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CHAPTER

1

Introduction to Surface Engineering for Corrosion and Wear Resistance

SURFACE ENGINEERING is a multidisciplinary activity intended to tailor the properties of the surfaces of engineering components so that their function and serviceability can be improved. The *ASM Handbook* defines surface engineering as “treatment of the surface and near-surface regions of a material to allow the surface to perform functions that are distinct from those functions demanded from the bulk of the material” (Ref 1). The desired properties or characteristics of surface-engineered components include:

- Improved corrosion resistance through barrier or sacrificial protection
- Improved oxidation and/or sulfidation resistance
- Improved wear resistance
- Reduced frictional energy losses
- Improved mechanical properties, for example, enhanced fatigue or toughness
- Improved electronic or electrical properties
- Improved thermal insulation
- Improved aesthetic appearance

As indicated in Table 1, these properties can be enhanced metallurgically, mechanically, chemically, or by adding a coating.

The bulk of the material or substrate cannot be considered totally independent of the surface treatment. Most surface processes are not limited to the immediate region of the surface, but can involve the substrate by

Table 1 Surface engineering options and property benefits

Surface treatment/coating type	Primary property benefits
Changing the surface metallurgy	
Localized surface hardening (flame, induction, laser, and electron-beam hardening)	Improved wear resistance through the development of a hard martensitic surface
Laser melting	Improved wear resistance through grain refinement and the formation of fine dispersions of precipitates
Shot peening	Improved fatigue strength due to compressive stresses induced on the exposed surface, also relieves tensile stresses that contribute to stress-corrosion cracking
Changing the surface chemistry	
Phosphate chemical conversion coatings	Used primarily on steels for enhanced corrosion resistance, increased plating or paint adhesion, and for lubricity (e.g., to increase the formability of sheet metals)
Chromate chemical conversion coatings	Enhanced bare or painted corrosion resistance, improved adhesion of paint or other organic finishes, and provides the metallic surface with a decorative finish
Black oxide chemical conversion coatings	Used for decorative applications, e.g., the “bluing” on steel gun barrels
Anodizing (electrochemical conversion coating)	Used primarily for aluminum for increased corrosion resistance, improved decorative appearance, increased abrasion resistance (hard anodizing), improved paint adhesion, and improved adhesive bonding (higher bond strength and durability)
Steam treating	Used on ferrous powder metallurgy parts to increase wear resistance and transverse rupture strength
Carburizing	Used primarily for steels for increased resistance to wear, bending fatigue, and rolling-contact fatigue
Nitriding	Used primarily for steels for improved wear resistance, increased fatigue resistance, and improved corrosion resistance (except stainless steels)
Carbonitriding	Used primarily for steels for improved wear resistance
Ferritic nitrocarburizing	Improved antiscaffing characteristics of ferrous alloys
Diffusion (pack cementation) chromizing	Improved molten-salt hot corrosion
Diffusion (pack cementation) aluminizing	Improved oxidation resistance, sulfidation resistance, and carburization resistance
Diffusion (pack cementation) siliconizing	Improved oxidation resistance
Boronizing (boriding)	Improved wear resistance, oxidative wear, and surface fatigue
Ion implantation	Improved friction and wear resistance for a variety of substrates
Laser alloying	Improved wear resistance
Adding a surface layer or coating	
Organic coatings (paints and polymeric or elastomeric coatings and linings)	Improved corrosion resistance, wear resistance, and aesthetic appearance
Ceramic coatings (glass linings, cement linings, and porcelain enamels)	Improved corrosion resistance
Slip/sinter ceramic coatings	Improved wear resistance and heat resistance
Hot-dip galvanizing (zinc coatings)	Improved corrosion resistance via sacrificial protection of steel substrate
Hot-dip aluminizing	Improved corrosion and oxidation resistance of steel substrate
Hot-dip lead-tin alloy-coatings (terne coatings)	Improved corrosion resistance of steel substrate
Tin plate (continuous electrodeposition)	Improved corrosion resistance of steel substrate
Zinc-nickel alloy plate (continuous electrodeposition)	Improved corrosion resistance of steel substrate
Electroplating	Depending on the metal or metals being electrodeposited, improved corrosion resistance (e.g., nickel-chromium multilayer coatings, and cadmium and zinc sacrificial coatings), wear resistance (e.g., hard chromium coatings), electrical properties (e.g., copper and silver), and aesthetic appearance (e.g., bright nickel or decorative chromium plating)
Electroless plating	Improved corrosion resistance (nickel-phosphorus) and wear resistance (nickel-phosphorus and nickel-boron)
Mechanical plating	Improved corrosion resistance
Weld overlays	Improved wear resistance (hardfacing alloys) and corrosion resistance (stainless steel or nickel-base overlays) and dimensional restoration (buildup alloys)
Thermal spraying	Primarily used for improved wear resistance (many coating systems including ceramics and cermets), but also used for improved corrosion resistance (aluminum, zinc, and their alloys) and oxidation resistance (e.g., MCrAlY), thermal barrier protection (partially stabilized zirconia), electrically conductive coatings (e.g., copper and silver), and dimensional restoration
Cladding (roll bonding, explosive bonding, hot isostatic pressing, etc.)	Improved corrosion resistance
Laser cladding	Improved wear resistance
Carbide (salt bath) diffusion	Used primarily for steels for improved wear resistance in tooling applications
Chemical vapor deposition (CVD)	Improved wear (e.g., tools and dies), erosion, and corrosion resistance; also used for epitaxial growth of semiconductors
Physical vapor deposition (PVD)	Improved wear (e.g., tools and dies) and corrosion resistance, improved optical and electronic properties, and decorative applications

exposure to either a thermal cycle or a mechanical stress. For example, diffusion heat treatment coatings (e.g., carburizing/nitriding) often have high-temperature thermal cycles that may subject the substrate to temperatures that cause phase transformations and thus property changes, or shot-peening treatments that deliberately strain the substrate surface to induce improved fatigue properties. It is the purpose of this book, and in particular Chapters 4 to 6, to review information on surface treatments that improve service performance so that metallurgists, chemists, mechanical engineers, and design engineers may consider surface-engineered components as an alternative to more costly materials.

Surface Engineering to Combat Corrosion and Wear

The Economic Effects of Corrosion and Wear. The progressive deterioration, due to corrosion and wear, of metallic surfaces in use in major industrial plants ultimately leads to loss of plant efficiency and at worst a shut-down. Corrosion and wear damage to materials, both directly and indirectly, costs the United States hundreds of billions of dollars annually. For example, corrosion of metals costs the U.S. economy almost \$300 billion per year at current prices. This amounts to about 4.2% of the gross national product.

However, about 40% of the total cost could be avoided by proper corrosion prevention methods. Table 2 provides a breakdown of the cost of metallic corrosion in the United States. Similar studies on wear failures have shown that the wear of materials costs the U.S. economy about \$20 billion per year (in 1978 dollars) compared to about \$80 billion annually (see Table 2) for corrosion during the same period. Table 3 illustrates the extent of wear failures by various operations within specific industrial segments. Highway vehicles alone use annually $14,600 \times 10^{12}$ Btu/ton of energy represented in lost weight of steel and 18.6% of this energy could be saved through effective wear-control measures.

Table 2 Cost of metallic corrosion in the United States

Industry	Billions of U.S. dollars	
	1975	1995
All industries		
Total	82.0	296.0
Avoidable	33.0	104.0
Motor vehicles		
Total	31.4	94.0
Avoidable	23.1	65.0
Aircraft		
Total	3.0	13.0
Avoidable	0.6	3.0
Other industries		
Total	47.6	189.0
Avoidable	9.3	36.0

Source: Ref 2

Table 3 Industrial operations with significant annual wear economic consequences

Industry	Operation	Loss mass(a), 10 ¹² Btu
Utilities (28% total U.S. consumption)	Seals	185
	Accessories	120
	Bearings	55
	Reliability	145
	Total	505
Transportation (26% total U.S. consumption)	Brakes	(b)
	Valve trains	(b)
	Piston ring assemblies	(b)
	Transmission	(b)
	Bearings	(b)
	Gears	(b)
	Total	(b)
Mining	Ore processing	22.80
	Surface mining	13.26
	Shaft mining	10.70
	Drilling	5.58
	Total	52.34
Agriculture	Tillage	16.85
	Planting	2.47
	Total	19.32
Primary metals	Hot rolling	14.30
	Cold rolling	0.14
	Total	14.44

(a) Assumes 19.2×10^6 Btu per ton of energy represented in lost weight of steel.
 (b) Lost mass not estimated. Source: Ref 3

Corrosive Wear. Complicating matters is the fact that the combined effects of wear and corrosion can result in total material losses that are much greater than the additive effects of each process taken alone, which indicates a synergism between the two processes. Although corrosion can often occur in the absence of mechanical wear, the opposite is rarely true. Corrosion accompanies the wear process to some extent in all environments, except in vacuum and inert atmospheres. Corrosion and wear often combine to cause aggressive damage in a number of industries, such as mining, mineral processing, chemical processing, pulp and paper production, and energy production. Corrosion and wear processes involve many mechanisms, the combined actions of which lead to the mutual reinforcement of their effectiveness. As listed in Table 4, 17 synergistic relationships among abrasion, impact, and corrosion that could significantly increase material degradation in wet and aqueous environments have been identified.

The combined effects of corrosion and wear can also lead to galvanic corrosion in some applications, such as crushing and grinding (comminution) of mineral ores. Wear debris and corrosion products that are formed during comminution affect product quality and can adversely affect subsequent beneficiation by altering the chemical and electrochemical properties of the mineral system (Ref 5–8). Electrochemical interactions between minerals and grinding media can occur, causing galvanic coupling that leads to increased corrosion wear. More detailed information on galvanic corrosion can be found in Chapter 2.

Methods to Control Corrosion. Owing to its many favorable characteristics, steel is well suited and widely used for a broad range of engineering applications and is referenced here to demonstrate the various corrosion-control steps that can be considered. Steel has a variety of excellent mechanical properties, such as strength, toughness, ductility, and dent resistance. Steel also offers good manufacturability, including formability, weldability, and paintability. Other positive factors include its availability, ferromagnetic properties, recyclability, and cost. Because steel is susceptible to corrosion in the presence of moisture, and to oxidation at elevated temperatures, successful use of these favorable characteristics generally requires some form of protection.

Methods of corrosion protection employed to protect steel include:

- Altering the metal by alloying, that is, using a more highly alloyed and expensive stainless steel rather than a plain carbon or low-alloy steel
- Changing the environment by desiccation or the use of inhibitors
- Controlling the electrochemical potential by the application of cathodic or anodic currents, that is, cathodic and anodic protection
- Applying organic, metallic, or inorganic (glasses and ceramics) coatings

Application of corrosion-resistant coatings is one of the most widely used means of protecting steel. As shown in Table 1, there are a wide variety of coatings to choose from, and proper selection is based on the component size and accessibility, the corrosive environment, the anticipated

Table 4 Synergistic relationships between wear and corrosion mechanisms

Abrasion

Removes protective oxidized metal and polarized coatings to expose unoxidized metal, in addition to removing metal particles.
Forms microscopic grooves and dents for concentration cell corrosion.
Increases microscopic surface area exposed to corrosion.
Removes strain-hardened surface layers.
Cracks brittle metal constituents forming sites for impact hydraulic splitting.
Plastic deformation by high-stress metal-mineral contact causes strain hardening and susceptibility to chemical attack.

Corrosion

Produces pits that induce microcracking.
Microcracks at pits invite hydraulic splitting during impact.
Roughens surface, reducing energy needed to abrade away metal.
May produce hydrogen with subsequent absorption and cracking in steel.
Selectively attacks grain boundaries and less noble phases of multiphase microstructures, weakening adjacent metal.

Impact

Plastic deformation makes some constituents more susceptible to corrosion.
Cracks brittle constituents, tears apart ductile constituents to form sites for crevice corrosion, hydraulic splitting.
Supplies kinetic energy to drive abrasion mechanism.
Pressurizes mill water to cause splitting, cavitation, and jet erosion of metal and protective oxidized material.
Pressurizes mill water and gases to produce unknown temperatures, phase changes, and decomposition or reaction products from ore and water constituents.
Heats ball metal, ore, fluids to increase corrosive effects.

Source: Ref 4

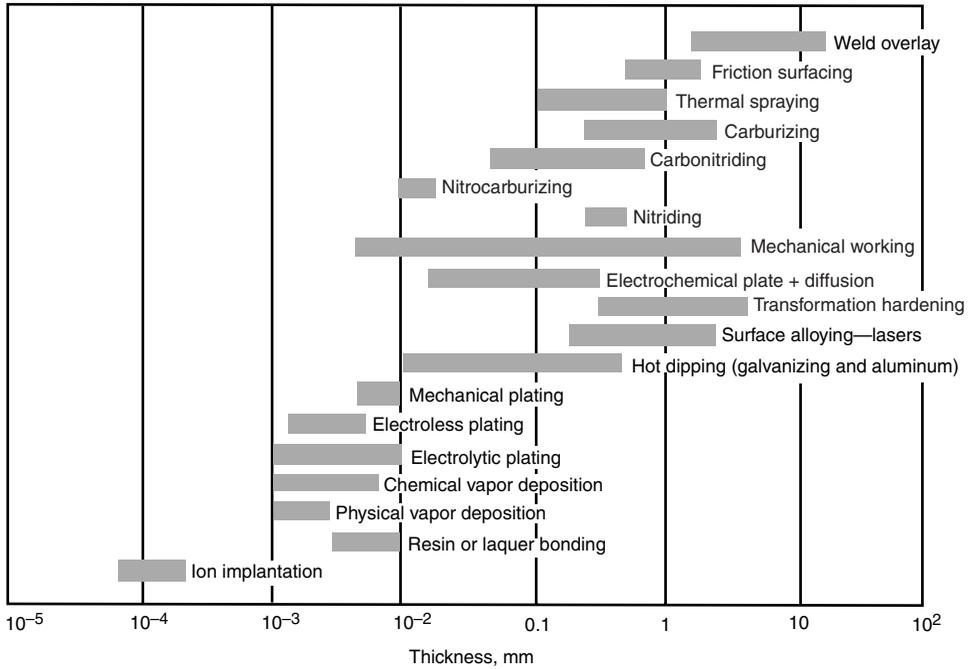


Fig. 1 Approximate thickness of various surface engineering treatments

temperatures, component distortion, the coating thickness attainable (Fig. 1), and costs. Many of these selection criteria are addressed in Chapters 6 to 8 in this book.

Painting is probably the most widely used engineering coating used to protect steel from corrosion. There are a wide variety of coating formulations that have been developed for outdoor exposure, marine atmospheres, water immersion, chemical fumes, extreme sunlight, high humidity, and moderately high temperatures (less than about 200 °C, or 400 °F).

The most widely used corrosion-resistant metallic coatings are hot-dipped zinc, zinc-aluminum, and aluminum coatings. These coatings exhibit excellent resistance to atmospheric corrosion and are widely used in the construction, automobile, utility, and appliance industries.

Other important coating processes for steels include electroplating, electroless plating, thermal spraying, pack cementation aluminizing (for high-temperature oxidation resistance), and cladding (including weld cladding and roll-bonded claddings). Applications and corrosion performance of these coatings are described in Chapter 6 in this book.

Methods to Control Wear. As is described in Chapter 3 in this book, there are many types of wear, but there are only four main types of wear systems (*tribosystems*) that produce wear and six basic wear control steps (Ref 9). The four basic tribosystems are:

- Relatively smooth solids sliding on other smooth solids
- Hard, sharp substances sliding on softer surfaces
- Fatigue of surfaces by repeated stressing (usually compressive)
- Fluids with or without suspended solids in motion with respect to a solid surface

As shown in Fig. 2, the wear that occurs in these tribosystems can be addressed by coatings or by modifications to the substrate metallurgy or chemistry.

The six traditional techniques applied to materials to deal with wear produced in the preceding tribosystems include:

- Separate conforming surfaces with a lubricating film (see Chapter 3 in this book).
- Make the wearing surface hard through the use of hardfacing, diffusion heat treatments, hard chromium plating, or more recently developed vapor deposition techniques or high-energy processes (e.g., ion implantation).
- Make the wearing surface resistant to fracture. Many wear processes involve fracture of material from a surface; thus toughness and fracture resistance play a significant role in wear-resistant surfaces. The use of very hard materials such as ceramics, cemented carbides, and hard chromium can lead to fracture problems that nullify the benefits of the hard surface.
- Make the eroding surface resistant to corrosion. Examples include the use of cobalt-base hardfacing alloys to resist liquid erosion, cavitation, and slurry erosion; aluminum bronze hardfacing alloys to prevent cavitation damage on marine propellers or to repair props that have

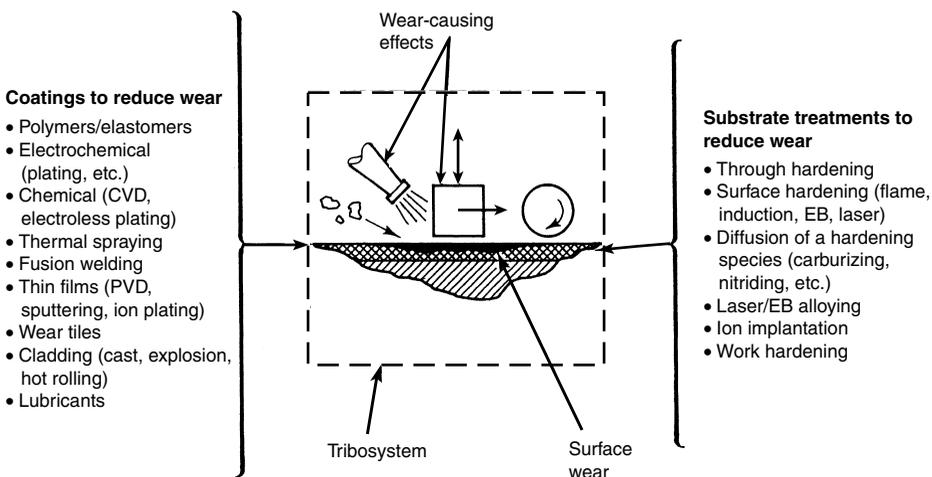


Fig. 2 Surface engineering processes used to prevent wear. CVD, chemical vapor deposition; PVD, physical vapor deposition; EB, electron beam

suffered cavitation damage; nickel-base hardfacing alloys to resist chemical attack; and epoxy-filled rebuilding cements used to resist slurry erosion in pumps.

- Choose material couples that are resistant to interaction in sliding (metal-to-metal wear resistance). Hardfacing alloys such as cobalt-base and nickel-chromium-boron alloys have been used for many years for applications involving metal-to-metal wear. Other surface-engineering options include through-hardened tool steels, diffusion (case)-hardened surfaces, selective surface-hardened alloy steels, and some platings.
- Make the wearing surface fatigue resistant. Rolling-element bearings, gears, cams, and similar power-transmission devices often wear by a mechanism of surface fatigue. Repeated point or line contact stresses can lead to subsurface cracks that eventually grow to produce surface pits and eventual failure of the device. Prevention is possible through the use of through-hardened steels, heavy case-hardened steels, and flame-, induction-, electron beam-, or laser-hardened steels.

More details on these surface-engineering techniques can be found in Chapters 5 through 8 in this book.

Material/Process Selection (Ref 10). Faced with the wide range of possibilities indicated in Table 1 and the discussions on “Methods to Control Corrosion” and “Methods to Control Wear,” selection of surface engi-

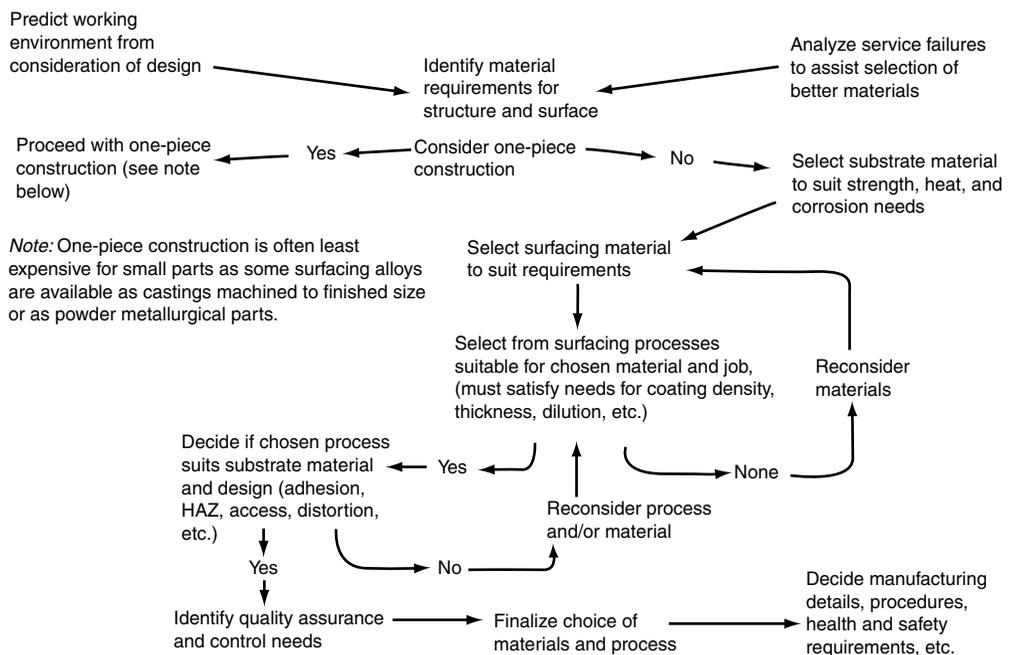


Fig. 3 Checklist for surface engineering material/process selection. HAZ, heat-affected zone

neering material and process may seem difficult, but it is normally straightforward. Often there are constraints placed on the choice because of availability (e.g., laser melting and/or alloying are not widely used, and these processes can only be obtained by a special arrangement with laser job shops). In many cases there is a precedent, but when considering a new problem it helps to follow a checklist of the type shown in Fig. 3.

The sequence of decisions to be made covers several fundamental points. The first is the need to be clear about service conditions, based on experience or plant data. This is the key to material selection. The second decision is the choice of application process for the material. This involves the question of compatibility with the coating material; that is, not all materials can be applied by all processes. A further question of compatibility arises between both material and process with the substrate, for example, whether distortion from high-temperature processes be tolerated. All these issues are covered in subsequent chapters in this book (see, in particular, Chapters 7 and 8).

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