Review

# Recent advances of superhard nanocomposite coatings: a review

Sam Zhang*, Deen Sun, Yongqing Fu, Hejun Du

*School of Mechanical and Production Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore*

## Abstract

In this paper, a review of the present status of the research and technological development in the field of superhard nanocomposite coatings is attempted. Various deposition techniques have been used to prepare nanocomposite coatings. Among them, reactive magnetron sputtering is most commonly used. Nanocomposite coating design methodology and synthesis are described with emphasis on the magnetron sputtering deposition technique. Also discussed are the hardness and fracture toughness measurements of the coatings and the size effect. Superhard nanocomposite thin films are obtainable through optimal design of microstructure. So far, much attention is paid to increasing hardness, but not enough to toughness. The development of next generation superhard coatings should base on appropriate material design to achieve high hardness and at the same time high toughness.
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## 1. Introduction

Nanostructured coatings have recently attracted increasing interest because of the possibilities of synthesizing materials with unique physical–chemical properties [1–4]. Highly sophisticated surface related properties, such as optical, magnetic, electronic, catalytic, mechanical, chemical and tribological properties can be obtained by advanced nanostructured coatings, making them attractive for industrial applications in high-speed machining [5,6], tooling [6,7] optical applications [8,9] and magnetic storage devices [10–13] because of their special mechanical, electronic, magnetic and optical properties due to size effect. There are many types of design models for nanostructured coatings, such as nanocomposite coatings, nano-scale multilayer coating, superlattice coating, nano-graded coatings, etc. Designing of nanostructured coatings needs consideration of many factors, e.g. the interface volume, crystallite size, single layer thickness, surface and interfacial energy, texture, epitaxial stress and strain, etc., all of which depend significantly on materials selection, deposition methods and process parameters [14–16].

A nanocomposite coating comprises of at least two phases: a nanocrystalline phase and an amorphous phase, or two nanocrystalline phases. Nanocomposite coatings exhibit hardness significantly exceeding that given by the rule of mixture. Hard materials usually refer to materials with hardness greater than 20 GPa. Materials with hardness above 40 GPa are classified as superhard, and those with hardness above 80 GPa are often called ultra-hard materials. Nanocomposite coatings can be hard, superhard or even ultra-hard, depending on coating design and application. Extensive theoretical and experimental efforts have been made to synthesize and study these nanocomposite coatings with superhardness and high toughness.

This paper reviews the present status of the research and technological development in the field of superhard nanocomposite coatings covering design concepts and preparation methods with emphasis on magnetron sputtering. Coating hardness and fracture toughness measurements are also discussed.

## 2. Design methodology for nanocomposite coating

In bulk materials, grain boundary hardening is one of the possibilities for hardness improvement. The same is true for films or coatings. With a decrease in grain size,

*Corresponding author. Tel.: +65-6790-4400; fax: +65-6791-1859.

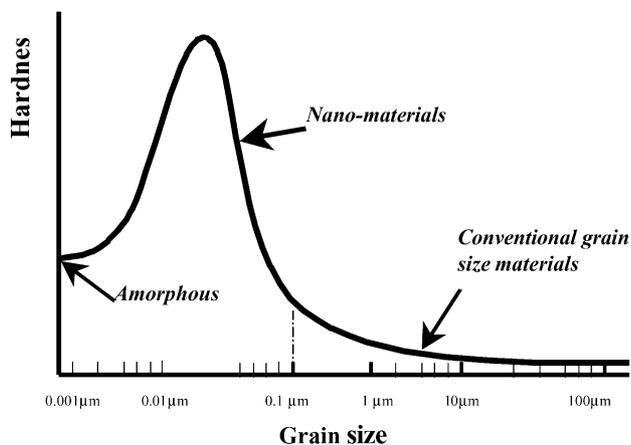*E-mail address:* msyzhang@ntu.edu.sg (S. Zhang).

Fig. 1. Hardness of a material as a function of the grain size [17].

the multiplication and mobility of the dislocations are hindered, and the hardness of materials increases according to the 'Hall–Petch' relationship: $H(d) = H_0 + Kd^{-1/2}$. This effect is especially prominent for grain size down to tens of nanometers (cf., Fig. 1). However, dislocation movement, which determines the hardness and strength in bulk materials, has little effect when the grain size is less than approximately 10 nm. At this grain size, further reduction in grain size brings about a decrease in strength because of grain boundary sliding. Softening caused by grain boundary sliding is mainly attributed to large amount of defects in grain boundaries, which allow fast diffusion of atoms and vacancies under stress [17,18]. As such, further increase in hardness requires hindering of grain boundary sliding. This can be realized through proper microstructural design, i.e. by increasing the complexity and strength of grain boundaries [19]. Since different crystalline phases often exhibit different sliding systems and provide complex boundary to accommodate a coherent strain thus preventing formation of voids or flaws [20], multiphase structures are expected to have interfaces with high cohesive strength. Apart from hardness, good mechanical properties also include high fracture toughness. It is quite straightforward to think that a high fracture toughness can be obtained in the nanocomposite coatings due to the nano-size grain structure as well as deflection, meandering and termination of nanocracks [21]. However, in order to obtain superhardness, usually plastic deformation is strongly prohibited, and dislocation movement and grain boundary sliding are prevented, thus probably causing a loss in ductility. Today, more and more researchers realize that a certain degree of grain boundary diffusion and grain boundary sliding are necessary in order to improve toughness of nanocomposite coatings. The following few types of design methods have been put forth for superhard high toughness nanocomposite.

First, a combination of two or more nanocrystalline phases provides complex boundaries to accommodate coherent strain, which result in the increase of coating hardness. In this case, the phases involved must show a wide miscibility in solid state, display thermodynamically driven segregation during deposition, and have certain chemical affinity to each other to strengthen the grain boundaries [19,20]. Successful examples include $TiN–TiB_2$, $Ti–B–N$, $(Ti, Si, Al)N$, as well as other metal–nitride and carbide/boride systems [15,22–24]. Second, segregation of nanocrystalline phases to grain boundaries of the first phase to generate the grain boundaries strengthening effect, and stops grain growth [1,25,26]. Though this composite design could significantly increases hardness and elastic modulus, it may not be able to improve toughness [27] because dislocation movement is prohibited and crack opening becomes the main mechanism of relieving strain. If the cohesive strength of the interface is not sufficient to withstand the local tensile stress at the crack tip, unstable crack propagation and debonding of the nanocrystals occur.

To address this problem, Miterer et al. [24] formed hard nanocrystalline phases within a metal matrix, such as TiN in Ni [28], ZrN in Ni [14], Zr–Y–N [29], ZrN in Cu [30,31], CrN in Cu [32]. The hardness of these coating systems varied from 35 GPa to approximately 60 GPa. In these coatings, one metal may be converted into nitride in the form of hard nanocrystalline phase and the other transported into the growing film unreacted. High hardness could be obtained for compounds showing a wide miscibility gap in the solid state but a certain chemical affinity to each other to form high strength grain boundaries. In this case, both the dislocation mechanism and the grain boundary mechanism contribute to the hardness [33–35], while the existence of a metal matrix improves toughness. However, there could be poor toughness and thermal stability problems [27]. Dislocation movement initiated from grain boundaries may be prohibited because of the small separation of grains in the metal matrix. This gives rise to poor toughness. Diamond-like carbon (DLC) based or metal matrix nanocomposite coatings may undergo structural change at 300–500 °C. This is the thermal stability issue. Thermal stability of nanocomposite coatings is yet another important property in mechanical applications. Hardness decreases upon annealing due to relaxation of compressive stress built up during deposition, and due to rapid diffusion at higher temperatures [36]. Grain boundary sliding depends on temperature, thus the mechanisms of preventing grain boundary sliding in room temperature may not be useful at elevated temperatures. One way of improving thermal stability of the coating is to include elements of high thermal stability, such as yttrium, in the coating. Another way is to modify the interface complexity, such as using a ternary
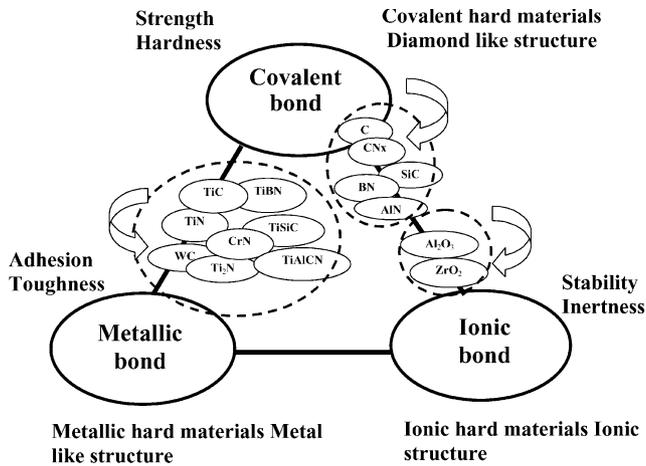
Fig. 2. Hard materials for nanocomposite coatings in the bond triangle and changes in properties with the change in chemical bonding [39].

system that displays immiscibility and undergo spinodal decomposition and segregation at high temperatures [5].

Another way is to embed nanocrystalline phases in an amorphous phase matrix [15,37,38]. DLC, amorphous carbon nitride or other hard amorphous materials (with high hardness and elastic modulus) have been recognized as the primary candidates for the amorphous matrix while nano-sized refractory nitrides, such as TiN, $Si_3N_4$, AlN, BN, etc., used as strengthening phases. A variety of hard materials can be used in nanocomposite coating design. Fig. 2 shows potential hard materials [39]. Nanocrystalline TiC has been embedded in DLC matrix to produce a nanocomposite of hardness of 32 GPa [40,41]. Veprek et al. [42,43] imbedded 4–11 nm TiN crystals in amorphous $Si_3N_4$ matrix and obtained a coating hardness of 50–70 GPa. Recently, Zhang et al. [37] prepared TiCrCN nanocomposite coatings with hardness of 40 GPa, in which 8–15 nm TiCrCN crystals were embedded in an amorphous DLC matrix as shown in Fig. 3. In this design, the size, volume percentage and distribution of the nanocrystals need to be optimized in order to obtain a compromise between superhardness and toughness. The distance between two nanocrystals should be within a few nanometers. Too large a distance will easily cause a crack to propagate in matrix, while too close to each other will cause the interaction of atomic planes in the adjacent nanocrystalline grains. The nanocrystalline grains should have random orientation (i.e. high angle grain boundaries) to minimize incoherent strain and facilitate many nanocrystalline grains to slide in amorphous matrix to release strain and obtain high toughness. The amorphous phase must possess high structural flexibility in order to accommodate coherent strains without forming dangling bonds, voids, or other defects. The presence of amorphous phase on the boundaries helps to deflect and terminate nanocracks in addi-

tion to the enhancement of grain boundary sliding, thus improving coating toughness.

To design a nanocomposite coating with both high hardness and high toughness, one must take all the above into consideration. Probably the best way is to use ternary, quaternary or even more complex systems, with high strength amorphous phase as matrix (such as a-$SiN_x$, a-BN, a-C, etc.) and hard transition metal-nitride nanocrystals (such as TiN, $W_2N$, BN, etc.) as nanocrystalline phase to increase grain boundary complexity and strength. These nanocrystalline phases should be refractory and immiscible with each other, and could result in compositional modulation, segregation and high thermal stability of the nanostructure. The aim is to maximize interfaces and form well-defined spinodal structure at interfaces. The structure should be stable at a temperature of 1000 °C or above. Of course, there is tedious work needed for the selection of different materials, optimization of grain size, volume percentage and distribution of these nanocrystals in the amorphous structures thus obtaining both superhardness and high toughness [27]. Following this idea, Veprek [25,38] produced nc-TiN/a-$Si_3N_4$/a- and nc-$TiSi_2$ nanocomposite coating with unbelievable hardness of 105 GPa [16], and the coating retains the hardness after annealing to 900–1000 °C [44].

## 3. Synthesis methods

Different techniques are now available for preparation of nanocomposite coatings. The most promising methods are magnetron sputtering and chemical vapor deposition (CVD) [5,38,44,45], although other methods, such as laser ablation [46], thermal evaporation [47], ion beam deposition [48] and ion implantation [49], are also used
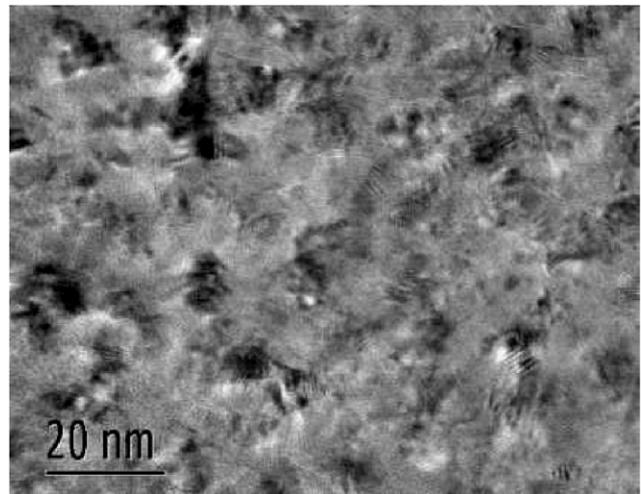
Fig. 3. TEM micrograph of TiCrCN nanocomposite coating showing nano-sized TiCrCN crystals embedded into the amorphous DLC matrix [37].

by various researchers. High deposition rate and uniform deposition for complicated geometries are the advantages of CVD method compared to sputtering. However, the main concern for CVD method is that the precursor gases $TiCl_4$, $SiCl_4$ or $SiH_4$ may pose problems in production because of their corrosive nature and danger of fire hazard. Moreover, the incorporation of chloride in protective films deposited from plasma CVD may induce interface corrosion problems during exposure to elevated temperatures under working condition. For most application, a low deposition temperature is required to prevent substrate distortion and loss of mechanical properties. This is difficult to realize in CVD processes.

Magnetron sputtering and pulsed-laser deposition were combined to fabricate superhard and tough nanocomposite coatings [40]. In general, the choice of specific deposition technique is made on consideration of coating application, coating thickness, desired coating properties, cost and production output available from the process, and temperature limitation of the substrate, etc. At present, significant effort is devoted to prepare nanocomposite coatings using reactive magnetron sputtering since this technology is a low-temperature and a far less dangerous method compared with CVD. Also, it can easily scale up for industrial application. Co-sputtering of single element targets allows independent regulation of each source by changing the power density thus enables adjustment of chemical stoichiometry of the resultant compound. A wide range of hard/superhard nanocomposite coatings has been synthesized using sputtering method [50–53].

Precision control and determination of grain size is important for nanocomposite coatings. In magnetron sputtering process, many basic process parameters affect the grain size of the coatings including substrate temperature, substrate ion current density, bias voltage, partial pressure of reactive gas (e.g. nitrogen for nitrides) and post-annealing temperature. Magnetron sputtering can operate at low temperatures to deposit films with controlled texture and crystallite size. A minimum temperature is required to promote growth of crystalline phase to the required diameter and/or to allow a sufficient diffusion within the segregating system. A temperature ceiling exists, however, to prevent significant grain growth and grain boundary segregation. Optimized target power density and bias voltage are also needed. Low-energy ion bombardment is preferred in the synthesis of nanocomposite coatings. The kinetic energy of bombarding atoms/ions is transferred into small areas of atomic dimensions and quickly converted into their close vicinity, causing extremely fast cooling process and produce dense films. The crystallite size generally increases with increase in substrate bias [32]. In the transition metal-nitride coatings, such as Ni–Cr–N and Zr–Y–N systems, partial pressure of nitrogen

has a great effect on crystallite size in the coating [29,53]. The concentration of the 'alloying element', such as the Cu concentration in TiN–Cu, Si concentration in nc-TiN/a-$Si_3N_4$, $Si_3N_4$ fraction in the nc-TiB/a-$Si_3N_4$ and nc-$W_2N$/$Si_3N_4$ also has significant effect on the size of the crystallites in the coatings [21,54,55].

## 4. Evaluation of mechanical properties

Good mechanical properties of a coating require high hardness, high toughness, low friction, high adhesion strength on substrate, good load support capability and chemical and thermal stability, etc. Of all these, hardness is probably of number one importance for an industrial coatings especially in tribological applications. At present, nanoindentation is regarded as a good method in hardness determination of thin films and coatings. In nanoindentation test, a diamond indenter is forced into the coating surface. The load and depth of penetration (the indentation profile) is recorded, from which the hardness and elastic properties are calculated. However, calculation methodology varies: the Oliver and Pharr method [56–58]; the deformation energy method [59–61]; the force indentation function method [36,62,63], the Joslin–Oliver method [64,65] and the energy density method [66], etc. Usually, the hardness of the same coating varies depending on evaluation method. Therefore, it is important that the calculation method is presented when presenting hardness data. Hardness of a coating is also affected by residual stress built up during deposition, usually a few GPa for superhard coatings. Such a large stress could cause significant exaggeration of hardness reading [42,67]. Veprek and Argon [6] suggested that the real hardness values are either measured with a low stress ($< 1$ GPa) in coating or measured after stress-relief annealing above 400–500 °C. For coatings based on DLC, however, annealing at such a temperature produces structural changes, thus is not suitable.

Nanoindentation is now a routine in hardness testing, but there is not yet a standard method for quantitative evaluation of fracture toughness of a coating. Fracture toughness measures the ability of a material to resist the growth of a pre-existing crack or flaw. At present, most researchers use ultra-low load indentation to evaluate fracture toughness [58,63,68,69]. After the indentation, when no cracking occurs, the coating is said to have good toughness. However, quantitative description requires measurement of crack length, which is relatively easier in thick coatings (a few micron meters) but extremely difficult in thin films even under scanning electron microscope [70]. This method also depends on the type of the indenter used. If the indenter is not sharp enough (like the Vickers Indenter widely used), cracking does not occur even under relatively high load. But that does not mean the coating is really tough because the

Stage 1



First Ring-Like Through-Thickness
Crack Formation

$2C_{R1}$

t

Stage2

Delamination and
Buckling

$2C_{DR}$

Stage3

Partial Spalling
Formation

Second Ring-Like
Through-Thickness
Crack Formation
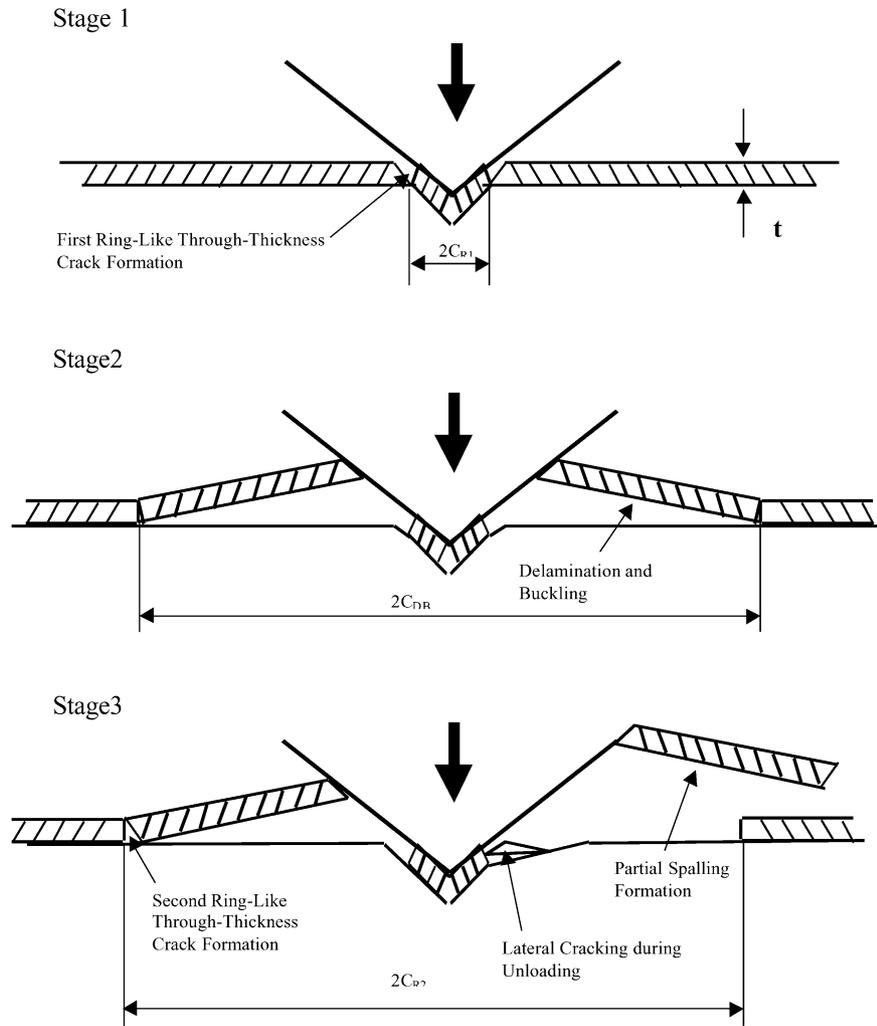
Lateral Cracking during
Unloading

$2C_{R2}$

Fig. 4. Schematic of various stages in nanoindentation fracture for the coatings/substrate systems [72].

indentation stress resulted does not reach the cracking threshold. This happens in most brittle materials [71].

Another method is based on energy release in through-thickness cracking in a coating obtained from a step observed in the indentation profile [72]. The fracture process progresses can be viewed as occurs three stages depicted in Fig. 4: in stage 1, the first ring-like through-thickness crack form in the contact area around the indenter; in stage 2, delamination and buckling occur around the contact area at the coating–substrate interface due to high lateral pressure; in stage 3, the second ring-like through-thickness crack and spallation are generated by high bending stresses at the edges of the buckled coating. The area under the indentation profile is the work done by the indenter during elastic–plastic deformation of the coating/substrate system. The strain energy release in the first/second ring-like cracking and spallation can be calculated from the corresponding steps in the loading curve. Fig. 5 illustrates the indentation profile in such a process. In Fig. 5, OACD is the

loading curve and DE is the unloading curve. The energy difference before and after the crack generation is the area ABC. This energy will be released as strain energy to create the ring-like through-thickness crack. The fracture toughness of an ultra-thin film can be written as:

$$K_{IC} = \left[ \frac{E}{(1-v^2)2\pi C_R} \frac{U}{\tau} \right]^{1/2} \qquad (1)$$

where $E$ is the elastic modulus, $v$ is the Poisson's ratio, $2\pi C_R$ is the crack length in the coating plane, $\tau$ is the coating thickness, and $U$ the strain energy difference before and after cracking. This method was used to assess the fracture toughness of thin amorphous carbon thin films [70,71].

Adhesion of coating to the substrate is always another big concern for industrial coatings. Scratch adhesion test is commonly used to evaluate the coating adhesion strength. However, actually this only reveals load bear-
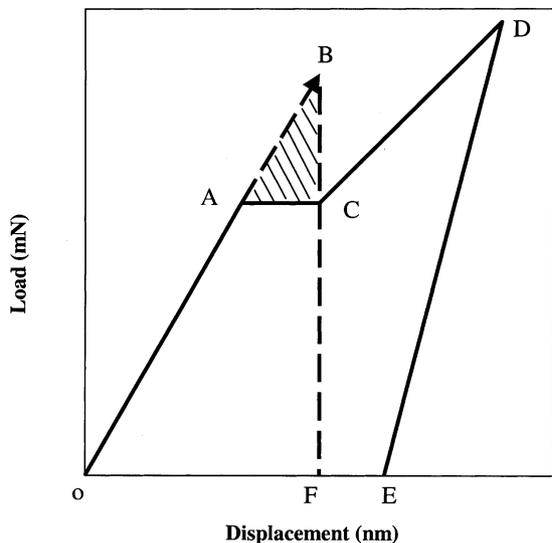
Fig. 5. Schematic diagram of a load–displacement curve, showing a step during the loading cycle and associated energy release [72].

ing capacity of the coating rather than the true adhesion between the coating and the substrate, since there are many factors that influence the results, including substrate hardness, coating surface roughness, coating hardness, coating thickness, loading rate, indenter radius, and friction between the coating and the indenter. Adding a functionally graded layer [73] or a bonding layer [74] in between the coating and the substrate are two important ways to improve coating adhesion. The functions of this interlayer include (1) facilitating good bonding, (2) relaxation and modification of the stress distribution, (3) providing a supporting layer, (4) imparting better chemical stability to substrate, (5) increasing the hardening depth.

## 5. Summary

Superhard nanocomposite thin films are at the beginning of their development, and appear to have a wide range of applications. Various deposition techniques have been used to prepare nanocomposite coatings. Among them, reactive magnetron sputtering is most commonly used. So far, much attention is paid to increasing hardness, but not enough on toughness. Superhard nanocomposite thin films are obtainable through optimal design of microstructure. It is clear that the development of next generation superhard coatings should base on appropriate material design for both high hardness and high toughness. In this nanocomposite field, many issues exist that need vigorous theoretical treatment and experimental verification. These include, but not limited to, effect of the change of the lattice parameter, the role of the crystallite size, the nature of the grain boundaries, the effects of impurities, multipha-

se and nanostructure, the formation mechanism and the reasons behind thermal stability. Until then the strengthening mechanism of nanocomposite coatings will be better understood and excellent coatings be engineered and fabricated.

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