over the binary ZrN. Further wear studies for this paper are planned to conduct in a controlled atmosphere, hopefully to change the dominant wear mechanism from oxidation to plastic deformation.

6.3 Paper 3

In this paper on ZrN/Zr_{0.63}Al_{0.37}N multilayers, we show that both hardness and fracture resistance of the multilayer coatings are tunable by changing the thickness of the Zr_{0.63}Al_{0.37}N layer. The thickness of the Zr_{0.63}Al_{0.37}N layer was systematically changed, to trigger a layer thickness dependent structural transformation and hence the mechanical properties of the multilayers. Monolithic and multilayers of ZrN/Zr_{0.63}Al_{0.37}N coatings were grown by reactive unbalanced magnetron sputtering, the thickness of Zr_{0.63}Al_{0.37}N was varied between 2 nm and 30 nm. The monolithic Zr_{0.63}Al_{0.37}N grown at 700 °C exhibit nanostructure, containing ZrN and AlN rich domains with incoherent interfaces. When the same composition is sandwiched between ZrN layers the structure is completely altered and it depends on the thickness of Zr_{0.63}Al_{0.37}N layer. The cubic phase is stable up to a layer thickness of 5 nm, a semi coherent w-AlN is observed at 10 nm layer thickness, and breakdown of semi-coherent growth mode occurs at a layer thickness of 30 nm. To find the local compositions inside nanosized grains of monolithic and multilayer coatings, three dimensional atom probe studies were performed. Results show comparable segregation of ZrN and AlN between monolithic and multilayer coatings, hence we interpret the structural changes as a result of the competitive balance between the

interface energy and strain energies under kinetically limited growth conditions. Indentation induced fracture studies shows significant improvement of fracture resistance for the multilayers of 2 nm $\text{Zr}_{0.63}\text{Al}_{0.37}\text{N}$ with metastable cubic AlN phase. The likely toughening mechanism was related to the contact induced phase transformation of metastable *c*-AlN phase relieving the tensile stress around the contact.

6.4 Future work

Future work will be more focused on deeper understanding of mechanical behavior of coatings both for arc deposited and magnetron sputtered composites and multilayered structures. Some of the required improvements in the ongoing work and potential future ideas are:

6.4a Hardness

Paper 1 shows that indentation induced deformation of Zr-Si-N nanocomposite is dominated by grain boundary sliding, which is not the case for the nanocomposite of Ti-Si-N. These contrasting deformation mechanisms explain why the nanocomposite of Zr-Si-N is soft but not in case of Ti-Si-N. There is a fundamental need to understand the origin of such a contrasting deformation mechanism in spite of similar microstructure, similar crystal structure of the host lattice. A detailed theoretical and experimental investigation of the interfaces between the TiN/ZrN and amorphous-SiN_x phase could be a good starting point.

It was shown in paper 1 that a hardness about 4 GPa can be improved by solid solution strengthening of Si in the lattice of ZrN. Classical dislocation theories suggest such a hardening mechanism can be further accelerated if a non-symmetrical distortion can be induced in the lattice by the appropriate alloying. Further work is required to explore such a mechanism.

6.4b Toughness

There are very few options at hand to enhance the toughness of the inherently brittle coatings. Indentation induced fracture studies of Zr-Si-N coatings show microstructure dependency of the fracture behavior. These results motivate further investigation on different coatings to arrive at the optimal grain size, morphology, and microstructure to enhance the toughness of these coatings. Crack deflection and branching is evident for fine columnar structured coatings, dedicated electron microscopy imaging and elemental spectroscopy is required to confirm the local sources for such deflection, such as columnar boundaries.

Since the characteristic microstructural length scales tend to be shorter than the size of the fracture process zone, the nanocomposite microstructure of hard coatings may not offer great resistance to crack propagation. The choice of nanocomposite coatings for toughness demanding applications should also be critically reviewed in the light of the relative ease of radial crack propagation.

Multilayers show a layer thickness dependent hardness, but less was known about its influence on toughness. Indentation induced fracture studies of ZrN/Zr_{0.63}Al_{0.37}N multilayers show a systematic layer thickness dependent fracture resistance for the multilayers. But the detailed toughening mechanisms are not known, which motivates future work in this direction.

Significant improvement in fracture resistance of 15 nm ZrN/2 nm Zr_{0.63}Al_{0.37}N multilayer coatings was explained by the proposed toughening mechanism of stress induced transformation of *c*-AlN to *w*-AlN (paper 2), this mechanism must be confirmed by detailed microscopic evidences. Exploitation of such a phenomenon can offer a higher degree of freedom to tune the toughness of the hard coatings.

6.4c Tribolayer

The ongoing work in paper 3 highlights the fact that good hardness and toughness does not guarantee good wear resistance. The wear process is very specific to a given contact pair and sensitive to sliding conditions. The coating communicates with the environment and forces through the tribo-layer, the composition and microstructure of the coatings should aim at evolving a stable tribo-layer for better performance. The sliding wear test on Zr-Si-N coatings show that tribo-layer of nanocomposites coatings offer superior resistance to tribo-oxidation but the detailed atomic scale mechanisms are not clear. This phenomenon will be explored further.

6. Summary and future work

Included Papers

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<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-106763>