SUPERHARD COATINGS

Raymond L. Boxman, Tel-Aviv University, Tel-Aviv, Israel; Stan Veprek, Technical University Munich, Garching, Germany; Vladimir Zhitomirsky, Tel-Aviv University, Tel-Aviv, Israel, and Avi Raveh, NRC-Negev, Beer Sheva, Israel

Contributed Original Article

Hardness is the ability to resist plastic deformation under an applied penetrating load. Historically, hardness of materials was compared by the ability of one material to scratch another, and the 1-10 Mohs scale was established based on a selection of 10 minerals with vastly different hardness. Modern technology uses indentation by a diamond indenter with various standardized shapes (Vickers, Knoop, Berkovich), and defines hardness by the ratio of the indenter load to the area of the plastically deformed indentation that’s left behind after the load is removed, expressed in units of kg/mm², or in GPa. Hardened steels generally have a hardness less than 10 GPa, while typical hard nitride and carbide coatings (e.g. of TiN and TiC applied to cutting tools) might have a hardness of 20-30 GPa. Materials whose hardness exceeds 40 GPa are termed “superhard.”

Hardness is one of the main properties of a material which determines its ability to resist wear when subjected to frictional forces. However, hard materials are often brittle, expensive, and difficult to form. One strategy to design components which are tough, inexpensive, and easy to produce, and yet wear resistant, is to choose a material for the body of the component which fulfills the first 3 requirements, and to deposit a coating of a second, hard or superhard, material to minimize wear. Of particular interest for low wear are coating materials with a high ratio of hardness-to-elastic modulus, H/E.

Deposition of superhard, nano-composite coatings by plasma processing was the subject of DESHNAF, a 35 month “coordination action” which concluded on 31 December 2006. DESHNAF was funded by the European Union and was executed by a consortium comprised of Euro-Consultants, Tel Aviv University, Ben Gurion University, Technical University of Munich, Max Plank Institute of Plasma Physics, Deutsches Zentrum für Luft- und Raumfahrt, University of Surrey, and University of Sheffield. DESHNAF conducted 5 workshops and several literature surveys – full documentation may be found on the DESHNAF website: www.DESHNAF.net. The culminating public event of the DESHNAF project was the International Conference on Superhard Coatings, held from 27 Feb to 1 March, 2006 at Kibbutz Ein Gedi in Israel. A total of 55 papers were presented on techniques for depositing, characterizing and applying superhard coatings, as well as solving problems connected with interface purity and thermal stability. Abstracts of the papers presented may be found at the conference website, www.hardcoat.org. A special issue of Surface and Coatings Technology devoted to Superhard Coatings and comprised of selected papers from the conference was published recently.

Basically there are two types of superhard coatings: (1) coatings comprised of materials which are intrinsically superhard, such as diamond, amorphous diamond-like carbon (DLC), cubic BN, and B₄N₂, and (2) engineered materials whose superhardness is a result of ion bombardment, alloying, nano-layering or nano-structuring hard materials. This latter type can be divided into several groups:

(a) Thin coatings in which the hardness is due to a complex, synergistic effect of ion bombardment during their deposition by plasma enhanced chemical or physical vapor deposition (PECVD or PVD). The ion bombardment engenders nano-grain development, densification, point defects and high compressive stresses, and leads to improved hardness, morphology, structure and nanostructure, and has been studied and reviewed by many researchers. 

(b) Multi-component nitride, carbide, and boride coatings, having a single-phase crystalline structure (such as ternary (Ti,Nb)N), which have a hardness greater than either material alone, as a result of solid solution hardening.

(c) Nanocomposite coatings which are formed by self-organization due to thermodynamically driven spinodal phase segregation. Examples are nanocomposites consisting of transition metal nitride nano-crystals embedded within an X-ray amorphous covalent nitride.

(d) Multilayer superlattice structures, produced by sequentially depositing up to 1000 alternating layers of two hard nitrides, carbides, and/or borides, (e.g. TiN/TiN, TiN/TaN, TiN/CrN, or TiC/TiB₂) and having a layer thicknesses of few nm, and a total coating thickness of few μm.

A successful recipe for fabricating group-c nano-structured superhard coatings is to co-deposit, on a heated substrate, materials which will form under equilibrium conditions at least two phases – a hard crystalline phase such as TiN which will comprise the largest volume of the coating, and a second material which is immiscible with the first phase. Figure 1 shows a transmission electron micrograph (TEM) of nc-TiN/a-Si₃N₄ nano-composite, showing a nano-structure typical for spinodally segregated binary systems. Under proper conditions there will be a tendency for the hard material to coalesce as nano-crystallites, separated one from the other by a continuous amorphous phase of the second material, such as nc-Me₆N/a-Si₃N₄ (where Me represents a metal such as Ti, Zr, V, W, Ti₆Al₁₄ and nc and a indicate nano-crystalline and X-ray amorphous phases, respectively). Examples include nc-TiN/a-BN, nc-MeC/a-C, nc-TiN/a-BN/a-TiB₂, and nc-TiN/a-Si₃N₄/nc-TiSi₁₄/a-TiSi₂. The thickness of the continuous phase is only 1-2 monolayers. This interfacial nano-layer (e.g., Si₃N₄) is more stable than bulk Si₃N₄ and it is sufficient to stabilize the nano-crystallite surfaces, and to retard cracks from propagating from one nano-crystallite to another.

The hardness of binary nano-composites, such as nc-Me₆N/a-Si₃N₄, generally do not exceed 50-60 GPa, whereas that of 70-80 GPa was achieved for ternary nc-TiN/a-Si₃N₄/a-TiSi₂ and about 100 GPa – for quaternary nc-TiN/a-Si₃N₄/a-TiSi₁₄/a-TiSi₂. Figure 2 shows the load dependence of the hardness of 3.5 μm thick coatings of the above quaternary material, in comparison with a 1 μm thick single-phase nc-diamond coating and a single-crystal bulk diamond. The hardness of the quater-
nary nano-composite at low loads was ~100 GPa, i.e., comparable with bulk diamond, then slightly decreased at a load of 100 mN because of the influence of the soft substrate.

Measuring the hardness of superhard coatings is technologically challenging. In general, the penetration depth of the indenter must be less than ~5% of the coating thickness, to prevent strain induced in the substrate from influencing the measurement. However, in some cases, surface effects may influence the measurement. Detecting and measuring small indentation areas is difficult and time consuming, and hence modern nano-indentation instruments typically rely on measuring the indenter displacement-load curve. However, when superhard coatings are indented, and the hardness of the coating is on the same order of magnitude as the hardness of the indenter, the instrument must be carefully calibrated to take into account strain in all elements of the instrument, and the exact shape of the indenter tip. This shape changes with wear when indenting superhard materials, and thus maintaining calibration is difficult. Because of these difficulties, some investigators only rely on conventional micro-hardness measurements with relatively large loads, which may only be performed on relatively thick coatings.

Superhard coatings prepared by the thermodynamically driven spinoval phase segregation have high thermal stability. Their hardness and grain size (which depend on nano-structure and composition), are not changed by annealing up to 1100°C, as shown in Figure 3 for nc-TiN/a-SiN<sub>x</sub> coatings deposited by PACVD on a Si substrate. Researchers have employed different methods to investigate the thermal stability of superhard coatings: (a) measuring the hardness at room temperature after annealing at high temperatures, as studied by Herr and Brozeit; and by Veprek et al.; (b) measuring the hardness dependence on composition (the segregation stability and diffusion between substrate and coating), as studied by Veprek et al. and Zeman et al.; (c) measuring the superlattice period stability as a function of annealing temperature in multi-layer superlattice coatings; and (d) measuring the biaxial stresses of the coatings in the as-deposited state and the stress relaxation during the heat treatment.

Various structures and compositions of superhard coatings exhibit similar hardness but completely different thermal stability. This depends on the relationship between different hardness enhancement mechanisms and the distinct thermal stability behavior of the superhard coatings. Multi-layered and nano-composite material systems fabricated by spinodal phase segregation exhibit significant thermal stability whereas coatings whose hardness enhancement is due to energetic ion bombardment soften upon annealing to 450 – 550 °C (see Ref. 14 and references therein).

Nano-layers and nano-structures in superhard coatings need a well-defined interface having high cohesive strength. This is because the 3 – 4 nm grains do not deform plastically because there is no dislocation activity, and the well-defined interface hinders grain boundary sliding.

One of the most challenging applications of hard and superhard coatings is improving the performance and life of cutting tools. There are three main economic advantages. With expensive tools such as hobs, tooling cost can be reduced by extending the lifetime. With all tools, including inexpensive “throw-away” insert tools, the ability to machine at higher speeds allows expensive automated machining centers to have higher productivity and hence lower costs per part. Finally, when the tool coating allows the elimination or minimization of coolants and lubricants, the machining cost can be reduced by 20% or more.

In machining operations, hardness, or even superhardness, is not sufficient. The coating, to be successful, must fulfill multiple requirements including having excellent adhesion to the substrate, and being stable at the high temperature encountered by the cutting edge. This high temperature accelerates stress relaxation, re-crystallization and grain growth, diffusion between the coating and substrate, and oxidation. To operate successfully under these conditions, the coating must have high oxidation resistance, low miscibility between the coating components in order to prevent diffusion between them, resistance to inter-diffusion between the coating and substrate materials, low solubility at high temperatures in both the substrate and work piece materials, and low residual compressive stress. In some applications, the ratio of the hardness to the elastic modulus (H/E) substantially influences performance. Coatings with high H/E perform particularly well in abrasion, erosion and impact wear, but are also beneficial in minimizing sliding wear and corrosion.

Superhard coatings have been found to super-perform on many cutting tools under a wide range of machining conditions, increasing the life time typically by a factor of 3 to 4 or more. For example, for drilling into a composite of aluminum alloy and graphite fiber reinforced carbon, which is used in the aerospace industry, only very expensive drills made of cemented carbide and coated with polycrystalline diamond could be used previously. Application of superhard nano-composite coatings increased the tool life time by a factor of 2. Moreover, worn coatings can be stripped and the expensive tool re-coated up to 5-times, which is not possible with the diamond coatings. However, there is no universal coating which is optimal for every situation. For every given high volume application, it is worthwhile to test alternatives. And finally, there is

continued on page 26
SUPERHARD COATINGS
continued from page 25
a continuing desire to develop improved coatings to obtain better yet performance for a wide range of applications.

REFERENCES