TECHNICAL PAPER

Tribological and Decorative Coatings

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Introduction

While protective and decorative coatings serve different functions, they share similar sets of material and deposition requirements critical for specialty optics. Decorative coatings also provide protection to softer substrate materials against wear and corrosion, enabling lower weight products based on coated plastics to replace metal substrates. Hard wear-resistant coatings are metallic in appearance and are based on compounds of carbides, nitrides, carbonitrides, borides and oxides. They are generally opaque as opposed to optical interference coatings. Different functional applications require specific deposition conditions that include layer composition, thickness and substrate temperature tolerance. The high energy aggressive cathodic arc process produces µm-thick dense compositions with no color shift. Enhanced PVD processes such as High-Power Impulse Magnetron Sputtering (HIPIMS) continue to show promise of high performance at a fraction of the coating thickness. A large variety of sputter tools involve reactive gas control and custom target and geometrical considerations. Applications of decorative and tribological coatings range from consumer to military, space and sea environments.

Applications

Tribological coatings are used in applications that are exposed to severe contact forces under which normal thin-film coatings would fracture and lose adherence, thereby forfeiting their protective function. The reduction of abrasive and adhesive wear between contacting surfaces requires low friction coefficients, high hardness to resist abrasive wear that can result in stress cracking, erosion and fatigue [1]. Wear occurs is several forms: adhesive welding between metals, shearing, abrasive, high-speed particle impact, erosive, corrosive, and high temperature induced chemical interaction [2]. Welding does not occur between ceramic and ceramic-metal surfaces because ceramic materials are harder and less reactive than metals. Examples of coatings that are subject to these forms of wear include: metal cutting tools, mechanically contacting surfaces operating at high temperatures, optical surfaces exposed to high-velocity sand and water impact, and surfaces exposed to contact abrasion and corrosive liquids. Due to their increased durability properties, tribological coatings are employed in applications ranging from machining and medical implants, to military air and sea vehicles, commercial decorative metals and polymer surfaces.

An example of opti-tribo coatings currently used in commercial applications has been adapted from previous military technological requirements. Supersonic aircrafts encounter high impact velocities of sand, dust and rain, any of which can degrade the optical transmission by erosion or micro-fracturing. Thermal IR nighttime imagery is available on high-end cars in the consumer market. The imagers require a Germanium IR window that is protected with a DLC layer against erosion from blowing sand and rain. Environmental protection for military operations in harsh environments has been provided by DLC, GeC, BN, and other coatings. Previous issues of CMN have addressed some of these topics [3].

Materials That Increase the Wear Life of Surfaces

Assuming the surfaces in contact are smooth and free of asperities and roughness, reduction of mechanical wear relies on decoupling the relative forces associated with sliding. Sliding friction force is proportional to the contacting area and coefficient of friction (COF), and can be reduced with the deposition of coating materials that are hard, adherent and possess a low COF. Many high-vacuum and high-temperature applications such as in-space optical instruments, and jet or rocket components cannot make use of lubricants to reduce COF. Temperature and relative humidity influence friction of dry surfaces.

A well-known tribological material, diamond-like carbon (DLC) layers have one of the lowest COFs available in thin-film form. Materials used for increased wear resistance and that are generally more available, are based on the transition metal compounds of C, N and O. These compounds produce carbide, nitride, boride, chrome and aluminum oxide compositions with high hardness. Wear-resistant materials include SiC, Si_3N_4, AlN, HfN, TaN, TiC, TiN, ZrN, and combinations of these (see Table 1).

Composition	**Color**	**Hardness (kgf/m^2)**	**Process**	Reference
TiN	Golden-yellow	2400	Cath. Arc	3
ZrN	Golden-green	3200	Cath. Arc	3
HfN	Yellow-green	2750	Cath. Arc	3
TiCxN1-x	Reddish	2450-2900	Cath. Arc, PVD	3, 4
ZrCxNy	Silver-gold-violet	--	PVD	4
(Ti, Al)ON	Gold-dark blue	--	PVD	4

Table 1. Compositions, colors, and hardness of tribological and decorative coatings produced by cathodic arc and reactive sputter processes.

In addition to high adhesion hardness and lubricity, ductility is an important aspect of improving wear characteristics. Coatings brittle in nature are subject to impact damage through cracking and loss of protection of the substrate. The inclusion of one or more ductile material layers provides energy dissipation that might otherwise be transferred at maximum force into the coating and interface. Ductility is imparted through structural and material characteristics. Coatings that are subject to impacting forces require special design to protect and survive with minimum damage.

Durable Decorative Coatings

Many consumer products require reflective coatings that mimic polished metal surfaces such as aluminum and chrome mirrors, and colored objects. Coatings on these types of polymers provide the benefit of lower weight cost and high-volume production of small and large 3-D surface shapes. Household appliances, bathroom furnishings, clothes dryer doors, automotive parts, and jewelry are a few of the most popular applications that use protected or durable reflecting coatings on plastic bases, thus resembling solid metal forms. Hard coatings provide the required scratch resistance [4, 5].

As opposed to interference-generated colors (golden-yellow, golden-green, yellow-green, reddish, silver-gold-violet, and gold-dark blue), the spectrum of available colors for decorative coatings is determined by selective absorption imposed by the chemical composition. In the case of semi-transparent layers, the morphology and thickness of the film can additionally influence color. Composition-determined color is established by the deposition parameters such as reactive gas composition and pressure and deposition rate. Doping with carbon is a tool that can also control color in some compositions.

An example of windows that appear to be gold is shown in Figure 1 below. The windows are coated with a thin semi-transparent gold layer that reflects the gold color and transmits a limited amount for interior lighting. Architectural glass is coated using PVD by large area coaters at the glass manufacturer.

Figure 1. Gold-coated windows of Mandalay Bay Casino-Hotel, Las Vegas, reflecting the setting sun. Photo by Samuel Pellicori.

Decorative coatings exposed to weather and abrasive wear environments require adequate mechanical durability to extend their lifetimes. The coatings might be reflective only or might require some transmission of light. Reflective colors available in hard durable coatings are listed in Table 1 (see above) along with their hardness and deposition process.

Transparent Hard Coatings for Optics

Many optical applications require abrasion-resistant coatings compatible with glass or polymers. Some of the most useful metal oxide compounds include ZrO_2, In_2O_3, HfO_2, Al_2O_3, and Y_2O_3, in addition to mixtures of these oxide compounds. Previous CMN newsletters have discussed the theory behind the improvements produced by adding small percentages of “dopants” to a base oxide compound [5]. Summarizing the findings, the additive discourages crystallite formation, creating porous and structurally weak and unstable microstructures. The deposited film is amorphous and dense, and therefore more environmentally stable than the pure parent material. Available mixtures include Yttria- and Alumina-stabilized ZrO_2, SiO_2, TiO_2 ($LaTiO_4$) [5, 6].

Deposition Processes for Tribological and Decorative Coatings

When looking at the deposition processes for tribological and decorative coatings, electroplating is used for some metal substrates. CVD processes were initially used for decorative and tribological coatings but have since been supplemented or replaced by PVD processes for higher durability or color fastness. These processes include low-temperature high-rate activated reactive (ARE), magnetron sputtering, and ion plating [2]. Cathodic arc deposition offers high deposition energy and rates, and it's easier to control total pressure as opposed to controlling partial pressures in the other processes.

Life-extending coatings for machine tools require a high-speed deposition process to build up the required tens-of-micrometer thick layers. An efficient process is filtered cathodic arc deposition. Low surface friction properties would not be possible if particulate inclusion and rough microstructure that are often associated with thick coatings were present. By filtering the beam, the largest particles are diverted from the beam, resulting in a smooth dense film layer.

Decorative and architectural windows and products coating use magnetron sputtering in roll coaters for high volume large area production.

As requirements for durable decorative and functional wear-resistant coatings evolve, the materials and processes will progress to meet new challenges. Materion provides sputtering targets for the large area glass industry, including a newly patented Zirconium Oxide (ZrO_2) based sputtering target. To learn more about our complete offerings, including our advanced chemicals, visit Materion.com/advancedmaterials.

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