Nanocomposite Hard Coatings for Wear Protection

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Abstract

Nanocomposite thin films successfully promote hardness, oxidation resistance, improved wear behavior, and other properties relevant for wear-reducing coatings. Such coatings are composed of nanocrystalline grains of transition-metal nitrides or carbides surrounded by an amorphous hard matrix. The properties of nanocomposite coatings, especially hardness, are directly linked to nanostructure. The codeposition of the amorphous and nanocrystalline phases of different compositions results in different morphologies, which in turn affect the coating's properties. A maximum hardness ranging from 30 GPa to reported values above 60 GPa has been observed for most nanocomposite coatings. To obtain enhanced hardness, the domain size of the nanocrystalline phase must be below 10 nm, while the thickness of the amorphous layer separating the nanocrystals must be maintained at only a few atomic bond lengths. The prime reason for the hardness enhancement is the absence of dislocation activity.

Keywords: nanocomposites, elastic properties, superhard coating materials, thin films.

Introduction

The use of protective coatings in modern applications where friction is involved has been instrumental in new developments such as energy-efficient car engines and dry-machining technologies. The protective action of such coatings is, on the one hand, based on reduced wear due to increased hardness and thus less severe deformation. On the other hand, reducing the shear forces between two sliding surfaces is a way to improve the performance of a tribosystem (a system involving two or more surfaces, together with liquids, debris, and other material, all participating in relative shear motion). In short, high hardness and low friction coefficients are two key parameters for coatings used for wear reduction. Nanocomposite thin films are a new class of materials that meet these requirements to a large extent.

Nanostructured thin films have attracted considerable attention as wear-protective coatings due to their outstanding properties relative to single-phase materials. Their increased hardness makes them interesting candidate materials for applications under extreme conditions. In addition to high hardness and low friction coefficients, other aspects such as thermal stability, coat-

ing toughness, and interface toughness are decisive parameters for their usability as protective coatings.

Routes to Increased Hardness

Perhaps the most intensively investigated route to enhanced performance in protective coatings is increasing their hardness. Hardness is defined as the resistance of a material to plastic deformation. Plastic deformation of crystalline materials occurs predominantly by dislocation movement under applied load; hence, a material with enhanced hardness has a higher resistance to dislocation movement. For a single-phase material, this means that the shear modulus increases.¹ TiN is a classic multipurpose coating material, with a hardness value of 23 GPa. Increased hardness in TiN was achieved by introducing ternary elements such as TiCN,² TiAlN,³⁻⁵ and TiZrN.² In these cases, hardness was increased up to 33 GPa, most likely through an increase in the shear modulus.

Hardness enhancement can also be achieved by introducing mechanical stresses into almost any coating.^{6,7} In most cases, stress-hardened coatings will fail prematurely under mechanical load. Enhanced

hardness obtained in this way is, therefore, of practical interest only in those cases where low loads act on the coated surface during use.

Another way to obtain high resistance to dislocation movement and plastic deformation is to preclude the formation of stable dislocations. More than 30 years ago, it was theoretically⁸ shown that the introduction of phase boundaries with alternating elastic properties in a solid material should enhance the strength of such a layered material. The individual layers must be thin enough to preclude the operation of Frank-Read dislocation sources. This concept was experimentally verified in a variety of material combinations in the form of multilayers deposited by magnetron sputtering.⁹⁻¹² Most of these multilayer combinations are superlattice coatings with alternating heteroepitaxial layers. Superlattices are periodic multilayer structures, usually of materials with matched common properties (structural, electronic, magnetic, etc.). Typically, hardness can be enhanced by a factor of two or three as long as the layer period does not exceed the thickness that enables dislocation activity. For most of the nitride materials, this value is of the order of 10 nm. It was shown that a difference in shear modulus between the two materials is an important factor in achieving hardness enhancement.¹³ Coherence stresses originating at the interfaces due to differences in the lattice parameters were shown to be of minor importance to the hardness enhancement.¹⁴

In analogy to superlattice coatings nanostructured in the growth direction (atomically sharp phase boundaries after several nanometers), the suppression of dislocation activity also can be realized in isotropically nanostructured materials (i.e., in nanocomposite materials) as long as the frequency of occurrence of phase boundaries is the same in all directions. This means that a material consisting of equiaxed or isotropic crystallites with a grain size of <10 nm separated from each other by a second phase should exhibit the same suppression of dislocation movement. Isotropic nanostructuring of materials thus provides an ample range of possibilities for enhancing the mechanical properties of a coating without having to follow the demanding experimental requirements of superlattice coatings.

Isotropic Nanocomposites: The TiN-Si₃N₄ System

Attempts to codeposit silicon and TiN go back to the early 1980s, when Hirai and Hayashi¹⁵ used chemical vapor deposition to codeposit Si₃N₄ and TiN. At 1050°C, their process formed amorphous silicon

nitride with TiN crystallites of about 3 nm. At 1450°C, crystalline α - Si_3N_4 was deposited without signs of titanium incorporation. This early example illustrates one important prerequisite for the formation of nanostructured materials: only complete or near-complete immiscibility can lead to the phase separation that generates atomically sharp interfaces.

The first attempts to increase the hardness of TiN by adding silicon were carried out by Li and co-workers.¹⁶ They used plasma-assisted chemical vapor deposition (PACVD) to deposit silicon-containing nanocrystalline TiN in a silicon nitride matrix for a silicon concentration of 15 at.%. Hardness values of 6000 Vickers (60 GPa) were reported.¹⁶ Vepřek's group performed intensive studies on isotropic nanocomposites deposited by PACVD, mainly on nc-TiN/a- Si_3N_4 .¹⁷ Extremely high hardness values exceeding 100 GPa for nc-TiN/a- Si_3N_4 were reported by his group.¹⁸ They showed that hardness enhancement is also possible for other transition-metal nitrides, such as W_2N in conjunction with a- Si_3N_4 .¹⁹ Unbalanced magnetron (UBM) sputtering was used as an alternative technique for depositing nc-TiN/a- Si_3N_4 .^{20,21} Some authors attributed the increased hardness to silicon solid solutions formed in TiN,^{22,23} although no incorporation of silicon into the lattice of TiN could be detected below 1100°C.²⁴

The Nature of Nanohardness Enhancement

Figure 1 shows the nanohardness of nc-TiN/a- Si_3N_4 coatings that were deposited by closed-field UBM sputtering as a function of the silicon nitride fraction. Figure 2 shows a schematic cross section of a closed-field UBM sputtering-deposition system, a commonly used arrangement for obtaining high plasma densities.²⁵ The high density provided by the UBMs is further enhanced by forming a magnetic enclosure using alternating magnet orientation along the circumference of the vacuum vessel. This arrangement provides intense discharges that enable deposition at relatively low temperatures of 150–350°C. Substrate rotation is necessary in most physical vapor deposition (PVD) arrangements in order to evenly coat three-dimensional objects. For more on UBM sputtering, see the article by Münz in this issue.

Silicon-free TiN forms elongated crystallites that are several hundreds of nanometers long and tens of nanometers wide (Inset A in Figure 1). Minor amounts of silicon nitride cause a significant increase in nanohardness. From x-ray diffraction measurements (grain size and orientation), it was

Figure 1. Nanohardness of nc-TiN/a- Si_3N_4 as a function of silicon nitride fraction. Insets illustrate the schematic nanostructure at different compositions. Inset A: elongated crystallites several hundred nanometers in length are observed at silicon nitride fractions below 5 at.%. Inset B: at the hardness maximum, the coatings consist of isotropic TiN crystallites < 10 nm in size that are encapsulated by a thin layer (2–3 monolayers) of Si_3N_4 . Inset C: when the silicon nitride fraction in nc-TiN/a- Si_3N_4 is too high, the nanohardness approaches that of Si_3N_4 . Open squares indicate single-phase TiN and Si_3N_4 ; solid squares indicate two-phase TiN/ Si_3N_4 .

deduced that the partial covering of the growing TiN crystallites by Si_3N_4 interrupted grain growth and thus forced newly arriving TiN-forming species to renucleate.²⁶ The higher the silicon nitride content, the less possible it is to achieve undisturbed growth of TiN, and renucleation has to take place at very high rates. Therefore, TiN crystallites become very small at increased Si_3N_4 contents. At 15–20 at.% Si_3N_4 , the mean grain size of TiN does not exceed 7 nm; this size is too small for dislocation activities, and thus increased nanohardness is observed. Under mechanical loading, such a material can react only by grain-boundary sliding (i.e., by moving single, undeformed TiN nanocrystallites against each other). This process requires more energy than deformation by dislocation movement, therefore leading to higher hardness. Estimations of the mean grain separation at this composition show that only a few monolayers of silicon nitride separate the nanocrystallites (Inset B in Figure 1). At high silicon nitride fractions, the mean grain separation becomes so wide that ordinary crack propagation

Figure 2. Schematic illustration of a closed-field unbalanced magnetron sputtering deposition unit used for the production of nanocomposite coatings. The magnetic confinement enhances and concentrates the plasma discharge to the region where the work pieces are coated.

in Si_3N_4 takes place, and the hardness approaches that of Si_3N_4 (Inset C in Figure 1).²⁷ Materials of such compositions are no longer of interest as hard coatings,

but are used as electrically conductive diffusion barriers for copper metallization in microelectronics.²⁸

The evolution of nanohardness with the amorphous-phase fraction shows that two factors are important in order to enhance hardness: the crystallite size must be less than ~10 nm in the direction of the deformation to preclude dislocation movement, and the mean grain separation must be kept below 0.5 nm. Interestingly, hardness enhancement was recently reported for nanomultilayers of TiN/Si₃N₄ when the thicknesses of the TiN and the Si₃N₄ layers were 5 nm and 0.5 nm, respectively.²⁹ This finding illustrates the close relationship between the phenomena found in nanocomposites and nanomultilayer coatings.

Thermal Stability

If hardness enhancement arises from nanostructural conditions, then annealing to relax residual stresses should not affect hardness. Figure 3 shows a plot of the measured nanohardness and residual stress for two nc-TiN/a-Si₃N₄ coatings deposited by UBM-PVD with different silicon nitride contents that were annealed for 12 h at various temperatures in vacuum.³⁰ Coatings with 20 at.% Si₃N₄ (solid curves) have a grain size of $d = 7$ nm and do not show grain growth at temperatures of up to 950°C, and their originally high residual stresses are relaxed to a large degree. Hardness even increases to a certain extent. In con-

Figure 3. Measured nanohardness and residual stress for two nc-TiN/a-Si₃N₄ coatings with silicon nitride contents of 7 at.% and 20 at.% Si₃N₄, respectively, annealed at various temperatures in vacuum. The 12-hour annealing does not lead to grain growth (constant $d = 7$ nm) of the 20 at.% Si₃N₄ sample at any of the temperatures, and residual stresses in the coatings are relaxed at high temperatures. In contrast, the 7 at.% Si₃N₄ sample shows grain growth (from $d = 12$ nm to $d = 25$ nm) and thus hardness loss upon annealing.

trast, while residual stresses are relaxed at high temperatures in coatings with 7 at.% Si₃N₄ (dotted curves) and an initial TiN grain size of $d = 12$ nm, these coatings also lose their hardness due to grain growth (mean grain size increases to $d = 25$ nm at 900°C). If encapsulation by Si₃N₄ is complete, almost no grain growth is observed. Moreover, silicon nitride acts as an efficient barrier against the diffusion of oxygen into the coating. As a consequence, nc-TiN/a-Si₃N₄ coatings are highly oxidation-resistant.²⁷

Other Nanocomposite Hard Coatings

A hardness evolution similar to that observed in nc-TiN/a-Si₃N₄ can be observed in nc-TiC/a-C:H nanocomposites (where a-C:H is amorphous hydrogenated carbon) deposited by UBM-PVD. Hardness enhancement by a factor of about two is found at the same relative phase ratio, again with a crystallite size of about 5 nm at the hardness maximum.³¹ The same effect is obtained in hydrogen-free nc-TiC/a-C deposited by other techniques.^{32,33} Nanocomposites based on a-C or a-C:H show excellent frictional behavior because the amorphous carbon transforms into nanocrystalline graphite, which acts as a solid lubricant. Friction coefficients of 0.25 against steel can be achieved. UBM-PVD^{31,34} and pulsed laser desorption³⁵ are techniques with low thermal loads ($\leq 150^\circ\text{C}$) that are suitable for temperature-sensitive substrate materials.

A special class of nanostructured hard coatings was developed and described by Musil and co-workers.³⁶ These coatings consist of grains of the transition-metal nitrides ZrN or CrN surrounded by minor amounts of metals like copper³⁷ and nickel.³⁸ Hardness values exceeding 40 GPa were reported for ZrN-Cu and other combinations. Annealing experiments to 600°C, however, suggested that residual stresses, not the nanostructuring of the films,³⁹ caused the enhanced hardness in these materials.

Deposition Methods

In order to keep a deposition process economically viable and compatible with commonly used substrates, deposition temperatures should be kept below 500°C. The preparation of nanocomposite hard coatings requires ion-assisted techniques to provide sufficient reactivity during deposition at low temperatures. If the activity of nitrogen during the reaction is too low, titanium silicides will form and the deposited coatings will have a reduced toughness. The first process for depositing nc-TiN/a-Si₃N₄ utilized PACVD

with TiCl₄, H₂, and N₂ as the educts and SiCl₄¹⁶ or SiH₄ as the silicon source.¹⁹ Coatings of nc-TiC/a-C can also be produced by PACVD to achieve hardness values of 40 GPa,⁴⁰ however, the incorporation of chloride in PACVD may lead to premature interface corrosion. Furthermore, the elevated deposition temperatures ($\sim 500^\circ\text{C}$) may pose a limitation for certain substrates.

Industrially practical techniques must avoid processes using hazardous chemicals such as halogenated species or chemicals that require special exhaust systems. The drawbacks of these hazardous gases can be circumvented in PVD processes, where metallic educts (Ti and Si) and benign gases like Ar and N₂ are used.^{21,27} Methane³³ or acetylene³¹ can be used for the deposition of carbide nanocomposites instead of a carbon target. UBM-PVD is an efficient method for producing nanocomposite coatings of various compositions.^{21,26}

Two of the drawbacks of magnetron sputtering, namely, inefficient target use (only 25–40% of the material can be used) and the complex and costly electronic power-supply circuitry, can be circumvented by using arc PVD. This robust technique has proved its efficiency in numerous commercial installations worldwide. In arc PVD, a low-voltage, high-current arc burns between the cathode target and the anode, yielding higher deposition rates than those of conventional sputtering techniques. However, a serious disadvantage of arc PVD is the long-known droplet problem—the incorporation of large molten target particles in the growing film. Despite this limitation, nanocomposite coatings with enhanced hardness can be produced by arc PVD.⁴¹ The deposition of nc-TiN/a-Si₃N₄ requires the use of a combined process where titanium is arc-evaporated and silicon is sputtered from a magnetron.⁴² The first commercially available nanocomposite coatings (nc-TiAlN/a-Si₃N₄) were deposited by arc PVD and are available from SHM (Czech Republic) and Platit (Switzerland).

Pulsed laser desorption in conjunction with magnetron sputtering has been used to deposit nc-TiC/a-C because of the very high plasma density of the laser plume and the resulting complete atomization of the carbon.³⁵ The applications of this technique, however, are limited to small, flat substrates.

Summary

Nanocomposite hard coatings are a class of materials that exhibit increased hardness when certain conditions are met. The reason for their enhanced hardness is the absence of dislocations within the nanocrystalline phase. These materials deform

under load by grain-boundary sliding, a process providing a higher resistance to plastic deformation. To achieve this effect, the material must fulfill the following conditions: the crystallites must be smaller than ~10 nm, the mean grain separation by the second phase should remain below 0.5 nm, and the phases must have negligible mutual miscibility. Coatings that meet these requirements—for example, nc-TiN/a-Si₃N₄—display high hardness and excellent oxidation-resistance properties. Potential applications of these materials include high-speed chipping processes, extrusion devices, and injection-molding tools. High hardness, high toughness, and low friction against metallic counterparts can be achieved with nc-TiC/a-C and nc-TiC/a-C:H coatings. These coatings can be used for applications requiring high contact pressure and low friction. All nanocomposite hard coatings are deposited by ion-assisted techniques, among which magnetron sputtering and arc PVD are the most important.

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