Enhancing Operations:
Heat Treatment &
Surface Treatments & Processing

1. Cleaning
   - Chemical Cleaning
   - Mechanical Cleaning and Surface Preparation
2. Surface Treatments & Processing
   - Diffusion and Ion Implementation
   - Plating and Related Processes
   - Conversion Coatings
   - Physical Vapor Deposition
   - Chemical Vapor Deposition
   - Organic Coatings
   - Porcelain Enameling & Other Ceramic Coatings
   - Thermal and Mechanical Coating Processes

Introduction

- Cleaning:
  - Parts must be cleaned chemically/mechanically many times to remove films, oil, dirt and contaminants during production
  - Reasons for cleaning.
    - Prepare the surface for subsequent processing (coating or adhesive bonding)
    - Improve hygiene conditions for workers and customers
    - Remove contaminants that may react with the surface
    - Enhance appearance and performance of a product
- Surface Treatment:
  - Diffusion and Ion implantation - impregnate the surface with atoms of a foreign material.
- Surface processing:
  - Plating, Conversion Coatings, PVD, CVD, Organic Coatings, Porcelain Enameling & Other Ceramic Coatings and Thermal & Mechanical Coating
  - enhances the life and appearance without affecting the geometry and bulk properties.

Factors in Selecting a Method

- Contaminant (due to previous processing or factory environment) to be removed
  - Oil & grease, Solid particles (metal chips, abrasive grits, shop dirt, dust), Buffing & polishing compounds, Oxide films, Rust, and Scale
- The required Degree of cleanliness - the amount of contaminant remaining after a cleaning operation
  - A *wiping method* - wiped with a clean white cloth to observe an amount of soil on the cloth (non-quantitative but easy to use)
- Substrate material - to prevent any damaging reactions
  - *Aluminum is dissolved by most acids and alkalis*
  - *Steels are resistant to alkalis but react with virtually all acids*
- Purpose of the cleaning
- Environmental and safety factors
- Size and geometry of the part
- Production and cost requirements

Chemical Cleaning Processes I

Alkaline Cleaning (most widely used) - Uses an alkali to remove oils, grease, wax, and various types of particles (metal chips, silica, light scale) from a metallic surface
- Alkaline solutions include sodium and potassium hydroxide (NaOH, KOH), sodium carbonate (Na_2CO_3), borax ($Na_2B_4O_7$)
- Cleaning methods: immersion or spraying, usually at temperatures of 50-95°C (120-200°F), followed by water rinse

Emulsion Cleaning - Uses organic solvents (oils) dispersed in an aqueous solution
- The use of suitable emulsifiers (soaps) results in a two-phase cleaning fluid (oil-in-water), which functions by dissolving or emulsifying the soils on the part surface
- Can be used on either metal or nonmetallic parts
- Must be followed by alkaline cleaning to eliminate all residues of the organic solvent prior to plating

Chemical Cleaning Processes II

Acid Cleaning - Removes oils and light oxides from metal surfaces using acid solutions combined with water-miscible solvents, wetting and emulsifying agents
- Common application techniques: soaking, spraying, or manual brushing or wiping at ambient or elevated temperatures
- Cleaning acids include hydrochloric (HCl), nitric (HNO_3), phosphoric (H_3PO_4), and sulfuric (H_2SO_4)

Acid Pickling - A more severe acid treatment to remove thicker oxides, rusts, and scales
- The distinction between cleaning and pickling is a matter of degree
- Generally results in some etching of the metallic surface which serves to improve organic paint adhesion

Chemical Cleaning Processes III

Solvent Cleaning - removes Organic soils (oil and grease) from a metallic surface by dissolving them with chemicals
- Common application techniques: hand-wiping, immersion, spraying, and vapor degreasing
- *Vapor degreasing* (a solvent cleaning method) uses hot vapors of chlorinated or fluorinated solvents largely discontinued in the U.S. due to the chemicals hazard.

Ultrasonic Cleaning - Mechanical agitation of cleaning fluid by high-frequency vibrations (between 20 and 45 kHz) to cause cavitation - formation of low pressure vapor bubbles that scrub the surface
- Combines chemical cleaning and mechanical agitation of the cleaning fluid.
- Cleaning fluid is generally an aqueous solution containing alkaline detergents.
- Highly effective for removing surface contaminants.

Mechanical Cleaning and Surface Preparation

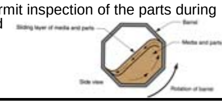
Physical removal of soils, scales, or films from the work surface by means of abrasives or similar mechanical action

- It serves other functions such as deburring, improving surface finish, and surface hardening
- Processes:
  - Blast finishing- High velocity impact of particulate media (Hard: Al_2O_3 and SiC and Soft: nylon beads) propelled by pressurized air or centrifugal force to clean and finish a surface
    - Most well-known method, *sand blasting,* uses grits of sand as the blasting media
  - Shot peening -High velocity stream of small cast steel pellets (called *shot*) is directed at a metallic surface to cold work and induce compressive stresses into surface layers
    - Used primarily to improve fatigue strength of metal parts
  - Mass finishing processes

Mass Finishing

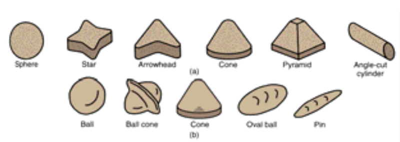
Finishing parts in bulk by a mixing action in a container with an abrasive media for the desired finishing action

- Usually for small parts & not economical for individual parts
- Processes include:
  - Tumbling - Use of a horizontally oriented barrel of hexagonal or octagonal cross-section in which parts are mixed by rotating the barrel at speeds = 10 to 50 rev/min
    - Finishing by "landslide" action - media and parts rise in the barrel as it rotates, then top layer tumbles down due to gravity
    - Drawbacks: slow, high noise levels, and large floor-space required
  - Vibratory finishing - Vibrating vessel subjects all parts to agitation with the abrasive media, as opposed to only the top layer as in barrel finishing
    - Processing times for vibratory finishing are significantly reduced
    - The open tubs in this method permit inspection of the parts during processing, and noise is reduced



Media for Mass Finishing

- Mostly are abrasive and some finishing operations such as burnishing and surface hardening
  - Natural media (corundum, granite, limestone) - generally softer and nonuniform in size
  - Synthetic media (Al_2O_3 and SiC) - greater consistency in size, shape, and and hardness
  - Steel - used for burnishing, surface-hardening, and light deburring operations



2. Surface Treatment and Processes

- Metal products except stainless steel and brass are usually coated by painting, plating, or other processes
  - Reasons
    - Provide corrosion protection of the substrate
    - Enhance product appearance, e.g., color or texture
    - Increase wear resistance and/or reduce friction
    - Increase electrical conductivity or resistance
    - Prepare a metallic surface for subsequent processing
    - Rebuild surfaces worn or eroded during service
- Nonmetallic materials are also coated
  - For a metallic appearance
  - For antireflection coatings on glass lenses
  - In the fabrication of semiconductor chips and printed circuit boards

Surface Treatment

- Impregnate the surface with foreign atoms:
  - **Diffusion** - Alteration of surface layers of a material by diffusing atoms of a different element into the surface, usually at high temperatures
    - The surface contains a high proportion of substrate material.
    - The diffused element has maximum percentage at the surface and rapidly declines with distance below surface.
    - Applications in metallurgy and semiconductor manufacture
  - **Ion implantation** - Embedding ionized particles into a substrate surface using a high-energy beam.
    - Alters the chemistry and physical properties of the layers near the substrate surface
    - Produces a much *thinner* altered layer and *different concentration profile* than diffusion
    - Alternative to diffusion which requires high temperatures.

Diffusion: Introduction

- Two main mechanisms
  - Vacancy (equilibrium defects) or substitutional
  - Interstitial
- Self-diffusion (vacancy diffusion)

  Arrhenius Eq. $\text{Rate of reaction} = Ce^{-Q/RT}$

  $R = \text{molar gas constant (8.314J/molK)}$

  $C = \text{rate constant, independent of temperature}$
- Activation energy to form and move vacancy

Metal	Melting	Range	Activation energy	
Zn (HCP)	419°C	240-418°C	91.6KJ/mol	21.9
Al (FCC)	660°C	400-610°C	165	39.5
Cu (FCC)	1083°C	700-990°C	196	46.5
α-Fe (BCC)	1530°C	808-884°C	240	57.7
Mo(BCC)	2600°C	2155-2540°C	460	110

- Interstitial – Diffusion of foreign atoms without changing the matrix crystal lattice(depending on the size of the atoms)

Steady-state Diffusion

- Fick's first law - Flux (the flow of atoms)

$$J = -D\frac{\partial C}{\partial x}$$

  – The diffusivity depends on the type of diffusion mechanism, the temperature, crystal structure, type of crystal imperfection present, the concentration of the diffusing species.
- Fick's second law $\frac{dC_x}{dt} = \frac{d}{dx}\left(D\frac{dC_x}{dx}\right)$

$$\frac{C_s - C_x}{C_s - C_o} = \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Diffusivity Data

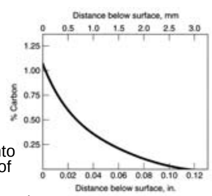
Diffusivities at 500°C and 1000°C for Selected Solute-Solvent Diffusion Systems

Solute	Solvent (host structure)	Diffusivity, m²/s 500°C (930°F)	1000°C (1830°F)
1. Carbon	FCC iron	(5×10^{-15})*	3×10^{-11}
2. Carbon	BCC iron	10^{-12}	(2×10^{-9})
3. Iron	FCC iron	(2×10^{-23})	2×10^{-16}
4. Iron	BCC iron	10^{-20}	(3×10^{-14})
5. Nickel	FCC iron	10^{-23}	2×10^{-16}
6. Manganese	FCC iron	(3×10^{-24})	10^{-16}
7. Zinc	Copper	4×10^{-18}	5×10^{-13}
8. Copper	Aluminum	4×10^{-14}	10^{-10} M†
9. Copper	Copper	10^{-18}	2×10^{-13}
10. Silver	Silver (crystal)	10^{-17}	10^{-12} M
11. Silver	Silver (grain boundary)	10^{-11}	
12. Carbon	HCP titanium	3×10^{-16}	(2×10^{-11})

*Parentheses indicate that the phase is metastable.
†M—Calculated, although temperature is above melting point.
Source: L. H. Van Vlack, "Elements of Materials Science and Engineering," 5th ed., Addision-Wesley, 1985.

Diffusion

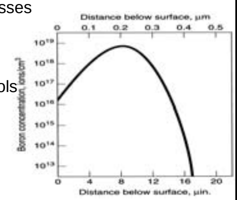
- To increase hardness and wear resistance
  – Carburizing, nitriding, carbonitriding, chromizing, and boronizing
- To increase corrosion resistance and/or high-temperature oxidation resistance
  – Aluminizing - diffusion of aluminum into carbon steel, alloy steels, and alloys of nickel and cobalt
  – Siliconizing – diffusion of silicon into steel part surface
- In semiconductor processing, *doping* (diffusion of an impurity element into the surface of a silicon chip) is used to change the electrical properties to make devices such as transistors and diodes.



in Iron

Ion Implantation

- Advantages
  – Low temperature processing
  – Good control and reproducibility of impurity penetration depth
  – Solubility limits can be exceeded without precipitation of excess atoms
  – No problems with waste disposal as in electroplating and many coating processes
  – No discontinuity between coating and substrate as in coating processes
- Applications
  – Nitrogen and Xenon Ions on cutting tools
  – Modifying metal surfaces to improve properties
  – Fabrication of semiconductor devices



in Silicon

Plating Processes

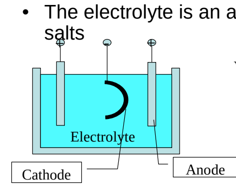
Coating of a thin metallic layer onto the surface of a substrate material by an electrolytic process in which metal ions deposited onto a cathode work material .

- Usually metallic & sometime plastic & ceramic parts
- Processes:
  – Electroplating (the most common plating process)
  – Electroforming - deposition of metal onto a pattern
  – Electroless plating - chemical reaction
  – Hot dipping - a molten bath instead of electrolyte
- Reasons for Plating
  – Corrosion, appearance, wear resistance, electrical conductivity, solderability & lubricity

Electroplating (*electrochemical plating)*

Electrolytic process in which metal ions in an electrolyte solution are deposited onto a cathode part

- The anode is generally made of the plating metal and thus serves as the source of the plate metal
- Direct current from an external power supply is passed between anode and cathode
- The electrolyte is an aqueous solution of acids, bases, or salts



Volume of metal plated: $V = CIt$

where C= plating constant

With the cathode efficiency: $V = ECIt$

The average plating thickness: $d = \frac{V}{A}$

Principal Electroplating Methods

- *Barrel plating* - performed in rotating barrels oriented either horizontally or at an oblique angle (35°) - suited to plating many small parts in a batch
- *Rack plating* –racks made of heavy-gauge copper wire and formed into suitable shapes for holding the parts and conducting current to them - used for parts that are too large, heavy, or complex for barrel plating
- *Strip plating* – a continuous strip is pulled through the plating solution by means of a take-up reel – suited to high production

19

Common Coating Metals

- *Zinc* - plated on steel products such as fasteners, wire goods, electric switch boxes, and sheetmetal parts as a sacrificial barrier to corrosion
- *Nickel* - for corrosion resistance and decorative purposes on steel, brass, zinc die castings, and other metals; also used as a base coat for chrome plate
- *Tin* - widely used for corrosion protection in "tin cans" and other food containers
- *Copper* - decorative coating on steel and zinc, either alone or alloyed as brass; also, applications in printed circuit boards
- *Chromium* - decorative coating widely used in automotive, office furniture, and kitchen appliance and one of the hardest electroplated coatings for wear resistance applications
- Precious metals (*gold*, *silver*, *platinum*) - plated on jewelry; gold is also used for electrical contacts

20

Electroforming

Electrolytic deposition of metal **onto a pattern** until the required thickness is achieved, after which the pattern is removed to leave the formed part

- The same process as electroplating with different purpose.
  - typical plating thickness is only about 0.05 mm or less, electroformed parts are often substantially thicker, so the production cycle is proportionally longer
- Metals: copper, nickel, and nickel cobalt alloys
- Typical applications: fine molds and dies (e.g., for lenses) and plates for embossing and printing
- Notable application: molds for CDs and DVDs.
  - Surface details imprinted onto a CD are measured in μm or μ-in (1 μm = 39.4 μ-in).
  - These details are readily obtained in the mold by electroforming

21

Electroless Plating

Plating driven entirely by chemical reactions - no external source of electric current is required

- Deposition of metal onto a part surface occurs in an aqueous solution containing ions of the desired plating metal - the workpart surface acts as a catalyst for the reaction in the presence of a reducing agent
- Electroless platable metals are limited: nickel and certain of its alloys, copper, and gold
- Notable application: copper for plating through-holes of printed circuit boards

22

Hot Dipping

Metal substrate (part) is immersed in a molten bath of a second metal to coated the part.

- Common substrate metals: steel and iron
- Coating metals: zinc, aluminum, tin, and lead
- Primary purpose is corrosion protection
- Processes
  - *Galvanizing* - zinc (Zn) coated onto steel or iron
    - By far the most important hot dipping process
  - *Aluminizing* - coating of aluminum (Al) onto a substrate
    - Excellent corrosion protection, in some cases five times more effective than galvanizing
  - *Tinning* - coating of tin (Sn) onto steel for food containers, dairy equipment, and soldering applications
  - *Terneplate* - plating of lead-tin alloy onto steel

23

Conversion Coating

A family of coating processes in which a thin film of oxide, phosphate, or chromate is formed on a metallic surface by electro/chemical reaction

- Immersion and spraying are the two common methods of exposing the metal surface to the reacting chemicals
- Reasons
  - Corrosion, preparation for painting, wear, lubricity, electrical resistance, appearance, and part identification
- Two categories
  - Chemical treatments – phosphate coating (Zn and steels) and chromate coating (Al, Cd, Cu, Mg and Zn)
  - Anodizing – An electrolytic treatment producing a stable oxide layer on Al and Mg.
- Common metals treated: steel (including galvanized steel), zinc, and aluminum

24

Chemical Conversion Coatings

Base metal is exposed to chemicals that form thin nonmetallic surface films

1. *Phosphate coating* - transforms base metal surface (e.g., steel, zinc) into phosphate film by exposure to phosphate salts and dilute phosphoric acid
   - Useful preparation for painting of automobiles
2. *Chromate coating* - transforms base metal (e.g., aluminum, copper, magnesium, zinc) into various forms of chromate films (sometimes colorful) using solutions of chromic acid, chromate salts, etc.

25

Anodizing

Electrolytic treatment that produces a stable oxide layer on a metallic surface

- Applications: aluminum and magnesium most common; also zinc, titanium, and other metals
- Dyes can be incorporated into the anodizing process to create a wide variety of colors
  - Especially common in aluminum anodizing
- Functions: primarily decorative; also corrosion protection

26

Physical Vapor Deposition (PVD)

A family of very versatile coating processes in which a material is converted to its vapor phase in a vacuum chamber and condensed onto a substrate surface as a very thin film

- Varieties of coatings: metals, alloys, ceramics and other inorganic compounds, and even certain polymers
- Varieties of substrates: metals, glass, and plastics
- Applications
  - Decorative coatings on plastic and metal parts such as trophies, toys, pens and pencils, watchcases, and interior trim in automobiles
  - Antireflective coatings of MgF_2 onto optical lenses
  - Depositing metal to form electrical connections in integrated circuits
  - Coating TiN onto cutting tools and plastic injection molds for wear resistance

27

Chemical Vapor Deposition (CVD)

Involves the chemical reaction between a mixture of gases and a **heated** surface substrate to form a solid film on the substrate.

- Reactions take place in enclosed reaction chamber and reaction product (metal or compound) nucleates and grows on surface to form the coating
- Wide range of pressures and temperatures in CVD
- Variety of coating and substrate materials possible

- CVD Variations
  - Atmospheric Pressure CVD
  - Low-pressure CVD
  - Plasma assisted CVD
- Applications
  - Industrial metallurgical processes (Mond process for reducing nickel from its ore)
  - Coated carbide tools, Solar cells, Refractory metals on jet engine turbine blades
  - Integrated circuit fabrication
  - Other applications for resistance to wear, corrosion, erosion, and thermal shock

28

Organic Coatings

Natural or synthetic polymers and resins is applied as liquids, which cures into thin surface films

- Advantages:
  - Wide variety of colors and textures possible
  - Capacity to protect the substrate surface
  - Low cost
  - Ease to apply
- Ingredients:
  1. Binders - give the coating its properties
  2. Colorings (Dyes or pigments) - provide color to the coating
  3. Solvents - dissolve the polymers and resins and add proper fluidity to the liquid
  4. Additives
- Powder coating - Dry, solid powders are melted to form a liquid film, which resolidifies into a dry coating.
  - Applications – spraying and fluidized bed

29

Ingredients

Binder holds the ingredients during and after application

- Common binders in organic coatings:
  - Natural oils (used to produce oil-based paints)
  - Resins of polyesters, polyurethanes, epoxies, acrylics, and cellulosics

Two **Coloring** types

1. *Dyes* - soluble chemicals that color coating liquid but do not conceal the surface beneath when applied
   - Coatings are generally transparent or translucent
2. *Pigments* - solid particles of uniform, microscopic size dispersed in coating liquid but insoluble in it
   - They not only color the coating; they also hide the surface below
   - to strengthen the coating

Solvents: Liquid that dissolve the binder and other ingredients in the liquid coating composition

- Common solvent: Aliphatic and aromatic hydrocarbons, Alcohols, Esters, Ketones, Chlorinated solvents

Additives:

- *Surfactants* to help spreading
- *Biocides* and *fungicides*
- *Thickeners*
- Heat and light *stabilizers*
- *Coalescing agents*
- *Plasticizers*
- *Defoamers*
- *Catalysts* to promote cross-linking

30

Application Methods

- Brushing and rolling
- Spraying
- Dip coating (immersion)
- Flow coating (showering)

Drying - process in which organic coating converts from liquid to solid
  - Many organic coatings dry by evaporation of their solvents

Curing - a conversion to form a durable film on the substrate surface
  - This involves a chemical change in the organic resin in which polymerization or cross-linking occurs to harden the coating

Example: Typical sequence in a mass production automobile:
1. Phosphate coat applied by dipping car body
2. Primer coat applied by dipping car body
3. Color paint coat applied by spray coating
4. Clear coat (for high gloss and added protection) applied by spraying

31

Porcelain Enameling

- Porcelain - A ceramic made from kaolin, feldspar & quartz
- *Porcelain enameling*: the technology to produce these ceramic coating materials
- Beauty, color, smoothness, ease of cleaning, chemical inertness and durability.
- Steps
  - Preparation of the coating material
  - Application onto the coating (Frit)
  - Drying
  - Firing (sintering at 800°C)
- Substrates: steel, cast iron, and aluminum as a vitreous porcelain enamel
- Products: sinks, bathtubs, lavatories, ranges, water heaters, washing machines, dishwashers, jet engine components, automotive mufflers, and electronic circuit boards.

32

Thermal & Mechanical Coating

- Thermal surfacing processes
  - **Thermal spraying** – spraying molten and semi-molten coating materials onto a substrate, which solidify and adhere to the surface (typically mechanical interlocking)
    - Coating materials: pure metals and metal alloys; ceramics (oxides, carbides, and certain glasses); other metallic compounds (sulfides, silicides); cermet composites; and certain plastics (epoxy, nylon, teflon, and others).
    - Substrates: metals, ceramics, glass, some plastics, wood, and paper
    - Heating technologies: oxyfuel flame, electric arc, and plasma arc
    - Applications
      - To rebuild worn areas on used machinery components
      - To salvage workparts that had been machined undersize
      - Corrosion resistance, high temperature protection, wear resistance, electrical conductivity, electrical resistance, electromagnetic interference shielding
  - **Hard facing** - alloys deposited as a weld onto a substrate material.
    - Distinguishing feature is that fusion occurs between coating and substrate to resist abrasive wear
    - Applications: coating of new parts and repair of heavily worn, eroded, or corroded part surfaces
  - **Flexible Overlay Process** – A cloth impregnated with hard ceramic or metal powders laid unto a substrate and heated to fuse the powders to the surface
- Mechanical Plating – Metallic powders are pounded onto the surface by the larger glass beads.

33