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REVIEW ARTICLE

Superhard nano-multilayers and nanocomposite coatings*

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Abstract This paper reviews the recent development of nano-multilayers and nanocomposite coatings. The hardening mechanisms and design of hard coating are discussed in details. Recent research on Ti/TiN and nitride/nitride multilayer, Ti-Si-N and Ti-Al-Si-N nanocomposite coatings is described, and the perspectives of the related research are proposed.

Keywords: **nano-structured materials, multilayer, nanocomposite, hardness.**

Nano-structured coatings have attracted increasing interest because of their unique physical and chemical properties. The properties such as hardness, high temperature stability, wear resistance, corrosion resistance, oxidation resistance[1,2], roughness, reflectivity, layer period, thermal stability[3,4], strength, and diffusion barrier, play very important roles in their applications in cutting tools, optics, optical magnetic storage[5] and microelectronics field[6], etc. In designing and fabricating nano-structured coatings, many factors, such as interface volume ratio, crystalline grain size, single layer thickness and bilayer period, surface and interfacial energy, texture, stress and strain, etc., must be considered, all of which closely relate to the deposition methods, materials selection and process parameters. The correlations between these deposition factors and the physical mechanism governing the superhard properties of these superhard nanocomposite coatings have attracted significant attention recently.

The superhard nano-multilayer and nanocomposite coatings reviewed in this paper have extensively potential applications. The wear resistance of the hard coatings directly affects the lifetime of the tools, and the hardness enhancement for the coatings on tools can enhance the wear resistance, and correspondingly increase the lifetime of the tools. Diamond is known to be the hardest material in nature, but the poor high temperature stability and the high chemical affinity of carbon to iron impede the application of diamond coated tools to high temperature and high speed machining tools. Since Koehler[7] reported that the epitaxial-grown heterostructures could enhance material strength, the novel hard nano-multilayer coatings have been developed rapidly. The hard and superhard multilayer coatings based on the modulation of reactive gases (Ti/TiN), target material (CrN/NbN), and deposition process parameters (bias voltage modulated TiN/TiN), etc., have been extensively reported, and a lot of models have been established to explain the hardening mechanism of these coatings. Very recently, Veprek[8] has developed Koehler's idea and proposed a theory and a designing method of superhard nanocomposite coatings, which attracts researchers' special attention.

1 Nano-multilayer coatings

New hard coatings can be developed based on a multiphase coating approach. The nano-multilayer coatings include metal/metal, metal/nitrides (carbides, borides), and nitrides (carbides, borides) /nitrides (carbides, borides), etc. Multiphase composite films tend to be dense and fine grained because columnar grain growth is interrupted by the nucleation of another phase. The presence of a large amount of interfacial area in multilayered structures can increase the hardness and wear resistance. In recent years, there have been many research reports about the multilayers, mainly the metal/nitrides (carbides, borides) and nitrides/nitrides.

1.1 Metal/nitrides (carbides, borides) multilayer

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As to the extensive data obtained for Ti/TiN multilayers grown by the reactive gases modulation, research interest is in understanding the mechanism of hardness enhancement. There are some discrepancies in both the maximum hardness and the critical period thickness reported in these studies, which can attribute to different techniques and different substrate temperatures used in these studies. Some reports[9, 10] showed that the hardness of Ti/TiN was significantly enhanced compared with that of the monolayer TiN, and the maximum hardness was obtained when the period was in the range from 5 to 10 nm. Daia et al.[11] investigated the hardness of Ti/TiN deposited by radio-frequency sputtering and found it increased with the decreasing period thickness from 20 to 2.5 nm and went beyond the rule-of-mixture value for samples with period thickness of $\Lambda < 5$ nm. The maximum hardness, 1.6 times higher than the value obtained by the rule of mixture, was obtained for $\Lambda = 2.5$ nm. The data of H (hardness) and period (Λ) gave a better fit with the Hall-Petch relationship. Other work did not confirm this report. Farhat et al.[12] found that the maximum hardness was obtained for $\Lambda = 10$ nm, far below the hardness of a thick TiN monolayer. The difference among these research reports possibly resulted from the different deposition parameters and layer thickness ratio. For tailoring of certain properties, it is essential to know the exact relationship between processing parameters and the corresponding thickness of the different single layers. Only rarely have these values been really measured; in most cases the multilayer period was deduced from the total coating thickness and the number of processing cycles, or sometimes with the aid of superlattice reflections in X-ray diffractograms. Dück et al.[13] adjusted the sputtering time and obtained single Ti and TiN layers of equal thickness. However, the hardness of these multilayers did not exceed those of monolayer TiN. Li et al.[14] studied the effect of layer thickness ratio on the hardness. Their experimental results indicated that the hardness of the multilayered film depended on both the modulation period and the thickness ratio $\lambda_{Ti/TiN}$ between Ti and TiN layers. The hardness was considerably enhanced when the modulation period was in the range of 35—60 nm for $\lambda_{Ti/TiN} = 1:1$, and it reached a maximum of 23 GPa. For $\lambda_{Ti/TiN} = 1:3$, the hardness enhancement appeared in the films with the modulation period of 20—70 nm, and the maximum value is 21.4 GPa, increased by 15% over 18.7 GPa calculated by rule of mixtures. One possible explanation of the above results is related to the high thickness ratio of Ti/TiN layers. For $\lambda_{Ti/TiN} = 1:3$, when the modulation period decreases, the Ti layer is too thin to form a sharp interface due to diffusion atoms mixing, so that the hardness enhancement is less than that for the film with $\lambda_{Ti/TiN} = 1:1$. Besides the hardness, the important effect of layer number and film thickness on the properties of multilayer has also been much investigated. Simmonds[15] reported that multilayer film showed enhanced (5-fold) scratch resistance compared to the conventional single layer film and the roughness increased with the increase of layer number. Mori et al.[16] reported that with the increase of multi-layer number the preferred orientation changed from [111] to [200], and the hardness, modulus and crystalline grain size increased when the total thickness was kept at 150 nm and the number of layers varied from 4 to 40. As the Ti/TiN multilayer is mainly deposited by alternating Ar/N_2 and Ar working gas, it leads to graded interfaces due to target poisoning and possible formation of the Ti_2N phase, which can increase hardness of the films. In order to explain the experimentally observed enhancement, more attention must be paid to interface characterization, and further experimental work is required to find the hardness dependence on structure of multilayers.

1.2 Nitrides/nitrides multilayer

For non-isostructural multilayers, the analysis of the hardness data is generally more complicated due to the epitaxial stabilization effect. That is, when two materials with different crystal structures that cannot form a coherent interface are deposited in a multilayer structure, one layer may crystallize in a metastable structure, which can form a coherent interface with the other layer. A metastable structure is almost always observed in multilayers with small layer thicknesses (< 2 nm) due to the extremely high amount of interfacial energy in this type of structure. The mechanical properties of this metastable structure are generally unknown, so it is difficult to predict the hardness of the composite. For the TiN/AlN multilayers, the AlN layer, which is normally hexagonal, is found to exist in the cubic NaCl-type structure for layer thickness below 2 nm, forming a coherent interface with the TiN. At this layer thickness, it is found that hardness increases dramatically up to 40 GPa, compared to the large layer thickness multilayers. Aside from the dislocation blocking mechanisms appearing in the isostructural multilayers, the bulk modulus, and presumably the hardness, of the AlN layer is much higher for the NaCl structure than that for the hexagonal structure. Therefore, by stabilizing a new crystal structure, the mechanical properties of the coating may be affected significantly. The idea behind these studies is to determine whether the TiN layers can stabilize the β-C_3N_4 compound, which has been theoretically predicted to have a bulk modulus comparable to diamond. Many useful investigations on CN_x have been carried out by Zheng et al.[18—25]. For cutting tool applications, hard and tough coatings are needed, and their thermal stability is also very important. Barshilia et al.[26] reported that the XRD data of heated TiN/CrN multilayers showed that the coatings were obtained with superlattice structure even up to 700 ℃ and oxide phases were detected only above 750 ℃. Single layer TiN and CrN coatings begun to oxidize even at 550 ℃ and 600 ℃, respectively. One way of improving thermal stability of multilayer is to ensure that two coupled layers are immiscible or two phases are not mixing, and the other is to dope some high thermal stability elements to material. Kim[27] investigated the high temperature stability of superlattice films of TiN/AlN nano-multilayers. In the range of 2.9—30 nm, the hardness of films with period thickness of $\Lambda = 3.2$ nm was higher than 30 GPa, while those with larger layer thickness were approximately 20 GPa. When the superlattice film was annealed, its microstructure remained unchanged at temperatures up to 1000 ℃ due to the combination of layers with immiscibility. Its hardness was also maintained after annealing. However, annealing above 1100 ℃ modified the microstructure abruptly, which resulted in the loss of hardness enhancement. Lewis et al.[28] confirmed that doping yttrium can improve the thermal stability and wear resistance for CrN/(Ti, Al)N multilayer. This improvement perhaps is related to yttrium diffusion to grain boundary and effective stress relaxation. The structure of their multilayer is shown in Fig. 1. Ion bombardment strongly influences film growth and the physical, chemical, structural and mechanical properties. The argon ions act like a "hammer effect" and the amount of defects and microvoids during film growth decreases. This improves the compactness of the coating and permits the improvement of mechanical properties. Thobor et al.[29] studied the influences of ion bombardment on the properties of TiN/AlN multilayer coatings and found that the improvement in hardness could be attributed to better densification of layers and to the presence of stresses.

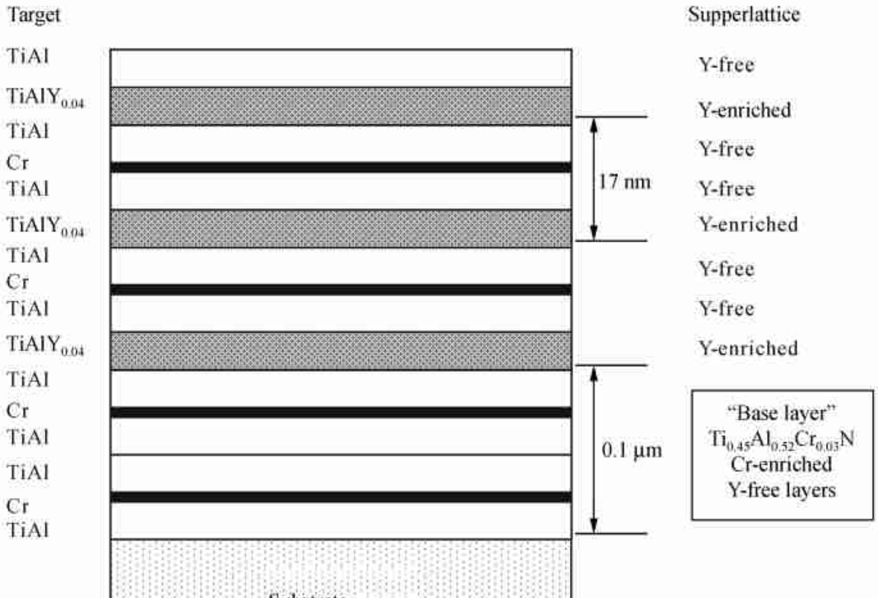

Fig. 1. Schematic diagram of the layered incorporation of yttrium in the CrN/(Ti, Al)N multilayer coating[28].

(Ti, Al) N thin films are widely used as protective coatings on steel and hard-metal tools. Their prevalence results from good mechanical and tribological properties as well as their high oxidation resistance. They are preferred partner in superlattice structures. Li et al.[30] reported multilayer TiN/($Ti_{0.5}Al_{0.5}$)N coatings deposited by plasma enhanced chemical vapor deposition (PECVD) which exhibited a higher hardness, adhesion strength and wear resistance compared to either monolayer TiN or ($Ti_{0.5}Al_{0.5}$)N coating. Si_3N_4 is a hard, high thermal stability and high chemical stability amorphous material. The amorphous phase has high structural flexibility, so it adapts itself to the shape and orientation of crystalline grain and to accommodate non-coherent strains coming from the random orientation of the grain. Xu et al.[31] studied amorphous Si_3N_4/nano-polycrystalline TiN nanostructured multilayer films and found that the hardness of the Si_3N_4/TiN multilayers was affected not only by the modulation periods, but also by the layer thickness ratio and deposition temperature. There existed a maximum hardness at a modulation period of 10.0 nm and layer thickness ratio ($\lambda_{Si_3N_4}/\lambda_{TiN}$) of 3/1. Chen et al.[32] found that the TiN/SiN_x multilayer coatings had high hardness (~45 GPa), low dry-friction coefficient (~0.06—0.11), excellent nanoscratch resistance (6 fold), improved oxidation resistance, and long contact fatigue life compared to TiN coatings. They investigated the effects of SiN_x layer thickness on thermal diffusion and found that at the SiN_x layer thickness of 0.8 nm or higher, the layer structure of TiN/SiN_x multilayer coatings was maintained for one hour after annealing at 1000 ℃ and the hardness was as high as 37 GPa. Xu et al.[33] studied the CrN/Si_3N_4 multilayers and found that the interfaces between the CrN and Si_3N_4 layers were very sharp because they did not form any interfacial phase. The results showed that the hardness values of the multilayers at different modulation periods are between those of constituent monolithic CrN and Si_3N_4 films. It is suggested that because there are no elastic modulus difference and no alternating stress fields in the interfaces between CrN and Si_3N_4 films, the superhardness effect does not appear in this system. With extensive data obtained from the above systems, research interest is in understanding the mechanism of the hardness enhancement. Although the mechanism is not yet completely understood on the atomic scale, it seems that a large number of interfaces or laminated structures play important roles in the improvement of tribological properties. To further understand the hardness enhancement of multilayer films, it is of interest to systemically study the relationship between the hardness and the microstructure of the films.

2 Nanocomposite coatings

The hardness of multiphase nanocomposite coatings nc-TiN/a-Si_3N_4/a- and nc-$TiSi_2$ prepared by Veprek[8] by means of plasma CVD reached 80—105 GPa. When the current density decreased to 1 mA·cm^{-2}, ternary TiN/a-Si_3N_4/a-$TiSi_2$, quaternary nc-TiN/a-Si_3N_4/a-, and nc-$TiSi_2$ nanocomposites could be obtained. Although the reproducibility of the total composition (i.e. Ti/Si ratio) was fairly good, the reproducibility of the hardness achieved was relatively poor due to insufficient control of the Si_3N_4 and $TiSi_2$ phase formation, which is probably associated with the narrow range for the coexistence of TiN, $TiSi_2$ and Si_3N_4 phases. Veprek pointed out that the maximum hardness was achieved when the nanocrystals are less than 10 nm in size and covered with approximately one monolayer of amorphous Si_3N_4. The decisive factor for the hardness of the nanocomposites formed of immiscible nitrides is percolation of the Si_3N_4, which is a wetting of the surfaces of the transition metal nitrides, and in the case of ternary and quaternary systems, also of the titanium silicide. Segregation of the immiscible phases during deposition results in the formation of a nanophase which is fairly free of flaws, and therefore possesses high superhardness, elastic recovery and resistance against crack formation. Their excellent work has attracted increasing interest in research on the ultra-hard nanocomposite coatings ($H > 80$ GPa). Liu et al.[34] investigated the normal grain growth kinetics in two-phase nanostructured films consisting of nanocrystallites embedded in an amorphous matrix using Monte Carlo simulations based on a modified Potts model. The simulation results have clearly shown that the amorphous matrix can lead to a remarkable decrease in grain size of the imbedded nanocrystallites. The hindering effect is sensitive to the volume fraction of the amorphous phase. As the volume fraction of the amorphous matrix increases, both the grain size and the kinetic growth exponent decrease nearly exponentially. Zhang et al.[35] recently systematically investigated the microstructure, surface morphology and mechanical properties of the two-phase nc-TiN/a-Si_3N_4 nanocomposite films synthesized by ion beam assisted deposition. A maximum hardness about 42 GPa was observed in a film with silicon content of 11.4 at.%. The improved mechanical properties of Ti-Si-N films with the addition of Si into TiN were attributed to their densified microstructure with development of fine grain size and reduced surface roughness. Figure 2 shows the TEM image from a Ti-Si-N film with Si content of 11.4 at.%. It can be seen that the nanometer-sized crystalline grains TiN inbedded in the amorphous Si_3N_4 matrix are clearly visible and in good agreement with Veprek's idea. Meanwhile, under the assumption that rough surfaces exhibit self-affine characteristic, they applied the kinetic scaling theory to determine the correlation functions of the growing surfaces. The values of roughness exponent α for TiN and Ti-Si-N (the hardest film) are 0.77 and 0.95, respectively. Jiang et al.[36] deposited nanocomposite films of Ti-Si-N by reactive unbalanced magnetron sputtering and found that in Ti-Si-N films the Si bonding status was in the form of Si_3N_4 with low Si contents ($<$ 14 at.%), while it was in the form of both Si and Si_3N_4 at high Si contents ($>$18 at.%). The quantification of surface roughening was achieved by calculating both vertical root mean square (rms) roughness and lateral correlation lengths of the film surface using the height-height correlation functions of measured AFM images. For all the Ti-Si-N films, a steady roughness exponent ($\alpha = 0.88 \pm 0.04$) was determined. Kim et al.[37] deposited Ti-Si-N films by a DC reactive magnetron sputtering technique with dual Ti and Si targets and obtained highest hardness value of approximately 38 GPa at a Si content of ~11 at.%, where the microstructure had fine TiN crystallites (approximately 5 nm in size) dispersed uniformly in an amorphous matrix. Nose et al.[38] investigated the influences of Si content and sputtering conditions on the properties of Ti-Si-N nanocomposite films prepared in an rf sputtering where the composite targets consisted of a Ti plate and Si or Si_3N_4 chips and the substrate was heated from room temperature up to ~573 K. The hardness and the crystallite size of the film as a function of the applied bias voltage were given. The maximum hardness value was 42 GPa at a bias of −10 V, but the crystallite size remained larger than 23 nm. From the above observations, the behavior of hardness increasing with decreasing crystallite size for nanocomposite films is very similar to that for multilayer coatings. The resistance on dislocation motion by distortions in crystal materials can be related to shear modulus differences. Compared to multilayer structure, the hardness enhancement for nanocomposite films can be explained as the result of sharp interfaces and biggish difference of shear modulus between two phases. The difference is: the nanocrystalline/amorphous nanocomposite system is isotropic, in other words, the orientation and distribution of two phases is in disorder. It is reasonable to suppose that the shear modulus of two phases is different (the structure and properties of two materials are different). The sharp interface observed in nc-TiN/a-Si_3N_4 nanocomposite is the result of immiscibility between two phases due to the chemical reason, while that in multilayer coatings is the result of adequate depositing technique and conditions.

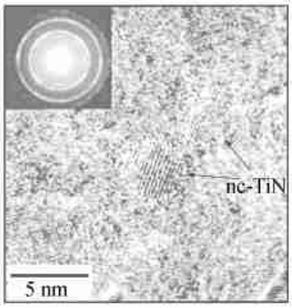

Fig. 2. High-resolution TEM plan-view image and its SAD pattern for a 50-nm-thick Ti-Si-N film with Si content of 11.4 at.%[35].

The hardness values of Ti-Si-N nanocomposite film in the above reports are far lower than that obtained by Veprek[8]. A possible explanation is that the a-$TiSi_2$ and nc-$TiSi_2$ phases were not observed in their films. The role of a-$TiSi_2$ and nc-$TiSi_2$ phases is strengthening the grain-boundary to block the dislocation motion and grain-boundary sliding. The differences of Si content and crystalline grain size corresponding to maximum hardness in these reports are obvious, so it is necessary to study the influences of Si content, crystalline grain size and depositing conditions on phase composition, hardness and other properties of nanocomposite films in detail.

TiN coatings have been applied to tools, dies, and mechanical parts to increase their lifetime and performance due to their attractive properties such as high hardness, good wear resistance, and chemical stability. One of the drawbacks of TiN is its limited oxidation resistance at high temperatures that can be reached during the process application. TiN exhibited obviously oxidation speed in 550—600 ℃ and TiN/Si_3N_4 exhibited obviously oxidation resistance. At

800 ℃ the oxidation speed of nc-TiN/a-Si_3N_4 with 12 at.% Si_3N_4 content is 10 fold slower than that of TiN and decreases further with the increasing of Si_3N_4 content but is accompanied by losses of hardness. The two step oxidation process is likely dominant in 600—1000 ℃. The first step characterized by oxygon slow diffusion to TiN nanocrystalite through Si_3N_4 is dominant from low temperature to 800 ℃. The increase of Si_3N_4 content in coatings means thicker Si_3N_4 layer covering TiN nanocrystallite and can result in slower oxidation speed. At the same time, the amorphous silicide tunnel is formed and the diffusion of oxygen to TiN decreases further. At above 820 ℃, the oxidation is characterized by recrystallizing and growing of TiO_2[39].

(Ti, Al)N exhibits good high temperature oxidation resistance and other superior performance compared with the other commercially available Ti based coatings. Several papers reported investigations on the dependence of the properties of these coatings on the Ti/Al ratio. Accordingly, the hardness monotonously increases with increasing Ti content up to approximately 60 at.% of the total metal content, and at above 70 at.% it strongly decreases again. The decrease in hardness is associated with the formation of the hexagonal wurtzite structure of AlN at a Ti content of less than approximately 20 at.%, and the decreasing effect of the solution hardening of the face center cubic TiN-like structure of the solid solution $Ti_{1-x}Al_xN$ at the higher side of the Ti content. Doping Si, embedding (Ti, Al)N nanocrystalline grain in the amorphous Si_3N_4 matrix can lead to an improvement of their properties. The (Ti, Si, Al)N nanocomposite coatings reported by Carvalho[40] exhibited a maximum hardness (54GPa) and a high elastic recovery (74%), and the thermal stable temperature reached 800 ℃. Generally speaking, the hardness of solid solution of (Ti Si, Al)N can reach 40 GPa and further enhancement needs formation of nanocrystalline phase/amorphous phase nanocomposite system. In (Ti, Si, Al)N quaternary complex system, the phase content greatly affects the structure and properties of nanocomposite films. Nakonechna et al.[41] prepared nanocomposite TiAlSiN thin films using cathodic arc-plasma and investigated the hardness affected by the Al content, the ratio of Al to Ti content varied within the range of 0.5—1.5, and the Si content did not exceed 3.5 at.%. The highest hardness (38—39 GPa) was obtained for samples with Al/Ti=1.0 and the lowest hardness values (30—33GPa) for samples with Al/Ti =1.5. Carvalho et al.[42] studied the effects of morphology and structure on the elastic behavior of (Ti, Si, Al)N nanocomposites using depth sensing microindentation and laser-acoustic (SAW) techniques. Both techniques indicated that Young's modulus of (Ti, Si, Al)N increased with Si content in the range of low amount of Si (<9 at.%), which can be attributed to a solution hardening. It seemed that a high amount of Si content induced the formation of amorphous phases and consequently a reduction of Young's modulus. Coatings having a columnar structure and high porosity with a large number of voids within crystallites showed a large difference (>20%) in elastic modulus obtained by the two techniques, when the laser acoustic values were smaller. When the films showed dense and very compact morphologies, the results achieved by both techniques were very similar. Therefore, the differences observed on the Young's modulus by both techniques were related to the pore volume within the material. It is very important to use ion bombardment techniques to densify the film and create strong grain boundaries. Ribeiro et al.[43] studied the effects of ion bombardment on properties of dc (direct current) sputtered superhard (Ti, Si, Al)N nanocomposite coatings. The XRD patterns of sputtered films revealed changes of the lattice parameter (from 0.418 nm to approximately 0.429nm) with the increase of the ion/atom arrival rate ratio. The lowest lattice parameter corresponded to a metastable phase where Si and Al atoms occupied Ti positions, while the highest lattice parameter corresponded to a system where at least a partial segregation of TiN and SiN_x phases already occurred, which can lead to the formation of a nanocomposite film of the type nc-TiAlN/a-Si_3N_4 and possibly nc-TiAlN/a-Si_3N_4/a-AlN. The mixture of the metastable phase with nanocomposite coating phases in some samples indicated that, in general, the segregation of TiN and SiN_x phases was not complete. An increase in ion bombardment corresponded to a hardness increase from 30 to 45 GPa, which helps the segregation of TiN and SiN_x phases. For (Ti, Si, Al)N nanocomposite coatings, understanding the increase of the hardness as a function of the coating composition and crystalline nature would be significant in realizing the hardening mechanisms of nanocomposite coatings and providing a guideline for designing and fabricating advanced composite materials.

Nanocrystalline TiC grains have been embedded in a hydrogen-free DLC matrix using a hybrid deposition technique, combining magnetron sputtering and pulsed laser deposition. The nanocrystalline grain sizes were maintained at the 10—20 nm level to restrict initial crack size and create a large volume of grain boundaries. The nanograins were separated within an amorphous matrix thickness above 2 nm to prevent interaction of atomic planes in the adjusted nanocrystalline grains and facilitate grain boundary sliding, but less than 10 nm to restrict the path of a straight crack. The hardness of the nanocomposite coatings was about 32 GPa for TiC/DLC with correspondingly high elastic modulus, and the hardness to modulus ratio was about 0.1. Single-phase materials with such high hardness would typically experience a brittle fracture once the load exceeded their elastic limit. The behavior of TiC/DLC composite coatings exhibited surface deformations, which visually appeared to be ‘plastic’. This was, however, not true plasticity since dislocation sources were prohibited. What we believe is that TiC grain boundary slides in the DLC matrix. Thus, the TiC/DLC coatings are hard and non-plastic at contact loads below their elastic limit, but their behavior will change to the described ‘plastic’ mode above this limit. This avoids brittle fracture at high levels of loading, and also creates the possibility to support high contact loads by local coating compliance and load distribution onto larger areas. Such self-adjustment of mechanical properties from hard to ductile resulted in dramatic improvement of scratch toughness characteristics. Scratch toughness was estimated at least 3—4 times above that of single-phase nanocrystalline TiC.

3 Hardening mechanism and design of superhard coatings

Hardness was defined as the resistance offered by a given material to external mechanical action. Generally speaking, hardness depends strongly on plastic deformation, which is related to creation and motion of dislocations. In a covalent crystal, in order to plastically shear it, electron-pair bonds must first be broken and then remade. According to solid-state physics, energetically breaking an electron-pair bond inside a crystal means that two electrons become excited from the valence band to the conduction band so the activation energy required for plastic glide is twice the band gap. Thus, the resistance force of band can be evaluated by energy gap E_g, and the hardness of covalent crystals should have the following form:

$$H(\mathrm{GPa}) = AN_aE_g, \qquad (1)$$

where N_a is the covalent bond number per unit area, A is a proportional coefficient, and E_g is the band gap. For polar covalent crystal, besides the covalent component, a partial ionic component has to be considered and Eq. (1) must be modified. But both theory and experiment confirmed that the main contribution to hardness comes from the covalent bond. In conclusion, three conditions should be met for superhard material: greater degree of covalent bonding, shorter bond length and higher coordination number.

Compared to bulk material, the film or coating consists of smaller crystallites and higher density of defects and so exhibits higher hardness. Now the explanations for the anomalous enhancement of hardness in nano-multilayer include modulus difference[44], coherent strain[45], structural barriers[46], Hall-Petch relationship[47], Brillouin zone effect[48], Orowan model[49], and solid solution[50]. All of the above mechanisms can explain the experimental phenomena with different levels of success, which is significant for designing hard coatings. Because of the great diversities, structure varieties and interface complexities of the nano-multilayer coating, research on it has been mainly done experimentally.

Koehler[7] first considered the modulus difference hardening on modulus difference isostructure epitaxially-grown multilayers. He found that dislocation motion was inhibited in a multilayered structure due to the image force on dislocations created by different dislocation line energies in each layer. By creating a multilayer structure in which the two layers have a low (layer A) and a high (layer B) shear modulus, a shear stress of the order of $G_A/100$ (where G is the shear modulus) would be required to drive dislocations through the structure. This shear stress is an extremely high value, which is the same order of magnitude as the theoretical strength of a solid. Koehler also noted that each layer should be as thin as a few mean free paths of dislocation motion so that dislocation creation cannot occur within the layers. Studies on TiN-based multilayers with VN, NbN, and alloys of $V_xNb_{1-x}N$ were performed by Shinn et al[51]. They found that VN and NbN had nearly equal shear moduli, and by varying the composition of the $V_xNb_{1-x}N$ layer in TiN/$V_xNb_{1-x}N$ multilayers, the lattice mismatch between the two layers can be changed without changing the shear modulus of the alloy layer significantly. All TiN/$V_xNb_{1-x}N$ multilayers showed strong hardness enhancements (~50%), and it was concluded that the lattice mismatch between layers had only a minor contribution to the hardness enhancement and modulus difference had the major contribution. Moreover, the diffusion between layers related to depositing conditions may decrease the modulation amplitude of shear modulus and decrease the hardness, so the sharp interface with less diffusion plays an important role in hardness enhancement.

The Hall-Petch relationship observed primarily for bulk material can be expressed as:

$$\sigma_s = \sigma_0 + kD^{-1/2}, \qquad (2)$$

where σ_s is the yield strength of polycrystalline material with grain size D, σ_0 is the yield strength of the same material with large grains, and k is a constant measuring the relative hardening contribution of the grain boundaries. The original model is based on the assumption that dislocations cannot move through grain boundaries, and dislocation pile-ups in one grain must initiate a dislocation source in an adjacent grain. If one of the interfaces in each pair of layers is impenetrable to dislocations, it may be reasonable to study the hardness behavior of multilayered materials by replacing the grain size with the multilayer period. It should be pointed out that the models from which Eq. (2) derived were based on grain sizes that were large enough to accommodate many dislocations. In a multilayer coating with a bilayer period of < 20 nm (where the hardest coatings are generally observed), only a few dislocations are present in a single layer, and more sophisticated models are necessary. Anderson et al.[52] have studied this problem in detail recently.

The model proposed by Chu and Barnett[44] is based on restricted dislocation movement between and within layers in the superlattice coating. For the first case, the difference of dislocation line energies for two layers is proportional to the difference of shear modulus for two materials. An additional energy is required to move the dislocation across layers. The interface width and shape may affect the dislocation motion, that is, more energy is needed for moving across narrow and sharp interface than that for diffused interface. When the layer thicknesses are very large, dislocations will move large distances without encountering an interface and will not experience significant image effects. The primary existing dislocations and dislocations created by Frank-Read source move more easily inside a layer than across layers. To find the maximum hardness, it is necessary to find the optimal layer thicknesses to inhibit dislocation motion across the boundaries between layers without having dislocation motion within a layer.

Research on hardening mechanisms of nano-multilayer coatings facilitates designing method for nanocomposite coatings. The recent depositing technique is almost non-equilibrium depositing process. There are a lot of defects in coatings. The measurement of hardness may induce sliding of dislocation, densification of structure and spreading of microcracks. The defects or other factors, which can resist spreading and propagating of dislocations, may enhance the hardness obviously. This is perhaps the most conceivable micro-mechanism to explain the property of nanocomposite coatings. The optimization of grain size and defect density is just the idea of enhancing the property of nanomultilayer.

In bulk materials, Hall-Petch relationship is especially prominent for grain size down to tens of nanometers. However, it 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 (inverse Hall-Petch). Softening caused by grain boundary sliding is mainly attributed to a large amount of defects in grain boundaries, which allow fast diffusion of atoms and vacancies under stress. So increase in hardness further requires hindering of grain boundary sliding. This can be realized by increasing the complexity and strength of grain boundaries. Since different crystalline phases often exhibit different sliding properties to accommodate a coherent strain and prevent formation of voids or flaws, multiphase structure is expected to have interfaces with high cohesive strength. Apart from hardness, good mechanical properties also include high fracture toughness. However, in order to obtain superhardness, usually plastic deformation is strongly prohibited, and dislocation movement and grain boundary sliding are prevented, thus a loss in ductility may be caused. Today, more and more researchers realize that a certain degree of grain boundary diffusion and grain boundary sliding are necessary to improve toughness of nanocomposite.

When wear resistance coating is applied to mechanical parts (mill, cutting tools), its temperature can reach more than 800 ℃ on cutting side. The parameters related to excellent coatings are not only the mechanical parameters but also the chemical stability (oxidation resistance), especially the high temperature toughness more important than hardness in application.

The first way to increase hardness of nanocomposite coating is to provide complex boundaries by means of a combination of two or more nanocrystalline phases. 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. Successful examples include nitride, carbide and boride systems. Segregation of nanocrystalline phases to grain boundaries of the first phase can generate the grain boundaries strengthening effect and stop grain growth, so it can significantly increase the hardness and elastic modulus but cannot improve the toughness. To address this problem, Miterer et al.[53] formed hard nanocrystalline phases within a metal matrix, such as TiN in Ni, ZrN in Ni, Zr-Y-N, ZrN in Cu, and CrN in Cu. In these coatings, one metal may be converted into nitride in the form of hard nanocrystalline phase and the other be transported into the growing film unreacted. In this case, both the dislocation mechanism and the grain boundary mechanism contribute to the improvement of surface hardness, but the existence of a metal matrix can improve toughness. However, the toughness and thermal stability are still poor. Dislocation movement initiated from grain boundaries may be prohibited because of the small separation of grains in the metal matrix, which can result in poor toughness. Grain boundary sliding depends on temperature, and the thermal activation facilitating grain boundary sliding has been confirmed, thus the mechanisms of preventing grain boundary sliding at room temperature may be not 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 system that displays immiscibility and undergoes spinodal decomposition and segregation at high temperatures.

Another way to increase hardness of nanocomposite coating is to embed nanocrystalline phases in an amorphous phase matrix. Diamond like carbon (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 nitride is used as strengthening phases, e.g. TiC/DLC, TiN/Si_3N_4, TiCrCN/DLC, etc. 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. Too large a distance between two nanocrystals will easily cause a crack to propagate in matrix, while a too short one 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. This can facilitate many nanocrystalline grains to slide in amorphous matrix to release strain. The toughness can be improved. The amorphous phase must possess high structural flexibility 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 addition to the enhancement of grain boundary sliding, thus it can improve the coating toughness. High hardness and high toughness is a contradiction and the optimization between them is necessary. Probably the best way is to use ternary, quaternary or even more complex systems, and the nanocrystalline phases should be refractory and immiscible with each other, which can result in compositional modulation, segregation and high thermal stability.

Some general principles to design a nanocomposite coating can be concluded from the above work on nc-TiN/a-Si_3N_4 and other nanocomposite coatings: One phase in composite must be hard enough to support load and hard transition metal nitride, carbide and some oxide are available candidate materials; the other phase must possess high structural flexibility to act as nano-cement and amorphous materials, for example, Si_3N_4, a-C, a-C:H, etc., are available candidates; the immiscibility between phases is a precondition to ensure the sharp change of elastic properties from one phase to the other.

4 Perspectives

Research on superhard nano-multilayer and nanocomposite coatings is still in progress now, and many existing issues need vigorous theoretical calculation and experimental verification. These include, in theory: the intrinsic factors and mechanisms of hardening, the maximum physical limitation of film hardness, the vigorous relation of hardness to microstructure of atoms and electrons; in experiment: the relation of mechanical properties to depositing parameters and chemical components, the method of measurement and characterization for ultra-hard coating; in application: the design of coatings with properties of wear resistance, corrosion resistance, thermal stability, high adhesion and others accommodating to special conditions in industry. To reach this aim, future systematic and hard research is required.

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