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SCHOOL OF INDUSTRIAL AND INFORMATION ENGINEERING

MATERIALS ENGINEERING AND NANOTECHNOLOGY

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# Surface Engineering

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## Author's preface

Dear Reader,
I am delighted to present this comprehensive collection of lecture notes for "`Surface Engineering`". These notes have been thoughtfully structured to closely align with the course curriculum, providing an invaluable resource for your studies.

These lecture notes are a culmination of extensive research and diligent note-taking, incorporating insights from professor lectures, course materials, textbooks, and other reputable sources. By bringing together these diverse resources, I aimed to provide you with a well-rounded understanding of the subject matter.

While every effort has been made to ensure accuracy and clarity, it is essential to acknowledge that errors or discrepancies may exist within these notes. The complexities inherent in the subject matter, coupled with the limitations of human interpretation, make occasional inaccuracies unavoidable. Therefore, I encourage you to approach these notes critically, supplementing your understanding with additional academic sources and seeking clarification from your professors or peers when necessary.

I have written these lecture notes using LaTeX, a precise typesetting system widely used in scientific and academic writing. Its utilization ensures a visually appealing and organized document, enhancing the overall readability and accessibility of the content.

I sincerely hope that these lecture notes will serve as a valuable companion throughout your academic journey. They are designed to supplement your learning experience, providing a comprehensive overview of the course material. Remember to approach these notes as a guide, actively engaging in discussions, seeking further insights and embracing the collaborative spirit of academia.

Wishing you success and an enriching learning experience.

📍 Milano, Italy
📝 February 6, 2026

# Contents

# 1 Introduction to Surface Engineering

**Surface engineering** is currently a field of lively interest, both in terms of its practical applications and scientific research activities. In both cases, as one can infer from its name, this discipline is based on the study and characterization of surfaces, which correspond to interfaces, both static and dynamic, that a medium exposes to the surrounding environment.

## 1.1 Historical Background

Surface engineering has origins that can be traced back to the dawn of humankind, as since the Stone Age, humans have shown particular interest and curiosity towards material surfaces, such as the finishing of flints used for hunting activities or the use of colored pigments for cave paintings.

**Figure 1:** Prehistoric cave painting.

However, progressing through historical epochs and with the introduction of new materials into society, the actual study of surfaces began roughly at the end of the eighteenth century, more precisely in 1784, when in England, industrial-scale rolling of a steel ingot was first implemented. Subsequently, in 1805, Luigi Brugnatelli, a colleague and admirer of the scientific work of Alessandro Volta, completed the first gold (Au) plating using an electrochemical reaction.

**Note**

In fact, through this pioneering experiment, he demonstrated how electricity, initially used solely for energy purposes, could also be useful for modifying the surface of a component.

Following this event, in the following years, numerous experiments were conducted, especially in Germany, the United States, and the Soviet Union, regarding increasingly sophisticated methods to alter the surface properties of materials.
Nowadays, these techniques are still under continuous development and, given their high versatility, are applied in various sectors, both for functional applications and decorative purposes.

### 1.1.1 Application Areas and Manufacturing Techniques

In conceptual terms, the birth of surface engineering can be traced back to the 1970s. In this historical context, indeed, this science expanded considerably due to growing interest in its discipline and its applications, becoming one of the main scientific topics concerning research activities.
Nowadays, it can be affirmed that this branch of engineering deals with the following three issues:

1. Characterization of manufacturing processes dedicated to producing surface layers, which can be applied to a component for both functional reasons and motivations related to its aesthetic appearance
2. Study of phenomena related to material surfaces, especially in chemical and physical aspects concerning the environment in which the component will be placed

3. Analysis of material performance, both regarding their surface finishes and the respective species adopted to achieve these finishes

**Note**

From a more general perspective, it will also be possible to understand that this engineering field is extremely useful for numerous application areas, ranging from functional purposes to decorative uses.

As for a possible distinction of the produced surface layers, these can be categorized into two main families:

- **Technological surface layers:** These are coatings created before a component is put into use through artificial processes conducted in the laboratory, specifically designed to confer specific properties to the surface of the component
- **Service-generated surface layers:** These are coatings formed through processes that occur during the life of a component, under specific application conditions

From the perspective of mechanical and chemical performance of materials, it can be reasonably stated that any product subjected to a surface engineering process will become a component defined by superior performance.
Furthermore, to distinguish the techniques used for modifying the surface properties of a material, the following situation can be considered:

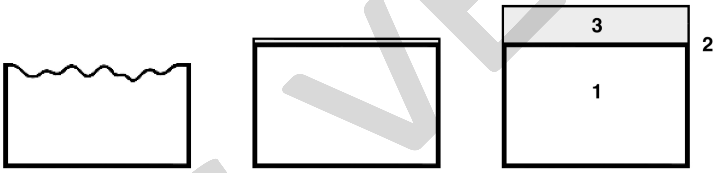

**Figure 2:** Schematic representation of techniques used for modifying the surface of a component. In the figure on the right, labeled respectively as 1, 2, and 3, you can recognize the substrate, the surface layer, and the coating.

In this regard, considering the image depicted above, there are indeed three different strategies related to surface treatments:

1. **Decremental approach:** This involves removing mass from the component's surface. By doing so, it becomes possible to obtain a different surface morphology from the same material
2. **Non-decremental approach:** This approach operates at a height that is practically equal to the initial one by applying very thin layers that are practically negligible in thickness
3. **Incremental approach:** In contrast to the decremental approach, this involves applying coatings that significantly increase the effective thickness of a medium

**Note**

In addition to these aspects, given the high number of possible solutions, techniques aimed at modifying the surface of a component can be further divided based on their modernity and the thickness they add to the component.

## 1.2 Surface Definition

> Surface
>
> Finding a consistent definition of the concept of **"surface"** is not at all simple, although it is still possible to assert that the surface of a component is always characterized by a structure and properties that are different from those possessed by the corresponding substrate.

The origin of this difference can be attributed to the following three aspects:

1. Different energy conditions, leading to a state of surface instability that may cause an increase in adsorption and desorption activities at the same interface
2. The combination of mechanical, thermal, electrical, physical, and chemical effects that occur during the manufacturing process of the component near its surface
3. The continuous or cyclical activity of these effects caused by the environment on the material, which always occur near its interface

**Note**

In other words, to provide a more comprehensive definition of the concept described above, it can be summarized that a surface corresponds to the physical boundary of a material that determines its extension in space.

### 1.2.1 Distinction of surfaces and their properties

In addition to what has been mentioned in the previous paragraph, it is also possible to define different types of surfaces, which can be characterized as follows:

- **Nominal surface** ▸ This corresponds to the measurement of the surface at the macroscale, which is usually used in blueprints to define the characteristic dimensions of a component to be produced in a simplified manner
- **Real surface** ▸ This is the surface that coincides with the actual interface of the material with the surrounding environment, taking into account its characteristic morphology
- **Observed surface** ▸ This corresponds to the measurement of the surface at the micro- and nanoscales, the precision of which will differ depending on the analysis technique used. Indeed, as we will see later, this parameter will be influenced by numerous aspects, such as the resolution of the instrument used and its sensitivity

> Surface Reactivity
>
> From a more practical standpoint, it is useful to talk about **surface reactivity**, which refers to the ability of a surface to interact with a generic component. Observing the particles present on the surface of a material, it can be noticed that they are less bound compared to those present in its volume.

Indeed, the excess energy resulting from unsaturated bonds will be converted into increased reactivity of a medium towards the surrounding system.

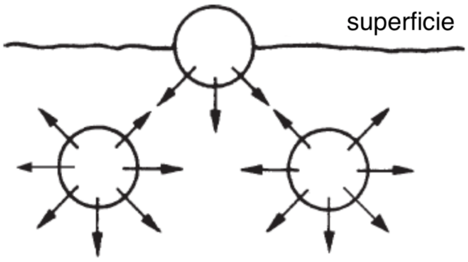

**Figure 3:** A schematic representation of the arrangement of particles in the volume and on the surface of a material, along with the corresponding bonds.

Obviously, as the conformation of a surface changes, so will the arrangement of atoms near it, meaning that surfaces with more complex morphologies will contribute a greater amount of free energy compared to simpler ones.

This aspect will be crucial for understanding a wide range of phenomena, such as adhesion between two surfaces.

**Figure 4:** Schematic representation of the comparison between two components having the same dimension but different morphologies relative to their surfaces. In particular, the case on the right will be characterized by a larger surface area, which is why the atoms arranged on it will collectively contribute more energy compared to the component on the left.

It is clear that by modifying the surface profile of a component, its reactivity towards the environment in which it will be placed can be controlled.

### 1.2.2 Surface Energy and Surface Tension

Talking about the thermodynamics of surfaces, we can define the concept of **surface energy** possessed by an interface as:

$$E_s = G_s = \frac{G - G_b}{A}$$

where $A$ corresponds to the area of the surface considered, $G$ is the value of the total Gibbs free enthalpy belonging to the system considered, while $G_b$ always consists of a term related to this thermodynamic function but will be of theoretical nature, as it will refer to the energy possessed by the system in case the particles arranged on its surface, such as atoms and molecules, have the same energy as those present in its volume.

In reality, often this term will be reduced to an index that will be more manageable from the point of view of the formulations defined by thermodynamics, which is precisely the **surface tension**, which will be calculated as:

$$\gamma = \left(\frac{\partial G}{\partial A}\right)_{P,V,n_i}$$

where the subscripts $P$, $V$, and $n_i$ correspond respectively to pressure, volume, and the number of moles, which by their own definition, in this case, will be considered constant within the

# Part II

# Industrial Processes

## 1 Metal Finishing

To fully understand industrial processes aimed at modifying the surface of a material, it is first necessary to focus on the study related to **metal finishing**, which encompasses all surface treatments related to the deposition of metallic materials and, more generally, to all materials that can be coated through such processes.

Indeed, nowadays, this sector is known for the vast number of procedures aimed at producing coatings of metallic nature, which allow imparting specific characteristics to base materials in order to obtain products destined for specific sectors.

> Electroplating & Electroless Plating
>
> The two main processes through which such surface layers can be obtained are **electroplating** (electrodeposition) and **electroless plating** (electroless deposition).
> In the first case, an electric current is used to conduct the deposition reaction, while in the second process, spontaneous redox mechanisms occur due to temperature, leading to the deposition of a metallic species onto a component.

Obviously, each of these two processes will be intended for specific materials, and the products obtained will also be significantly different from each other, especially regarding their properties and resulting performance.

### 1.1 Fundamental Parameters

> Metal Finishing Processes
>
> **Metal finishing processes** are, by their very definition, characterized as deriving from electrochemical reactions, i.e., oxidation-reduction processes.

Specifically, these processes take place within a system where the following three elements are present:

- A **substrate**, which refers to the component or part thereof that will undergo the surface treatment
- An **electrolyte solution**, which corresponds to an aqueous solution containing ions of the species intended to be deposited on the surface of the aforementioned component ("wet phase deposition"), as it will be immersed in it
- A **driving force**, which represents the means by which the oxidation-reduction reaction will occur and which will lead to the subsequent completion of the respective surface treatment

Obviously, each process will be defined by different parameters, which is why these deposition mechanisms will be extremely varied among them in terms of morphologies and application areas.

## 1.2 Electrodeposition

> Electrodeposition
>
> **Electrodeposition** is a surface finishing treatment characterized by the fact that the driving force in the system is an electric current, which provides the electrons necessary for the deposition process and reaches the **cathode**, i.e., the component to be coated, from the **anode**, which is a component similar to the species to be deposited, whose presence allows the electrical circuit to be closed.

Obviously, since the process in question is driven by the presence of an electron flow, the substrate material must necessarily be a **conductor** or a **semiconductor**; otherwise, the surface treatment considered here would not work.

> The goal is to deposit a coating consisting of a zero-valent metal through a reduction reaction, which will have a composition different from that of the substrate.

In practical terms, electrodeposition is characterized by being a relatively inexpensive process whose performance will vary depending on the materials chosen for the coating, which, as we already know, are numerous.
Additionally, this technique requires relatively simple and economical preparation; in this case, the only costs to consider are the price of the precursor chemicals for the coating species and the energy expenditure related to the use of electrical energy to generate the current used in the plating process.
In this regard, it is possible to affirm that through an electrodeposition process, coatings can be obtained from the following species:

- **Single metals**, such as tin (Sn), copper (Cu), nickel (Ni), chromium (Cr), and zinc (Zn), which will provide a coating with increasing performance as both their purity and thickness increase. For this reason, such materials will be used mainly for applications in corrosion protection
- **Metal alloys**, such as copper-zinc (Cu−Zn), copper-tin (Cu−Sn), lead-tin (Pb−Sn), and tin-nickel (Sn−Ni) alloys, which will allow obtaining a single layer with characteristics different from a multilayer coating obtained through the sequential application of individual electrodeposition processes. In this case too, their main applications will be related to corrosion protection and wear resistance. Obviously, being more complex materials, these coatings can also be used for much more specific purposes, such as sensor creation

**Figure 37:** Bolts coated with a zinc-nickel (Zn−Ni) metal alloy. This type of coating is still widely used in a variety of sectors, such as corrosion resistance fields. Indeed, zinc (Zn) alone, due to its low nobility, would not provide sufficient performance for such applications because of galvanic coupling phenomena.

- **Organic particles of various sizes**, such as Polytetrafluoroethylene (PTFE), i.e., Teflon, and carbon (C) derivatives and graphite within the metal matrices of composite materials.

Specifically, these will optimize numerous physical characteristics of the treated components: a clear example of this fact is the increase in the hardness of a substrate, which will also increase the wear resistance of the medium considered

**Note**

In general terms, it is also possible to observe how the deposition of a certain family of materials, both organic and inorganic, is more or less favored depending on the applications to which the coating will be destined.

### 1.2.1 Analysis of the plating system

As we already know, the first historical mentions related to electrodeposition date back to the early nineteenth century when Luigi Brugnatelli demonstrated that a thin layer of gold (Au) could be deposited on a silver (Ag) foil using a voltaic pile, i.e., through an electric current.
Over many years, electrodeposition has evolved substantially, but the fundamental concept underlying it has remained the same: indeed, in the technique in question, there will always be a mechanism for the surface deposition of a zero-valent metal layer on a conductive or semiconductive substrate, driven by a flow of electrons through an electrolytic solution. In this regard, the plating system related to these processes is defined as follows:

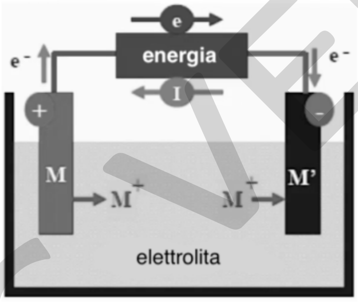

**Figure 38:** Schematic representation of the plating system used in a generic electrodeposition process.

from which image it will be possible to note how both the anode, where oxidation reactions will occur, and the cathode, which will undergo a reduction process, are immersed in an electrolyte that will carry the flow of ions within the system.
In this regard, the chemical reaction justifying the coating mechanism of the cathode is as follows:

$$M^{z+}_{(aq)} + ze^{-} \longrightarrow M_{(s)}$$

where M indicates the metallic element in question and z corresponds to the number of ions exchanged during the process.
However, this will not be the only reaction along with the oxidation reaction, as secondary reactions due to the presence of other elements in the system can also be observed.
Indeed, at the anode and cathode, respectively, secondary reactions of **oxygen evolution**[8] and **hydrogen evolution**[9] can be observed, which, if not adequately controlled, could lead to

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[8] Oxygen evolution:

$$2\,H_2O_{(l)} \longrightarrow O_{2(g)} + 4\,H^{+}{}_{(aq)} + 4\,e^{-}$$

[9] Hydrogen evolution:

$$2\,H^{+}{}_{(g)} + 2\,e^{-} \longrightarrow H_{2(g)}$$

defective coatings poorly adhered to the substrate, making them unusable.
In fact, the hydrogen evolution reaction corresponds to a process describing how hydrogen atoms (H) recombine to form molecular hydrogen ($H_2$): more precisely, this compound will have a much larger volume than the two initial particles, and if this phenomenon occurs near the surface of the component to be coated, it could lead to phenomena attributable to hydrogen embrittlement due to the development of internal stresses within the structure of the material.

In any case, to control the presence of these secondary reactions, two types of anodes can be used:

- **Inert anodes**, such as platinum (Pt), mixed metal oxides, and carbon-based compounds, which are sources of electrons that, however, do not take part in the aforementioned electrochemical reaction and consequently limit the hydrogen evolution reaction during a generic oxidation-reduction process
- **Sacrificial anodes**, such as nickel (Ni), copper (Cu), zinc (Zn), and tin (Sn), which, unlike the previous ones, consist of sources of electrons that will take part in the oxidation-reduction reaction and, in fact, will be consumed, leading to a much more aggressive hydrogen evolution reaction

**Note**

Alternatively, to obtain a specific product, it will still be possible to replace the material of the anode with a more suitable species, or secondary finishing processes can be carried out on the cathode to give it a specific property that would otherwise be impossible to achieve solely through the electrochemical process in question.

Furthermore, the concentration of ionic species within the electrolyte must necessarily be kept constant throughout the entire electrodeposition process, and the positioning of these elements will also be fundamental for the correct execution of the plating process. In fact, depending on the geometry of the medium to be treated, to ensure the obtaining of a homogeneous coating, multiple anodes will be used in different positions relative to the cathode, so as to ensure that the reduction reaction occurs on the entirety of the surface exposed by the component to be plated. Obviously, the choice of the number, position, and nature of the anodes will strongly depend on the objective to be achieved and the quality of the process to be conducted.

### 1.2.2 Faraday's Law

Let's continue the analysis related to electrodeposition by introducing a fundamental relationship in the context of oxidation-reduction processes, which is precisely **Faraday's law**. In fact, this relationship was formulated in 1833 by the chemist of the same name, and it allows us to define the quantity of reactants that have been transformed during an electrochemical reaction. Consequently, it enables us to determine how much a system has changed from its initial state following a plating process, quantifying the mass of the metal material deposited by applying a certain electric current over a certain period of time. This law is described by the following equation:

$$m_i = \frac{n_i M_i}{z} \frac{Q}{F} = \frac{n_i M_i}{z} \frac{It}{F}$$

where $m_i$ and $M_i$ correspond respectively to the mass of the species reacted in a time interval $t$ and the molar mass of the deposited species, $z$ is the stoichiometric number of electrons involved in the reaction, $F$ is **Faraday's constant**, which is defined by a value of 96 485 C/mol, while $Q$ is the value of the electric charge flowing within the plating system under consideration.

**Note**

In other words, this law allows us to predict the thickness of the coating produced by an electrochemical process, which is why this relationship is fundamental in the control of metal finishing processes.

### 1.2.3 Morphologies of Electrodeposited Layers

Another advantage of electrodeposition procedures lies in the ability to modulate the **morphology** of the created coatings, which will possess different properties depending on their microstructure. Among all the possible alternatives, we can mention the following cases:

- **Columnar** structure, characterized by grains oriented vertically to the plane defined by the treated substrate. However, the interfaces between them, i.e., the grain boundaries, will be highly reactive zones and therefore more sensitive to chemical attacks, such as corrosion

**Figure 39:** Schematic representation of an electrodeposited coating with a columnar structure

- **Layered** structure, which presents an orderly and periodic alternation of coatings of different components that provide additional thickness to the substrate and also effectively hinder the propagation of corrosion. However, this phenomenon will still occur, albeit with greatly extended timeframes

**Figure 40:** Schematic representation of an electrodeposited coating with a layered structure

- **Equiaxed fine grain** structure, where the presence of many grains, generally recognized as crystals with nanometric dimensions, and thus numerous grain boundaries, will provide the coating structure with very high mechanical performance

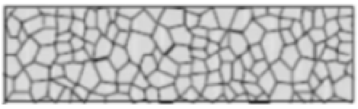

**Figure 41:** Schematic representation of an electrodeposited coating with a fine equiaxed grain structure.

- **Dendritic** structure, defined by the presence of roughness that significantly increases the surface area of the coating and therefore its reactivity to stimuli from the surrounding environment. Indeed, for this reason, this structure will primarily be used for sensor manufacturing

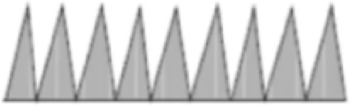

**Figure 42:** Schematic representation of an electrodeposited coating with a dendritic structure.

# 3 Nickel Plating

Having completed the analysis related to chromium plating processes, let's now continue our discussion on industrial coating procedures by studying **nickel plating**. Indeed, nowadays, this technique is also widely present in the market of metal finishes, and for this very reason, this surface treatment will be observable in numerous fields, especially concerning corrosion resistance applications.

## 3.1 Definition of the process and physical properties of nickel

**Nickel** (Ni) is a metal widely present in the Earth's crust, both in mineral form and within living organisms, namely plants and vegetables.
Regarding its physical properties, we can consider the following summary table:

**Table 6:** Some physical properties of nickel.

| **Property** | **Value** |
|---|---|
| Atomic weight | 58.7 g/mol |
| Crystal Structure | FCC |
| Melting Point | 1455 °C |
| Boiling Point | 2900 °C |
| Density | 8.9 g/cm$^3$ |
| Magnetism | Ferromagnetic |
| Valence | +2 |

Based on the data reported above (Table 6), besides being one of the **most aggressive allergens**, it is important to mention the following aspects:

- It is a **high-melting metal** ▸ consequently, similar to chromium (Cr), it will be very stable within a wide temperature range
- It is a **ferromagnetic material** ▸ therefore, nickel (Ni) will impart this property to the substrate on which it is deposited. Additionally, considering its ability to offer significant magnetic properties when associated with other elements such as iron (Fe) or cobalt (Co), this species is often used in the creation of alloys[14]. In this regard, such compounds are still widely used in the electronics sector, especially concerning the production of magnetic sensors

Furthermore, concerning the optical properties of the material, nickel (Ni) is inherently a very bright metal with a slightly softer color than chromium (Cr). Consequently, it will have a reflective appearance towards light and allow obtaining surface finishes very similar to those achievable through chromium plating.

**Note**

Additionally, in this case, it will be possible to use specific additives to make the nickel-plated layer **black**, which is an industrial requirement highly prevalent today.

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[14] However, in this case, it will be necessary to pay close attention to the elements present in such a compound, as phosphorus (P), reacting with the said component, will gradually nullify its magnetic properties, and consequently, the final product will not possess this characteristic.

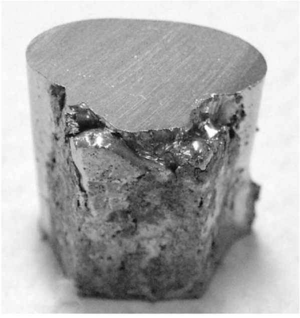

**Figure 64:** Nickel (Ni) in mineral form.

Nickel (Ni) is an element that can be deposited onto the surface of a metallic component through an electrodeposition process. Specifically, in this case, it will be possible to obtain relatively thick and uniform coatings characterized by high uniformity and significantly meaningful optical and mechanical performances.

In addition to these aspects, **nickel plating**, which corresponds precisely to the electrodeposition process by which a component will be coated with a layer of metallic nickel, will allow obtaining coatings both for functional purposes and for purely aesthetic, decorative applications.

In fact, unlike what we have seen previously with chemical nickel plating, we can identify three main areas of application for the aforementioned surface layers:

- **Barrier coatings**, where metallic nickel will shield and protect the substrate from corrosion and oxidation phenomena. In both cases, the nickel layer will act as a functional barrier, protecting the coated material from wear and tear caused by its working environment. Nickel (Ni) is inherently highly resistant to corrosion and thus stable in both acidic and alkaline environments. Consequently, it will be used in numerous applications, such as corrosion resistance support for chromium layers
- **Aesthetic coatings**, consisting of surface layers that will utilize the optical characteristics of nickel (Ni) to enhance the brilliance of a component. These coatings are still widely used, especially in decorative applications, as they allow obtaining much shinier metal finishes compared to those normally achievable through chromium plating
- **External layers**, which have both an aesthetic and functional role. In these cases, metallic nickel, deposited as the external coating of a component, will be in direct contact with the environment, leading to oxidation. This event is crucial, as nickel will protect the substrate from possible contamination, and its color will remain similar to the initial one, except for a slight opacification effect, which will be almost imperceptible. Considering this additional characteristic of the species in question, we can easily understand how it consists of a particularly advantageous metallic element from the standpoint of the quality of the coatings obtained

**Figure 65:** Suspensions made of steel springs that have undergone a nickel plating surface treatment, thus enhancing their performance against wear and corrosion mechanisms.

In this regard, we can affirm that surface coatings obtained through traditional nickel plating processes will not only be effective in protecting materials but will also exhibit a noteworthy aesthetic appearance.

### 3.1.1 Formulations

> In terms of production, the quality of the conducted nickel plating process will heavily depend on the choice of **formulation**, which essentially corresponds to the type of electrolytic solution defined based on the use of a salt aimed at promoting the deposition of metallic nickel on a component.

Obviously, for each formulation, given the different chemical compounds used, it is important to note how nowadays there are more specialized industrial sectors than others, both in terms of the quality of the produced coatings and regarding their chemical, physical, and morphological properties resulting from the related electroplating process.
Generally, it will then be possible to distinguish four types of formulations for nickel plating, which are:

- **Watts solutions**, which allow obtaining highly glossy nickel-plated coatings characterized by excellent mechanical performances and high surface hardness, especially in the case of hard nickel deposition. In this case, for the production of nickel-plated coatings, nickel sulfate ($NiSO_4$) and nickel chloride ($NiCl_2$) will be used as precursors.
  These compounds will also be responsible for the coloration of the plating bath, as in the former case, the solution will be blue, while in the latter case, it will be green

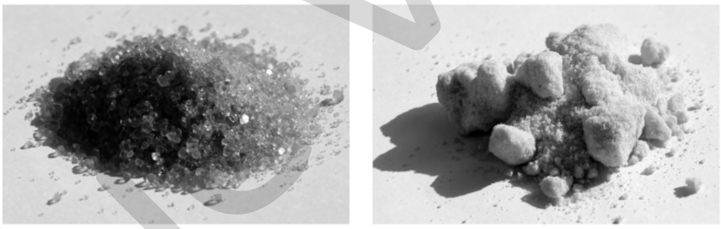

**Figure 66:** The two precursors related to Watts solutions in the form of crystalline powders, which are nickel sulfate ($NiSO_4$) on the left and nickel chloride ($NiCl_2$) on the right.

- **Chloride solutions**, which are specific for applications where it will be necessary for the nickel-plated coating to adhere highly to a substrate and to protect it from oxidation and corrosion. In this case, the use of chlorides, which are particularly aggressive chemical substances, will be indicated for the surface etching of components on which metallic nickel deposition is desired. This fact will be very common in the case of stainless steels, where the use of these species will indeed allow breaking down their native oxide formed by chromium (Cr) into an alloy through the so-called "chloride strike" mechanism, and then depositing the nickel (Ni) coating on the ferrous surface. From an industrial standpoint, their effect will consist of anodic dissolution of the said element: indeed, cloth bags containing nickel beads, which are sacrificial anodes, will be placed inside the tank.
  These beads will dissolve in the electrolyte and form an oxide layer on the cloth surfaces. However, this layer could represent a physical obstacle from the standpoint of dissolving the species to be deposited, so to avoid this, a certain amount of magnesium chloride (MgCl) will be added to the system.
  This compound will counteract the passivation mechanism of nickel (Ni) and thus improve the electrical conductivity of the electrolyte, preventing the oxide layer from accumulating

on the cloth surfaces. Obviously, to ensure the correct progress of the electroplating process of the metal in question, frequent maintenance interventions related to the cleaning of the bags used in the described process will be necessary, often carried out with brushes

**Figure 67:** Beads of nickel (Ni), which are widely used in formulations defined by chloride solutions.

- **Sulfamide solutions**, which, as we will see later, will be essential for stabilizing electroforming processes. These compounds indeed correspond to the main sources of $Ni^{2+}$ ions and, besides being economical, they will be stable, highly soluble, and also electrically conductive
- **Alloy solutions**, which, as their name suggests, consist of special formulations aimed at depositing metallic nickel on a component to create an alloy.
  Specifically, in this case, it will be possible to obtain nickel-iron ($Ni-Fe$) and nickel-cobalt ($Ni-Co$) alloys through co-deposition processes, which materials are indeed widely used in the manufacturing industry due to their high mechanical performances

Although the formulations mentioned above may be used for different scenarios, it is still possible to notice common aspects among these types of solutions.
In fact, in each of these cases, we can observe the following three aspects:

1. Boric acid ($H_3BO_3$) will always be present. This chemical compound acts as a **buffering agent**, allowing for specific pH regulation within a range of approximately 1.5 to 4.5. This is crucial in surface finishing processes, ensuring nominal conditions throughout the treated medium's surface.
   However, managing this compound can be problematic due to its toxicity and environmental impact. Compounds derived from boron (B) are toxic and polluting, rendering the plating bath unusable and requiring proper disposal. Therefore, the goal is to minimize the environmental impact by significantly reducing the concentration of boron within the chosen formulation
2. The temperature of the processes involved will fall within a defined range of 21 to 65 °C. Considering 55 °C as the average temperature for a generic electroplating process, these conditions yield better-quality nickel-plated layers. At this temperature, nickel layers are shinier and harder, and the electrolytic species have maximum electrical conductivity. Additionally, the current density used in this system will be approximately 3 to 7 $A/dm^2$, ensuring adequate deposition flow towards the component to be plated
3. Additives will be used to confer specific characteristics to the nickel-plated coating. These compounds are added to the formulation to make the plated surfaces shinier and more morphologically homogeneous

Furthermore, two crucial themes concerning industrial nickel plating facilities are agitation and filtration mechanisms of the electrolytic bath. Through these technical measures, it is possible to achieve even higher-quality coatings.
Regarding bath agitation, this can be achieved either through air or mechanical means, ensuring

## Part IV

# High-Temperature Deposition Processes

## 1 PVD and CVD Processes

Having concluded the part concerning conversion coatings and the technologies aimed at their industrial production, we will now address the study and characterization of vapor-phase deposition processes, which consist of **Physical Vapour Deposition (PVD) processes** and **Chemical Vapour Deposition (CVD) processes**.
These processes utilize physical and chemical technologies, respectively, to obtain surface layers as an alternative to electrodeposition and chemical deposition. Indeed, nowadays these two types of techniques are widely employed in industrial applications, such as in the field of microelectronics, as they allow obtaining surface finishes, generally metallic, of excellent quality and with significantly greater thickness compared to coatings obtained through immersion of a substrate in an electrolytic species.

### 1.1 Definition of Processes

> PVD & CVD Processes
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> **PVD** and **CVD** processes, as mentioned earlier, are processes that utilize vapor, i.e., a gaseous phase containing the species to be deposited, to produce coatings aimed at enhancing mechanical performance and protecting the structural integrity of the substrates to which they are applied.

The main advantage of these techniques, as we will see later on, is that it will be possible to obtain layers of both single materials and compounds and alloys formed by them, which will confer particular characteristics depending on their morphology.
However, as previously addressed both in electrodeposition and chemical deposition, these two techniques are extremely costly, mainly due to equipment such as reactors, pumping systems[22] with their respective pipelines, and the chemicals used: indeed, these processes will be slower than those related to immersion treatments and especially present a spatial limitation, as the deposition mechanisms will occur exclusively within a vacuum chamber, inside which the components to be coated must be arranged.

Consequently, although they are relatively simple industrial procedures to perform, it will still be necessary to consider that for different pressure intervals, there will be different **vacuum regimes**, i.e., low vacuum, medium vacuum, high vacuum, and ultra-high vacuum: obviously, as this factor varies, both the quality of the deposited layers and their respective deposition mechanism will change, also due to the fact that different pumps will be used for the two aforementioned processes.
In technical terms, CVD processes will be much more complex than PVD processes, as they will require both very specific chemical species and vacuum chambers equipped differently: in any case, nowadays both mentioned technologies will allow coating components both continuously and discontinuously, regardless of their size.

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[22] Especially concerning these elements, most of the expenses related to the examined facilities will be dedicated to their maintenance. In fact, over time, these pumps could wear out and therefore, under such conditions, they would no longer be able to develop a flow sufficient to ensure a certain pressure in the respective deposition chamber.

**Example 1.1** – (Printing of Banknotes)

An example related to the possible applications of these techniques is related to the printing of banknotes, a process that was initially carried out using nickel-plated plates for electrodeposition and subsequently hard chrome-plated: however, given their high rate of surface wear, over the years, this outer coating has been progressively replaced by a layer of metallic chromium obtained through vapor-phase chemical deposition, which indeed exhibits better abrasion resistance compared to those obtained through electrodeposition.

From an application standpoint, both processes will be highly selective, as it will be sufficient to cover the portion of a material that is NOT intended to be coated to expose its regions to be treated.

**Figure 117:** A turning tool, whose family of components is often treated through vapor-phase deposition processes. Note how only its tips, the areas subjected to high wear rates, are coated with a much harder material.

**Note**

Obviously, as we have already seen for other surface deposition techniques, it will be necessary to have both pretreatment processes, to ensure the maximum degree of adhesion between the coating and the substrate in question, and activation processes, also through plasmas, to make the surfaces of the component to be treated more reactive towards the deposition species.

### 1.1.1 Classification of Vacuum Deposition Technologies

**Vacuum deposition technologies**, including both PVD and CVD processes, are diverse nowadays, each characterized by different properties and industrial procedures. In general, these techniques can be differentiated based on their deposition rate and their step coverage, which refers to the ability of a deposition mechanism to uniformly cover every exposed interface of the component being treated.

In this regard, we can define the following chart:

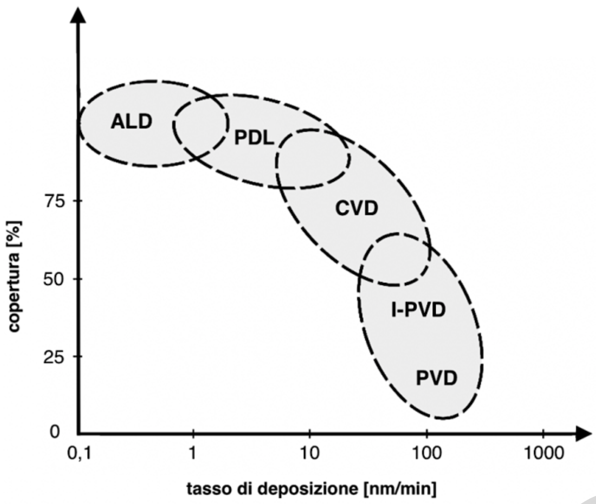

**Figure 118:** Graphical representation of different vacuum deposition techniques in terms of coverage and deposition rate. As evident from the diagram presented here, Atomic Layer Deposition (ALD) will be the slowest method but will provide the highest quality coatings, while PVD processes will be the fastest but characterized by greater superficial layer inhomogeneity. For this reason, they will be the most versatile among those listed here.

From this image, it can be observed that in these cases, deposition rates are much lower compared to those of deposition techniques we have previously studied, as they are typically in the range of nanometers per minute. Additionally, each vacuum deposition process can also be defined based on the thickness of the coatings it can produce: indeed, focusing solely on PVD and CVD processes for practicality, we generally observe thicknesses in the micron scale, where for the former, we have a range of values from 0.01 to 20 µm, while for the latter, thicknesses are typically around 0.1 to 500 µm.

> It is clear that, although these are more time and resource-intensive processes, through such techniques, coatings with thickness comparable to those studied previously can be obtained, and therefore, the deposited layers will be equally effective in terms of wear and corrosion resistance.

Specifically, the coverage of these coatings will be on average 40 to 50 %, which is lower than usual, so it will still be preferable to use layers produced by electrodeposition or chemical deposition to ensure better performance in practical applications. To be more specific, CVD processes allow obtaining coatings of higher quality, although they are slower to implement: these characteristics are indeed due to the nature of the processes themselves, as the chemical reactions occurring near the interfaces of the components to be treated allow for more effective coverage[23].
Additionally, CVD processes occur at temperatures of about 450 to 1200 °C due to the need for stable gaseous phases, while PVD processes can be carried out at much lower temperatures, typically from 100 to 450 °C: regarding this, it can also be inferred that coatings with different thermal resistance can be obtained, as in the former case, metals and ceramic materials are used, while in the latter, polymers can also be deposited.

**Note**

Consequently, we can affirm that the properties of the coating in question will depend on the base material, as it can tolerate different temperatures.

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[23] This fact is linked to the high operating temperature of the ALD process, which promotes the rearrangement of atomic morphology on the surfaces of the treated component.

### 1.1.2 Deposition Mechanisms and Thin Hard Coatings

As previously mentioned, the quality of coatings obtained from PVD and CVD processes will be closely dependent on both the substrate material to be coated and the process conditions, such as temperature and pressure, which will define a certain vacuum regime inside the treatment chamber.

> Regarding this, PVD processes will involve the vaporization of a target from which the metallic species to be deposited will be extracted: this commonly occurs through sputtering mechanisms, which can be implemented either through heating or ion bombardment.

As for CVD processes, as already mentioned, the situation will be much more complex: in this case, it will be necessary to mix gaseous precursors with reactive gases, such as molecular nitrogen ($N_2$), molecular oxygen ($O_2$), or carbon dioxide ($CO_2$), inside an environment with an inert atmosphere, typically defined by the presence of argon (Ar) or molecular hydrogen ($H_2$). By doing so, it will be possible to obtain coatings consisting of multiple materials such as nitrides, carbides, and oxides, such as TiN, TiC, $TiO_2$, and $Al_2O_3$, which will be characterized by being very thin, i.e., with a thickness of less than 10 µm, but at the same time extremely hard: these layers are indeed known as **"thin hard coatings"** and are widely used today due to their high mechanical performance, especially in tribological applications.

## 1.2 CVD Processes

Let's now focus on the analysis of CVD processes, as compared to what we presented in previous sections regarding PVD processes, such deposition techniques will be much more rewarding in terms of the quality of the produced coatings.
In general terms, each chemical vapor deposition process can be defined by the following scheme:

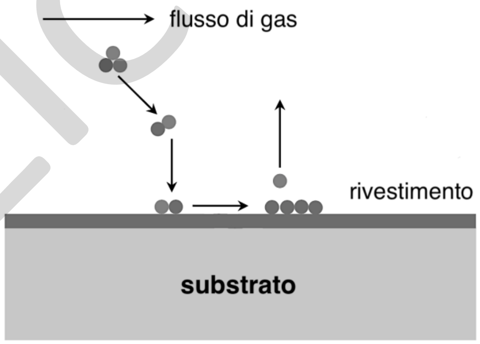

**Figure 119:** Schematic representation of the deposition mechanism of a generic CVD process, which involves diffusion phenomena triggered by the high temperature of the system in question.

From this image, we can observe how, in the presence of high temperature from both the substrate and the vacuum chamber, diffusive phenomena will lead to the adsorption and desorption of atomic and molecular chemical species coming from the gaseous mixture, which is precisely a vapor consisting of a precursor and a reactive gas.
In addition to this, through these chemical reactions, co-products can also be formed, which secondary compounds may be more or less useful depending on the properties of the coating intended to be obtained.

**Note**

Obviously, in this case as well, it will be possible to regulate the pressure of the system, thus optimizing the deposition mechanism and also the growth rate of the considered coating: indeed, this parameter can be controlled by temperature but can also be enhanced by external elements, such as a laser or a plasma.

### 1.2.1 Types of chemical reactions

As we already know, each CVD process will be associated with particular chemical reactions, as they define both the gases involved in the deposition process, i.e., the gaseous mixtures containing the precursors of the deposition species, and the products obtained from them.
In general, four main types of reactions can be observed, which consist of the following processes:

- **Pyrolysis**, which involves the thermal decomposition of gaseous species in proximity to the substrates to be coated. Two examples of this type of process are the decomposition reactions of silane ($SiH_4$) and nickel tetracarbonyl ($Ni(CO)_4$), represented as follows:

$$\mathrm{SiH_{4(g)}} \xrightarrow{650\,^\circ\mathrm{C}} \mathrm{Si_{(s)}} + 2\,\mathrm{H_{2(g)}}$$
$$\mathrm{Ni(CO)_{4(g)}} \xrightarrow{180\,^\circ\mathrm{C}} \mathrm{Ni_{(s)}} + 4\,\mathrm{CO_{(g)}}$$

  From these, it can be noted how the temperature referred to for these decomposition processes will be different depending on the thermal stability of the precursor used in the respective gaseous phase

- **Reduction**, which involves molecular hydrogen ($H_2$) as a reducing agent to decompose a gaseous species. This type of reaction can be related both to the reduction of silicon tetrachloride ($SiCl_4$), i.e.,:

$$\mathrm{SiCl_{4(g)}} + 2\,\mathrm{H_{2(g)}} \xrightarrow{1200\,^\circ\mathrm{C}} \mathrm{Si_{(s)}} + 4\,\mathrm{HCl_{(g)}}$$

  and to the deposition of very hard and compact coatings consisting of refractory materials, such as tungsten (W), according to the following process:

$$\mathrm{WF_{6(g)}} + 3\,\mathrm{H_{2(g)}} \xrightarrow{300\,^\circ\mathrm{C}} \mathrm{W_{(s)}} + 6\,\mathrm{HF_{(g)}}$$

  In this case, as noted in the previous point, the temperature used will be associated with the thermal stability of the species under examination

- **Oxidation**, which, as we already know, corresponds to a reaction that occurs through the interaction between molecular oxygen ($O_2$) and a material, leading to the formation of a surface oxide layer, which is indeed a very hard and thermally stable material. Two examples related to this type of reactions are the oxidation of silane ($SiH_4$) and the oxidation of aluminum chloride ($AlCl_3$), defined as follows:

$$\mathrm{SiH_{4(g)}} + \mathrm{O_{2(g)}} \xrightarrow{450\,^\circ\mathrm{C}} \mathrm{SiO_{2(s)}} + 2\,\mathrm{H_{2(g)}}$$
$$2\,\mathrm{AlCl_{3(g)}} + 3\,\mathrm{H_{2(g)}} + 3\,\mathrm{CO_{2(g)}} \xrightarrow{1100\,^\circ\mathrm{C}} \mathrm{Al_2O_{3(s)}} + 6\,\mathrm{HCl_{(g)}} + 3\,\mathrm{CO_{(g)}}$$

- **Complex reactions**, which lead to the obtaining of coatings with a significantly complex structure and very high hardness. In this case, being processes that are very articulated from a purely chemical point of view, the precursors will react at high temperature together

with other gases present in the vicinity of the surface of the medium to be treated, leading to the formation of a surface layer along with a gaseous coproduct.
In this case, numerous cases can be observed, as it is a procedure that is widely used today in industries dedicated to the production of advanced coatings. Indeed, among the multiple processes belonging to this category of chemical reactions, the following three examples can be mentioned:

$$\begin{aligned}
\mathrm{SiCl}_{4(g)} + \mathrm{CH}_{4(g)} &\xrightarrow{1400\,^{\circ}\mathrm{C}} \mathrm{SiC}_{(s)} + 4\,\mathrm{HCl}_{(g)} \\
\mathrm{TiCl}_{4(g)} + \mathrm{CH}_{4(g)} &\xrightarrow{1000\,^{\circ}\mathrm{C}} \mathrm{TiC}_{(s)} + 4\,\mathrm{HCl}_{(g)} \\
\mathrm{BF}_{3(g)} + \mathrm{NH}_{3(g)} &\xrightarrow{1100\,^{\circ}\mathrm{C}} \mathrm{BN}_{(s)} + 3\,\mathrm{HF}_{(g)}
\end{aligned}$$

From these reactions, it can be noted that the temperatures involved are equal to or greater than 1000 °C, especially due to properties of the elements involved in them

From the reactions mentioned above, it will be possible to infer the need to pay particular attention to the coproducts developed during these processes, as, in some cases, these could be toxic and could also damage the integrity of the respective vacuum chamber.

A very common example related to this fact is the action of hydrochloric acid (HCl), which compound corresponds to a very frequent coproduct in the aforementioned reactions and is still widely studied regarding the safety of industrial plants dedicated to operating according to this kind of processes.

### 1.2.2 Coating Morphologies

Each CVD process can provide a coating with a different morphology, especially when two metallic elements are used to form an alloy. Specifically, CVD can also be used as a subsequent surface treatment to electrodeposition, chemical deposition, and even to processes aimed at creating conversion coatings, in order to impart specific properties to components that have been previously treated.
In this regard, the following types of surface layers can be identified:

- **Single-component coatings**, which correspond to coatings entirely composed of a single material and, for that reason, are surface layers characterized by mechanical performance inferior to those of more complex coatings. Obviously, as we already know, the greater their thickness, the higher their respective performance will be, both in terms of wear and corrosion resistance

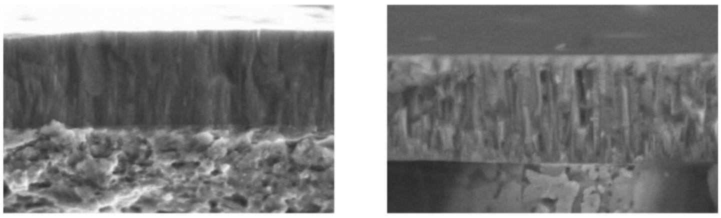

**Figure 120:** Photographs of single-component coatings. On the left, we have a sample of a substrate coated with titanium nitride (TiN), while on the right, we have a coating consisting of titanium carbonitride (TiCN). In both cases, although they are composed of a single component, the coatings observed here will be very hard.

- **Multicomponent coatings**, which, unlike the previous case, are surface layers consisting of multiple materials. The result of this type of process is therefore a structure with a mixed composition that will present better mechanical properties than single-component coatings

- **Graded coatings**, which correspond to surface layers defined by a variable composition depending on their depth relative to the interface of the base material, as we have seen in the case of coatings resulting from hot-dip galvanizing and sherardizing. These surface layers will be used especially for adhesion and wear resistance, as it is possible that the deposited coating material is very hard on the outside but soft and particularly compatible with the substrate on the inside

**Figure 121:** Photograph of a graded titanium nitride (TiN) coating deposited on an aluminum (Al) component. Note how the composition of the layer in question varies depending on the distance from the interface with the base material.

- **Multilayer coatings**, which, as the name suggests, correspond to surface layers consisting of multiple internal layers that are made of different materials.

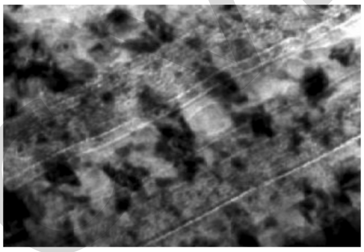

**Figure 122:** A photograph of a multilayer coating where nanoscale particles are dispersed inside, which will make it effectively a high-performance composite material.

These coatings are widely used today because of their mechanical properties, which are extremely optimized due to the synergy of the different elements deposited within the same layer

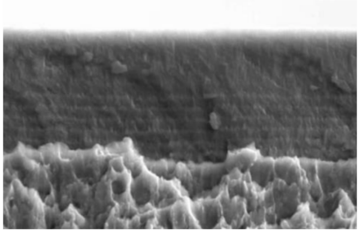

**Figure 123:** A photograph of a multilayer TiAlN coating, from which one can observe an evident stratification within.

- **Superlattice coatings**, which consist of multilayer coatings characterized by a much denser stratification. Indeed, these coatings will consist of layers with nanometric thicknesses, whose distance will be comparable to the lattice spacing of the crystalline lattices belonging