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Substrates for Tribological Coatings

Tribology is the science and technology of solid surfaces moving with respect to one another under load. Tribological coatings include ones used for wear resistance and abrasion resistance, such as those used for tool coatings. Wear and abrasion are typically inversely proportional to hardness—with fracture toughness, corrosion resistance, coefficient of friction, and adhesion between contacting surfaces also playing roles. The hardness of a material is measured by its resistance to surface deformation. If the coating is deposited on a rough surface, a "macro-columnar" morphology will be superimposed on the normal columnar morphology of atomistically deposited films, caused by geometrical effects, giving a less than fully dense deposit. If the film material is less than fully dense, it will compact under load, resulting in a lowered hardness value, as well as increased friction, wear and galling. Surface roughness and the angular distribution of the depositing vapor atoms are important in generating macro-columnar morphology, because of geometrical shadowing effects. It is best to have a smooth substrate surface to obtain a dense deposit.

The ability of a hard coating to carry a load depends on the load, load distribution, mechanical properties of the coating material, and the coating thickness. If the coating is deformed by the load, then some of the load will be carried by the underlying substrate material, and the mechanical properties of the substrate become important. The Vickers (HV) or Knoop (HK) hardness measurements are made by pressing a diamond indenter of a specific shape into a surface, with a known force. The hardness is then calculated by using an equation of the form "hardness (HV or HK) = constant (HV or HK) x p/d^2 (Kg/mm^2)," where p is the indentation force, and d is a measured diagonal of the indenter imprint in the surface.

Hardening of Surfaces by Diffusion

Treatment	Substrate	Microhardness (kg/mm^2)	Case Thickness (μm)
Carburizing	Steel: Low C, Med C, C-Mn Cr-Mo, Ni-Mo, Ni-Cr-Mo	650–950	50–3000
Nitriding (ion)	Steel: Al, Cr, Mo, V or W austinic stainless	900–1300	25–750
Carbonitriding	Steel: Low C, Med C, Cr Cr-Mo, Ni-Cr-Mo	550–950	25–750
Boriding	Steel: Mo, Cr, Ti, Cast Fe, Cobalt-based alloys, Nickel-based alloys	1600–2000	25–500

Testing for Hardness

Hardness measurements generally do not give much of an indication of the fracture toughness of the surface. Scratch tests and stud-pull tests will give a better indication. Scratching is typically performed by drawing a hard stylus over the surface with an increasing load. The surface is then observed microscopically for deformation and fracture along the scratch path. The acoustic emission from the surface during scratching can also give an indication of the amount of brittle fracturing that is taking place during scratching. The stud-pull test is performed by bonding a stud to the surface with a thermosetting epoxy, then pulling the stud to failure. If the failure is in the surface material, the failed-surfaces are observed for fracture and "pull-outs."

Hardening Substrate Surfaces

Substrate surfaces can be hardened, and dispersion strengthened, by forming nitride-, carbide- or boride-dispersed phases in the near-surface region by thermal diffusion of a reactive species into the surface. Steels that contain aluminum, chromium, molybdenum, vanadium or tungsten can be hardened by thermal diffusion of nitrogen into the surface. Typically, nitriding is carried out at 500–550 °C for 48 hr in a gaseous atmosphere, giving a "case" depth of several hundred microns. In carburizing, the carbon content of a low-carbon steel (0.1–0.2 percent) is increased to 0.65–0.8 percent by diffusion from a carbon-containing vapor at 900 °C. Carbonitriding can be performed on ferrous materials by diffusing both carbon and nitrogen into the surface. Nitrogen diffuses faster than the carbon, so a nitrogen-rich layer is formed below the carbonitrided layer and, if quenched, increases the fatigue strength of the carbonitrided layer. Hardening by boronizing can be done on any material having a constituent that forms a stable boride, such as Fe_2B, CrB_2, MoB or NiB_2.

Diffusion coatings can also be formed by pack cementation. In this technique, the diffusion coatings are formed by heating the surface in contact with the material to be diffused (solid-state diffusion) or by heating in a reactive atmosphere that will react with the solid material to be diffused, to form a volatile species, which is then decomposed on the substrate surface, and diffuses into the surface [*e.g.*, similar to chemical vapor deposition (CVD)]. Aluminum (aluminizing), silicon (siliconizing), and chromium (chromizing) are the most common materials used for pack cementation.

Ion Bombardment

The use of a plasma for ion bombardment enhances the chemical reactions and diffusion rates, and also allows heating of the substrate, and *in-situ* cleaning by sputtering. Typically, a plasma containing NH_3, N_2 or N_2-H_2 (9:1, *i.e.*, forming gas) is used along with substrate heating to 500–600 °C to nitride steel. The term "ionitriding" has been given to the plasma nitriding process. Bombardment from a nitrogen plasma can be used to plasma-nitride a steel surface prior to the deposition of a PVD-TiN coating. Plasma carburizing is done in a carbon environment. The table shows some surface hardnesses that can be obtained by diffusion processes.

Mechanical working of a ductile surface by shot-peening, or cold-working introduces work hardening and compressive stress, which makes the surface hard and less prone to microcracking. Shot peening is used on highly stressed, high-strength materials (*e.g.*, auto crankshafts) to increase the fatigue strength. Cold rolling may be used to increase fatigue strength of bolts and fasteners.

Thermal Stressing

Materials having a high-modulus, low-thermal conductivity, and a non-zero coefficient of thermal expansion, can be strengthened by heating the part, then rapidly cooling the surface while the interior cools slowly (*e.g.*, tempered glass). This places the surface region in a compressive stress and the interior in a state of tensile stress. The material then resists fracture, but, if the compressive surface layer is fractured, the energy released causes the material to fracture rapidly. If the compressive stress in the surface region is too high, the internal tensile stress can cause internal fracturing or void formation.

Thermal stressing of the substrate surface also occurs when depositing a hard coating that has a different coefficient of the thermal expansion (CTE) than the substrate. If the coating has a higher CTE than the substrate, it shrinks more on cooling than the substrate, putting the coating in tensile stress, and the substrate surface in compressive stress. This can result in microcraking of the coating. If the coating has a lower CTE than the substrate, the coating is put into compressive stress, and the substrate into tensile stress, which can produce cracking or void formation at the interface.

Ion Implantation

Ion implantation refers to the bombardment of a surface with high-energy ions (sometimes mass and energy analyzed) with sufficient force to allow significant penetration into the surface region. Typically, ion implantation uses ions having energies of 100 keV–2 meV, which gives penetration of several thousand Å, depending on the relative masses of the bombarding and target atoms. The most commonly used ion species, outside the semiconductor industry, are those of nitrogen (N^+). Bombardment is typically done at an elevated temperature (*e.g.,* 300 °C) with a bombarding dose on the order of $10^{17}/cm^2$. Other bombarding species can be used, including a combination of titanium and carbon implantation, which gives an amorphous surface layer at low temperatures, and carbide precipitation at high temperatures. Ion implantation of ceramic surfaces can reduce the fracturing of the brittle surfaces under load by the introduction of a compressive stress in the surface region, both by atomic peening and by surface-region amorphization, which is accompanied by a volume expansion. Amorphitizing the surface of ceramics improves fracture resistance, and provides better wear resistance, even though the surface hardness is decreased.

In some cases, it may be desirable to have a tough interlayer deposited on the substrate to aid in supporting the hard coating and provide corrosion resistance. Such materials might be nickel or tantalum, which are typically good adhesion interlayers for metallic systems. This layer may be diffused and reacted with the substrate prior to deposition of the hardcoat. o

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