Superhard Coating Materials

Yip-Wah Chung and William D. Sproul, Guest Editors

Abstract

"Superhard" coating materials are defined by hardness values that exceed 40 GPa. In this issue of *MRS Bulletin*, we focus on noncarbon-based superhard coatings, with the exception of a review of carbon nitride (CN) materials. Nanometer-scale multilayered nitride coatings were the first to show the superhard property, and these coatings have quickly made their way into industry as protective coatings for cutting-tool operations. Nanocomposite thin films also exhibit superhardness, and some of these materials have hardnesses approaching that of diamond. Cubic boron nitride (c-BN), which is naturally superhard, has proven very difficult to deposit at thicknesses exceeding 0.1 μm, but it is now reported that chemical vapor deposition techniques based on fluorine chemistries can produce c-BN films up to 20 μm thick. The search to produce cubic β-CN has led to the development of noncubic, fullerene-like forms of CN that are both hard and elastic, a very interesting combination of properties that has already been put to use in the hard-disk industry. Overall, the development of hard and superhard coatings during the past 20 years has been remarkable. We have progressed from trying (and often failing) to deposit hard coatings to now designing new nanometer-scale multilayered and nanocomposite coatings that exhibit excellent hardness properties and other high-performance characteristics.

Keywords: *carbon nitride, cubic boron nitride, nanocomposites, nanometer-scale multilayered coatings, superhard coating materials, superhard oxide materials, thin films.*

Interest in "superhard" coating materials, defined by hardness values in excess of 40 GPa, has increased significantly during the past 10–15 years. In nature, there are only two materials that qualify as superhard: diamond and cubic boron nitride (c-BN). Diamond is the hardest known material, with a hardness of 70–100 GPa depending on crystallographic orientation and purity; c-BN has a hardness of 50 GPa. Many researchers have tried to produce coatings that match or exceed the hardness of these materials. Much of the work has been directed at the deposition of diamond or diamondlike coatings, and there has been much success in this area. In this issue of *MRS Bulletin*, however, we look at other superhard coating systems that are not carbon-based, with the exception of a review of carbon nitride materials.

In the mid-1980s, researchers at Linköping University[1] in Sweden showed that it was possible to produce nanometer-scale multilayered coatings of titanium nitride and vanadium nitride with hardness values in excess of 50 GPa. Their discovery led to much research activity in this area, and many other nanometer-scale multilayered coatings have been investigated since this initial development. In this issue, we look at two contributions that are directly related to work in this field.

In the first article, Barnett et al. report on efforts to produce high-temperature stability in nanometer-scale multilayered coatings. The superhardness of these materials depends on maintaining a distinct layer structure, which can be destroyed by diffusion at high temperatures. To overcome this problem, Barnett et al. describe the use of immiscible layers to produce superhard coatings that maintain their hardness to temperatures in excess of 1000°C.

In the second article, Münz et al. look at industrial applications for nanometer-scale multilayered coatings. Much success has been achieved in adapting this technology for use in metal-forming operations. This work represents a rapid transfer of technology from the research stage to the routine use of these coatings in industry.

Related to nanometer-scale multilayered coatings are nanocomposite thin films. Some of these films have hardnesses approaching that of diamond. In his article, Patscheider discusses the effect of nanostructure on coating properties. These films usually have nanocrystalline grains of transition-metal nitrides or carbides surrounded by amorphous hard nitrides. The immiscibility of the amorphous and transition-metal nitrides is key in developing this structure. The amount of the amorphous material and the size and shape of the nanocrystalline grains have a direct influence on the hardness of the material. The hardness enhancement is due to restricted dislocation movement, as it is with nanometer-scale multilayered coatings.

It became apparent very early on that depositing c-BN coatings was difficult. In order to create the cubic phase instead of the hexagonal phase, stress had to be applied to the film. However, this stress caused delamination of the coating once the thickness of the film exceeded a few tenths of a micron. Thick c-BN films have eluded researchers for a long time. In this issue, Zhang et al. report on a method for depositing c-BN films at a thickness in excess of 20 μm. Their technique uses chemical vapor deposition based on fluorine chemistry. Thick c-BN films will find many useful applications, particularly in metal-cutting operations where the hardness and insolubility of c-BN in the work piece will lead to enhanced tool life.

In high-temperature applications, all of the nitride- and carbide-based superhard materials fail due to oxidation. One of the goals in researching new superhard materials has been to develop superhard oxide materials. In his article, Lowther shows how predictive computer modeling is being used to guide researchers in the quest to produce new superhard oxides.

The final article, by Hultman et al., is on resilient fullerene-like carbon nitride coatings. Carbon nitride first came to the notice of most researchers through the published work of Liu and Cohen.[2] They predicted that the cubic β-C_3N_4 form of carbon nitride might be as hard as or harder than diamond. This led to a flurry of attempts to produce this elusive material that continues even today. The guest editors of this issue were among those who have tried to deposit cubic β-C_3N_4, and like most researchers, they found it difficult to do. However, CN_x, where x is around 0.2–0.3, was found to be a very interesting hard material. It may even be a

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superhard material, but it is not as hard as diamond. Normally, most hard materials are very brittle, but CN_x is very elastic, which seems a contradiction. Hultman et al. show that CN_x has a fullerene-like structure, which gives this material its elastic property. They review the nature of the bonding between the carbon and nitrogen atoms and the issues involved in trying to determine the hardness of the material. The bonding between carbon and nitrogen atoms is key to the degree of elasticity, and this finding is important for the design of tough materials.

Overall, the development of hard and superhard coatings during the past 20 years has been remarkable. We have progressed from trying (and often failing) to deposit hard coatings to now designing new nanometer-scale multilayered and nanocomposite coatings that exhibit excellent hardness properties and other high-performance characteristics. Thick c-BN coatings will quickly find uses in industry, as will hard oxide coatings once they are available, and CN_x has already found industrial acceptance as a protective overcoat on virtually all hard-disk drives manufactured today.

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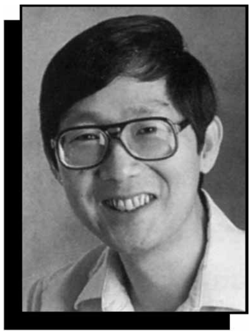

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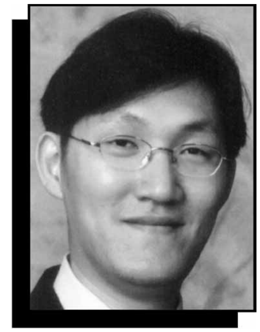
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such as AlN/TiN, AlN/VN, AlN/W, and AlN/NbN. This work focused on the stabilization of the metastable cubic AlN phase in nanolayers and the mechanical properties of the resulting nanolayered coatings.

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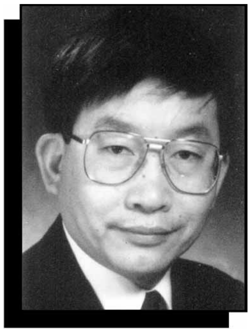

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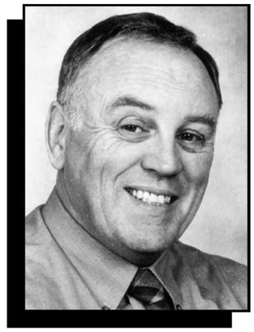

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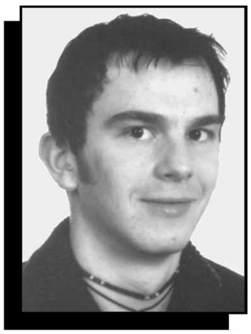

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