

CHAPTER «ENGINEERING SCIENCES»

METHODS OF OBTAINING METAL-OXIDE COATINGS ON METALLIC SURFACES AND THEIR FEATURES

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Abstract. Metal-oxide coatings play a crucial role in modern materials science, offering enhanced properties such as corrosion resistance, mechanical strength, and functional versatility. This study explores various methods for obtaining metal-oxide coatings, emphasizing their technological advancements and practical applications. The research systematically analyzes the main techniques, including chemical, physical, and vacuum-based deposition processes, highlighting their advantages and limitations. *The purpose* of this study is to classify and analyze existing methods of obtaining metal-oxide coatings and to determine the influence of processing parameters on their structural and functional properties. Special attention is given to electrochemical oxidation as a cost-effective and scalable approach. The research *methodology* is based on a comparative analysis of different deposition techniques, classification of processing parameters, and synthesis of experimental data. The study categorizes metal-oxide coating methods into chemical (chemical vapor deposition, sol-gel, chemical oxidation), physical (thermal spraying, laser-assisted deposition, ultrasonic treatment), and vacuum-based (magnetron sputtering, cathodic arc deposition, ion plating) techniques. *The results* indicate that electrochemical oxidation remains one of the most efficient and scalable methods for producing metal-oxide coatings with controlled thickness and composition. However, advancements in vacuum-based and laser-assisted technologies enable the

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fabrication of coatings with superior functional characteristics, expanding their applications in high-performance industries such as aerospace, energy, and biomedical engineering. *Practical implications.* The study provides insights into optimizing deposition methods to enhance coating performance while reducing processing costs. Understanding the correlation between synthesis parameters and coating properties facilitates the selection of the most suitable technique for specific applications. *The originality* of this research lies in its comprehensive analysis of modern deposition technologies for metal-oxide coatings, offering insights into development trends and potential industrial applications. The findings contribute to the advancement of functional coatings by improving process efficiency and material performance in diverse engineering fields.

1. Introduction

Metal-oxide coatings play a crucial role in modern materials science, providing protection and enhanced operational properties for structural materials. Their applications span various industries, including aerospace, electronics, biomedical, automotive, and energy sectors. Due to their high corrosion resistance, mechanical strength, and ability to modify functional properties, metal-oxide coatings have become an integral part of advanced technologies.

Aerospace components operate under extreme environmental conditions, requiring materials that can withstand high temperatures, oxidative environments, and mechanical stress. Metal-oxide coatings provide critical protection for aircraft engines, turbines, and structural components. A key application of these coatings in the aerospace industry is using thermal barrier coatings (TBCs) to improve the thermal and oxidation resistance of aircraft engines. Yttria-stabilized zirconia (YSZ) is widely employed as a TBC material due to its low thermal conductivity and high-temperature stability. Studies have shown that YSZ-based coatings effectively enhance the oxidation resistance of turbine blades and engine housings, thereby increasing operational efficiency and extending service life [1; 2].

The role of metal-oxide coatings in electronics remains essential for modern technological advancements. Indium tin oxide (ITO) is found to be extensively used in touchscreens, photovoltaic cells, and liquid

crystal displays (LCDs), providing a unique combination of high optical transparency and electrical conductivity. Its widespread application in flexible and transparent electronics has led to the development of next-generation display technologies, including organic light-emitting diodes (OLEDs) and advanced optoelectronic devices. Furthermore, ongoing research in ITO alternatives, such as doped zinc oxide and graphene-based coatings, aims to improve performance while reducing material costs [3].

Additionally, the integration of zinc oxide (ZnO) and titanium dioxide (TiO₂) in advanced semiconductor devices enhances sensor sensitivity and improves transistor performance, contributing to the development of more efficient electronic components. ZnO, with its wide bandgap and excellent piezoelectric properties, is particularly valuable in the production of high-frequency surface acoustic wave (SAW) sensors, ultraviolet photodetectors, and thin-film transistors. TiO₂, on the other hand, serves as a key material in resistive switching memories and perovskite solar cells, where its high dielectric constant and excellent charge transport properties enable significant improvements in device efficiency and stability.

Moreover, metal-oxide coatings are critical in the fabrication of transparent conductive electrodes (TCEs), which are essential for modern touch interfaces, smart glass, and energy-efficient windows. These coatings provide enhanced durability against mechanical wear, oxidation, and environmental degradation, ensuring the long-term functionality of electronic devices. Recent advancements in metal-oxide-based electronics also include their use in neuromorphic computing, where materials such as hafnium oxide (HfO₂) and aluminum oxide (Al₂O₃) are employed in memristors to mimic biological synapses, opening new avenues for artificial intelligence and brain-inspired computing [3].

The continuous evolution of metal-oxide coatings in electronics is driving improvements in performance, efficiency, and sustainability. Innovations in deposition techniques, including atomic layer deposition (ALD) and chemical vapor deposition (CVD), allow for precise control of thin-film properties, enabling the development of next-generation electronic components with enhanced functionality and reliability.

Biomedical engineering has significantly advanced by incorporating metal-oxide coatings, which enhance the performance, longevity, and

biocompatibility of medical implants and devices. These coatings provide essential functionalities such as corrosion resistance, antibacterial properties, and enhanced mechanical stability, making them indispensable in modern medical applications.

Titanium dioxide (TiO_2) coatings are extensively used in orthopedic and dental implants, promoting osseointegration by facilitating direct bone attachment and reducing the risk of implant failure. TiO_2 exhibits excellent antibacterial properties, preventing biofilm formation and lowering infection risks, a critical factor in implant success. Moreover, TiO_2 -based coatings have been explored for drug-eluting implants, where the surface can be functionalized to release antibiotics or growth factors to accelerate healing and reduce post-operative complications. The photocatalytic activity of TiO_2 also makes it useful in sterilization applications, where it can degrade organic contaminants under UV exposure, further improving infection control [4].

Zinc oxide (ZnO) coatings have gained attention for their antimicrobial effects, making them valuable components in wound dressings, catheters, and biomedical coatings that require infection resistance. ZnO nanoparticles are particularly effective in combating antibiotic-resistant bacteria, offering a promising alternative in the fight against hospital-acquired infections. Additionally, ZnO coatings have been investigated for their role in promoting wound healing by stimulating cell proliferation and collagen synthesis, making them highly beneficial in regenerative medicine applications [5].

Alumina (Al_2O_3) coatings are widely utilized for their superior wear resistance and chemical stability, enhancing the durability of joint prostheses and dental restorations. These properties contribute to reducing material degradation and extending implant lifespan. Beyond orthopedic applications, Al_2O_3 coatings are also employed in cardiovascular implants such as stents and heart valves, where their biocompatibility and corrosion resistance improve the reliability of these life-saving devices. Furthermore, Al_2O_3 coatings provide a strong diffusion barrier against ion leaching, which is critical in preventing metal ion release from implants into surrounding tissues, reducing potential inflammatory responses and allergic reactions [6].

Hydroxyapatite (HA) coatings, often combined with metal oxides, further enhance bone integration due to their chemical similarity to

natural bone minerals. HA-TiO₂ composite coatings have been shown to improve bone cell adhesion, accelerate mineralization, and enhance mechanical strength, making them an excellent choice for next-generation orthopedic implants. With the growing demand for smart biomedical coatings, researchers are developing multi-functional metal-oxide coatings that combine bioactivity, drug delivery, and real-time health monitoring [4]. Advances in nanotechnology and surface engineering allow for the creation of coatings with tunable properties, such as pH-responsive drug release or coatings embedded with biosensors for real-time diagnostics. These innovations are paving the way for a new era of personalized and responsive implant technologies, significantly improving patient outcomes and the long-term success of biomedical devices.

The energy sector relies on metal-oxide coatings for improving the longevity and efficiency of fuel cells, lithium-ion batteries, and solar panels. These coatings enhance electrochemical stability, thermal endurance, and overall energy efficiency, playing a crucial role in next-generation energy storage and conversion technologies. Lithium cobalt oxide (LiCoO₂) remains a leading cathode material in battery technology due to its high energy density and excellent electrochemical performance [7]. However, advancements in coating materials, such as lithium iron phosphate (LiFePO₄) and lithium nickel manganese cobalt oxide (LiNiMnCoO₂ or NMC), are emerging as alternatives that offer improved safety, longer lifespan, and reduced dependence on scarce resources. Additionally, protective oxide coatings, such as aluminum oxide (Al₂O₃) and magnesium oxide (MgO), are applied to battery electrodes to mitigate capacity fading and improve cycle stability by preventing unwanted side reactions between the electrolyte and active materials.

Yttria-stabilized zirconia (YSZ) serves as an effective electrolyte in solid oxide fuel cells (SOFCs), offering excellent ionic conductivity and chemical stability at high temperatures. Recent research explores doped ceria (CeO₂) and perovskite oxides as alternative electrolyte materials, aiming to reduce operating temperatures and enhance efficiency. In addition, oxide coatings based on lanthanum strontium manganite (LSM) and cobalt-based perovskites are used in cathodes to optimize oxygen reduction reactions, improving overall fuel cell performance and durability.

Anti-reflective coatings based on silicon dioxide (SiO_2) and titanium dioxide (TiO_2) enhance light absorption and energy conversion efficiency by minimizing reflection losses on photovoltaic surfaces. Advanced multilayer coatings incorporating hafnium oxide (HfO_2) and aluminum oxide (Al_2O_3) are also being investigated to further boost light transmission while maintaining excellent environmental durability. Additionally, transparent conductive oxide (TCO) coatings, such as tin-doped indium oxide (ITO) and fluorine-doped tin oxide (FTO), improve the efficiency of thin-film solar cells by facilitating better charge carrier transport [8].

Moreover, metal-oxide coatings are increasingly applied in concentrated solar power (CSP) systems, where selective absorber coatings based on nickel oxide (NiO) and tungsten oxide (WO_3) help maximize solar heat absorption while reducing thermal emittance. These innovations are critical in improving the operational efficiency and reliability of renewable energy systems, paving the way for more sustainable and high-performance energy solutions.

Black chromium coatings modified with aluminum and titanium are an effective protective barrier for AISI 304 stainless steel, shielding it from the harsh conditions of water-water energetic reactors (WWER-1000, WWER-440). High temperature and pressure in the reactor coolant accelerate intergranular, fatigue, and uniform corrosion, compromising the structural integrity of critical components. The application of these protective coatings significantly reduces the corrosion rate. It prevents the dissolution of oxide films, thereby enhancing the material's durability and extending its operational lifespan in aggressive environments [9; 10].

The choice of coating deposition methods depends on the required structure, thickness, adhesion to the substrate, and technological feasibility. Generally, all methods for obtaining metal-oxide coatings can be categorized into three main groups: chemical, physical, and vacuum-based methods (Figure 1). Each of these groups has its characteristics, determining their suitability for specific operating conditions.

A comprehensive analysis of existing methods for obtaining metal-oxide coatings allows for evaluating their advantages, limitations, and application areas. A detailed examination of the technological aspects of each method will provide recommendations for optimizing processes and improving the efficiency of coating deposition for various engineering applications.

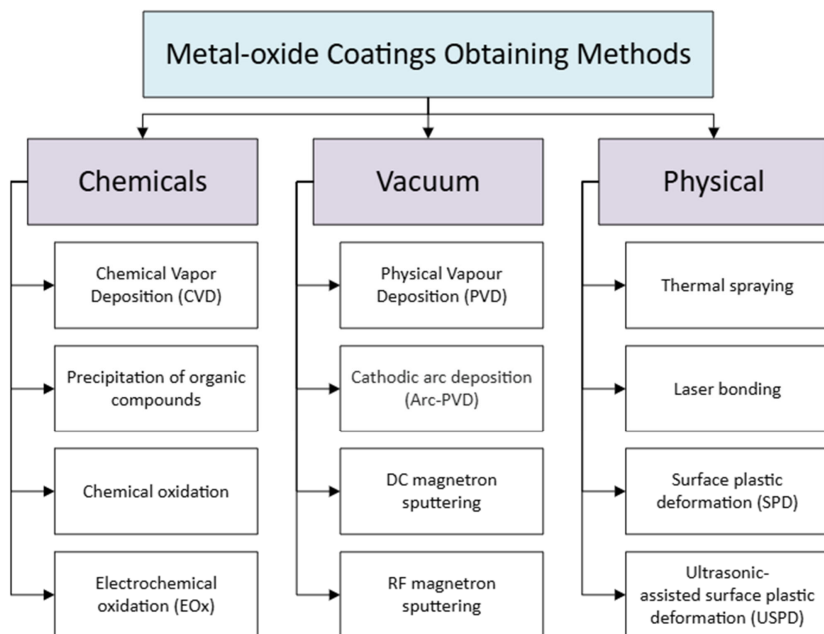


Figure 1. Methods of Obtaining Metal-oxide Coatings on Metallic Surfaces

2. Methods based on chemical processes

Chemical methods for obtaining metal-oxide coatings are widely employed due to their ability to form uniform, adherent, and functionally tailored coatings on various substrates. These processes involve chemical reactions that lead to the deposition of oxide layers, often providing enhanced corrosion resistance, thermal stability, and mechanical durability. Compared to physical methods, chemical approaches generally offer better coating uniformity, even on complex geometries, and can be performed under relatively mild conditions. However, some of these techniques require high temperatures, specialized chemical precursors, or extended processing times. This section presents key chemical methods for metal-oxide coating formation, including chemical vapor deposition (CVD), deposition from solutions of organometallic compounds, chemical

oxidation, and electrochemical formation, each offering distinct advantages and limitations.

The Chemical Vapor Deposition (CVD) Method is a well-known coating deposition technology introduced into the industry as early as the 1960s. It is widely used to produce functional materials, which can be applied as hard, corrosion-resistant, and heat-resistant coatings for micro- and optoelectronics, energy, and other industries [11].

The formation of metal-oxide coatings occurs through a chemical reaction of gaseous reagents on a heated material surface inside a sealed chamber, following these stages: the supply of vapor-phase particles to the material, adsorption of vapor-phase particles on the material surface, decomposition of reagents on the material surface and the formation of metal-oxide coatings, desorption of reaction products and their removal from the chamber. For example, to form a TiO_2 coating, steel samples were placed on graphite rods, which were inductively heated by radiofrequency to 750°C under vacuum. The thermal decomposition of $\text{Ti}(\text{OPr}^i)_4$ during film growth [12]:



Coatings produced by the Chemical Vapor Deposition (CVD) technology are typically homogeneous, exhibit high adhesion, and possess low porosity [11]. This method allows for the formation of metal-oxide coatings not only on flat surfaces but also on materials with complex geometries [13]. Another significant advantage, compared to other methods, lies in its relative cost-effectiveness and the simplicity of equipment requirements. However, this technology also has considerable drawbacks. One of the primary limitations is the necessity of high temperatures (600°C and above) to provide the kinetic energy required for metal-oxide coating formation, which restricts its application when coating materials with low melting points. Additionally, the process is toxic and poses a fire hazard due to using volatile reagents and the chemical interaction products involved [14].

Method of Deposition from Solutions of Organometallic Compounds.

The deposition of metal-oxide coatings from solutions of organometallic compounds is an established technique that enables precise control over the chemical composition and microstructure of the resulting coatings. This method relies on the decomposition of organometallic salts, particularly

metal alkoxides, leading to the formation of a sol, which subsequently undergoes a sol-gel transformation. The versatility of this approach allows for the deposition of coatings with tailored properties, including enhanced corrosion resistance, mechanical strength, and thermal stability [15].

The process consists of several key stages. The precursor solution is initially prepared by dissolving metal alkoxides in an appropriate solvent, often combined with stabilizing agents or catalysts to regulate hydrolysis and condensation reactions. The solution then undergoes controlled hydrolysis and polycondensation reactions, forming a stable sol with dispersed colloidal particles. This sol is subsequently applied to a metallic substrate via various deposition techniques such as dip-coating, spin-coating, or spray-coating, depending on the required coating thickness and uniformity. Once deposited, the sol gradually transforms into a gel, followed by a drying step to remove residual solvents. The final stage involves high-temperature treatment, typically between 200°C and 800°C, to achieve densification, crystallization, and enhanced adhesion of the oxide layer to the substrate.

A widely studied example involves the deposition of silicon-based coatings on AISI 316 stainless steel using silicon alkoxides as precursors. These coatings exhibit high corrosion resistance, particularly in aggressive environments, making them a viable alternative for metallic implants and biomedical applications. Additionally, titanium-based organometallic precursors, such as titanium isopropoxide, are frequently used to form TiO_2 coatings with photocatalytic and protective properties [16].

One of the most significant advantages of this method is the ability to precisely adjust the composition of the coating by varying the concentration of the initial components in the solution. This flexibility allows for incorporating multiple metal oxides, enabling the fabrication of composite coatings with enhanced functional properties. Moreover, the sol-gel approach promotes a high degree of homogenization of the precursor components, which reduces processing temperatures and facilitates the production of thick, uniform films. The relatively low-temperature processing makes this method suitable for coating temperature-sensitive substrates that cannot withstand the high temperatures required by techniques such as chemical vapor deposition (CVD).

Despite its advantages, the sol-gel method has some limitations. One of the main drawbacks is the lengthy processing time, as the gelation,

drying, and densification steps often require several days to complete. Additionally, environmental factors such as humidity and temperature fluctuations during the sol-gel transition can influence the final coating properties, requiring careful process control to ensure reproducibility. Furthermore, while the method effectively produces uniform coatings on flat and curved surfaces, challenges may arise in coating highly complex geometries without defects such as cracking or delamination [17].

Overall, the deposition of metal-oxide coatings from organometallic solutions remains a highly versatile and widely used approach in various industrial and research applications, including protective coatings for biomedical implants, electronic devices, and high-temperature oxidation-resistant surfaces. Continued advancements in precursor chemistry and process optimization are expected further to expand the capabilities and applicability of this method.

The chemical oxidation method is widely used for forming oxide films on metal surfaces, offering an efficient and relatively simple approach to improving corrosion resistance, aesthetic appearance, and functional properties. This process involves immersing the metal in oxidizing solutions or molten salts that contain active oxidizing agents such as chromates, nitrates, and permanganates. Depending on the chemical composition of the oxidation bath and the process conditions, the resulting oxide coatings can vary in thickness, porosity, and protective characteristics.

The kinetics of chemical oxidation depends on the diffusion of reactants through the solution and the oxide layer itself. The process generally follows the parabolic rate law, which indicates that oxidation slows down as the oxide layer thickens due to increased diffusion resistance. The oxidation rate is influenced by several factors:

1. **Reaction at the Metal-Solution Interface.** Initially, the metal reacts with oxidizing species in the solution, forming a thin oxide layer. The nucleation and growth of oxide films are influenced by temperature, pH, and the availability of active oxidizing agents.

2. **Ion Migration and Oxide Growth.** Once the initial oxide film is formed, further oxidation occurs through the inward diffusion of oxygen anions (O^{2-} , OH^-) and outward migration of metal cations (M^{n+}). The rate of diffusion through the oxide layer determines the overall growth kinetics.

3. Passivation and Stability. At a critical thickness, the oxide film may become a diffusion barrier, slowing down further oxidation and leading to passivation. However, aggressive environments or chloride-containing solutions may disrupt the protective layer, causing localized corrosion or pitting.

Chemical oxidation is broadly categorized into acidic and alkaline oxidation processes. Acidic oxidation typically utilizes strong oxidizing acids, including nitric (HNO_3), orthophosphoric (H_3PO_4), and hydrochloric (HCl) acids, often combined with additional components such as calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) and manganese compounds to influence film properties. This type of oxidation is commonly employed to create thin, dense oxide layers that enhance adhesion and corrosion resistance. Alkaline oxidation, on the other hand, is performed in solutions containing hydroxides, such as sodium or potassium hydroxide, along with oxidizing agents like sodium nitrite (NaNO_2) or potassium permanganate (KMnO_4). The process is usually conducted at temperatures ranging from 30 to 180°C, with variations in concentration and temperature significantly affecting the oxide layer's microstructure and performance [6].

The resulting oxide layers serve multiple industrial purposes. In aerospace and automotive applications, chemical oxidation produces coatings that improve wear resistance and reduce friction on moving components. In architectural and decorative applications, chemically oxidized layers provide an attractive finish, particularly for stainless steel and aluminum alloys. Furthermore, controlled chemical oxidation processes are employed in electronics and microfabrication to create functional oxide films that modify electrical conductivity, surface energy, or optical properties.

A practical example of chemical oxidation was demonstrated in research where colored oxide films were obtained on AISI 304 stainless steel using an aqueous solution containing H_2SO_4 – 490 g/L, CrO_3 – 250 g/L, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ – 7 g/L, ZnSO_4 – 5 g/L, and MnSO_4 – 4 g/L. The inclusion of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ enhanced the wear resistance of the oxide film, while ZnSO_4 stabilized the coloring potential, and MnSO_4 accelerated the coating formation process. The ability to manipulate the composition of the oxidation bath enables fine-tuning of the coating's mechanical and optical properties, making this technique highly adaptable for various industrial applications [18].

However, despite its advantages, chemical oxidation has notable limitations. The protective layers formed through this process generally exhibit lower corrosion resistance than coatings obtained via electrochemical methods, as they tend to be thinner and more porous. Additionally, certain chemical oxidation processes involve toxic or environmentally hazardous chemicals, necessitating strict waste disposal and treatment protocols. Forming uniform, defect-free coatings on complex geometries can also be challenging, requiring precise control of bath composition, temperature, and immersion time.

To further enhance the performance of chemically oxidized coatings, post-treatment processes such as oil impregnation, sealing in hot water, or additional chemical passivation are often employed. These secondary treatments help to reduce porosity, improve wear resistance, and extend the service life of the coatings, making them more suitable for demanding environments. Continued research in this field focuses on developing greener oxidation processes that eliminate hazardous reagents while maintaining or even improving coating performance.

In summary, the chemical oxidation method remains an important and versatile technique for producing protective oxide films. While it is widely utilized for decorative, functional, and anti-corrosion applications, its effectiveness can be further optimized through careful selection of oxidation conditions and post-treatment strategies.

The electrochemical oxidation (EO_x) method is a widely used technique for depositing metal-oxide coatings, leveraging electrochemical reactions to form protective and functional oxide layers on metallic surfaces. Widely applied to materials such as stainless steel, titanium, and aluminum alloys, involves the controlled electrochemical growth of an oxide layer in an electrolyte solution under the influence of an external current. This process involves the application of an electric current to a conductive solution or molten salt bath containing metal ions, leading to the formation of an adherent oxide film on the substrate. The ability to precisely control deposition parameters makes EO_x a highly effective approach for engineering coatings with tailored physicochemical properties [19].

The electrochemical oxidation process follows a complex mechanism governed by electrochemical kinetics and ionic transport phenomena. The key steps in the formation of oxide layers include:

1. Ion Transport and Surface Adsorption

When an external potential is applied, metal cations (M^{n+}) dissolve into the electrolyte, while oxygen-containing anions (O^{2-} or OH^-) migrate towards the metal surface. The applied voltage influences the migration of ions and dictates the rate at which oxidation occurs.

2. Oxide Nucleation and Growth

Oxide layer formation begins with the adsorption of oxygen species on the metal surface, leading to the formation of an initial passive layer. The growth mechanism can be described by the Pilling-Bedworth ratio, which defines the volume expansion between the metal and the resulting oxide film. A ratio greater than 1 generally indicates a compact, protective layer, whereas a ratio below 1 results in porous or non-adherent coatings.

3. Diffusion-Controlled Oxide Layer Thickening

As the oxide layer thickens, the rate of oxidation becomes limited by the diffusion of oxygen ions and metal cations through the oxide layer. The applied current density and electrolyte composition significantly impact the final microstructure and porosity of the coating.

4. Passivation or Breakdown

In some cases, a stable and protective oxide layer is formed, preventing further oxidation (passivation). However, under aggressive electrochemical conditions, the oxide layer may degrade due to pitting corrosion or mechanical stress, reducing its protective efficiency.

One of the key benefits of the electrochemical oxidation method is its ability to produce coatings with exceptional mechanical and chemical characteristics. Oxide layers formed via this process exhibit high hardness, superior wear resistance, low porosity, and excellent corrosion protection, making them suitable for harsh environments. The method is extensively used in aerospace, biomedical, energy, and electronics industries, where durable protective coatings are essential.

A distinct advantage of EO_x is the precise regulation of coating thickness, which is particularly important for minimizing material waste and conserving expensive or rare metals. By adjusting parameters such as voltage, current density, electrolyte composition, and deposition time, it is possible to achieve oxide layers with specific thicknesses and microstructures. This level of control allows for the formation of dense, uniform coatings, which enhance the performance of coated materials [21; 22].

Recent research has demonstrated the effectiveness of electrochemical oxidation in improving the properties of metal surfaces. Studies [19] have focused on the structural and phase analysis of TiO_2 -based composites, revealing the potential of electrochemical oxidation for creating coatings with enhanced thermal and chemical stability. Another study by [20] analyzed the structure and anticorrosion properties of oxide coatings on AISI 304 stainless steel, highlighting the significant improvement in corrosion resistance achieved through electrochemical oxidation techniques. The work of Junqueira et al. [21] provided insight into the morphological, chemical, and mechanical characteristics of anodic coatings on stainless steel, demonstrating the potential of this method for improving surface hardness and adhesion properties. Additionally, research by Shen et al. [22] investigated the formation of Al_2O_3 coatings on stainless steel/aluminum composites via micro-arc oxidation, confirming the capability of electrochemical oxidation in producing dense and wear-resistant ceramic coatings.

One of the key advantages of electrochemical oxidation is its ability to modify the microstructure of the oxide layer to enhance specific performance characteristics. Coatings with tailored porosity, crystallinity, and adhesion strength can be obtained by adjusting electrolyte composition, applied voltage, and processing time. This adaptability allows for the optimization of coatings for various applications, including aerospace, biomedical, and energy sectors. Additionally, the method provides a sustainable and cost-effective alternative to other high-temperature deposition processes, as it can be performed under ambient conditions and requires relatively simple equipment [20].

Despite its numerous benefits, electrochemical oxidation has certain limitations. While highly protective, the oxide layers formed through this method may exhibit higher porosity compared to coatings produced by chemical vapor deposition or thermal spraying. This can impact the barrier properties of the coating, requiring post-treatment processes such as sealing or impregnation with corrosion inhibitors to improve long-term stability. Furthermore, the choice of electrolyte plays a crucial role in determining coating quality, as some solutions may introduce impurities or lead to non-uniform layer formation.

Nevertheless, electrochemical oxidation remains one of the most versatile and widely researched methods for enhancing the surface properties of metals. With ongoing advancements in electrolyte formulations and process optimization, this method is a promising approach for developing high-performance oxide coatings with applications in harsh environments requiring superior durability and protection.

3. Methods Based on Vacuum Technologies

The Physical Vapor Deposition (PVD) method encompasses a wide range of deposition processes that employ various physical vapor-phase technologies. These include evaporation, sputtering, laser ablation, or ion plating, all of which displace solid materials in the form of atoms or molecules [23]. The displaced atoms or molecules are transported through a vacuum or low-pressure environment and condense onto different substrates, forming thin solid coatings. Additionally, in a process known as reactive deposition, these atoms or molecules interact with gases introduced into the deposition chamber, forming new compounds.

The process of forming metal-oxide coatings using PVD technology can be divided into three key stages: generation of vapor-phase evaporation and sputtering; transport of vapor species from the initial target to the substrate; nucleation and growth of the coating on the substrate. During PVD processes, each stage can be independently controlled, allowing precise regulation of the coating's structure, properties, and deposition rate [23].

Studies have shown [24] that at a critical temperature of approximately 500°C, Al_2O_3 undergoes a phase transition into an amorphous modification. Nitrogen was introduced into the deposition process to stabilize the structure at higher temperatures to counteract this transformation. As a result, the $\text{TiAlN-Al}_2\text{O}_3$ coating obtained through this method exhibits high hardness, superior wear resistance, and a refined microstructure [25].

Cathodic arc-deposition (Arc-PVD). The method is based on using a vacuum arc to generate a flow of highly ionized metallic plasma, which is formed by the evaporation of the cathode material. Applying a high negative potential to the substrate promotes its effective cleaning through the sputtering of the surface by ions of the deposited material, as well as activating the diffusion of atoms into the substrate. This ensures strong adhesion of the coating to the substrate material. Introducing a reactive

gas into the vacuum chamber enables the synthesis of coatings based on compounds with high physical and mechanical properties.

When the vacuum arc is ignited on the surface of the cathode target, a cathode spot is formed, from which the cathode material evaporates and is further ionized in the electric field near the cathode. The resulting plasma is almost fully ionized and contains multicharged ions along with a droplet phase of the target material, with the fraction of the droplet phase being approximately 10% for low-melting-point metals and about 1% for refractory metals.

Among the various approaches to improving functional coatings, the concept of multilayer coatings appears to be the most promising. Such coatings can meet a wide range of often conflicting requirements, including low friction, high wear resistance, diffusion barrier properties, high interlayer adhesion strength, reduced internal stress levels, and a balanced combination of hardness and toughness.

In addition, combined coatings can be formed, including metastable and multicomponent structures that alternate and combine different properties of individual layers in a single coating.

DC magnetron sputtering. DC sputtering is a thin film deposition technique that uses direct current (DC) to deposit films from electrically conductive target materials onto a substrate. It is commonly used for applying metal coatings due to its cost-effectiveness, efficiency, and ability to produce uniform, high-quality thin films when working with conductive materials [26].

DC magnetron sputtering enhances this process by using magnets behind the target to trap positively charged ions near the target surface. The deposition occurs within a vacuum chamber to eliminate contaminants that could interfere with the film formation. A high-purity inert gas, typically argon, is introduced inside the chamber. When subjected to a DC or pulsed-DC current, the gas ionizes, enabling the sputtering process.

In this setup, the metal target serves as the negative electrode (cathode), while the substrate acts as the positive electrode (anode). Applying a DC electrical current ionizes the argon gas, causing its ions to collide with the negatively charged target material. These high-energy collisions dislodge metal atoms from the target, releasing them into the plasma – a mixture of ionized argon atoms and electrons. The substrate, positioned in the path of

this vapor flux, allows the metal atoms to condense onto its surface, forming a thin film coating of the target material.

While DC sputtering is highly effective for conductive metals, it is less suitable for dielectric materials. These materials can accumulate charge, leading to arcing and electron flow disruptions, which result in an uneven deposition rate. Excessive accumulation of positive ions may even cause the sputtering process to halt, requiring a system reset to resume operation.

A certain percentage of oxygen is added to the working gas atmosphere to obtain oxide coatings by direct current magnetron sputtering. This method of obtaining thin-film structures is called reactive magnetron sputtering.

For example, in [27], the influence of oxygen flow rate on the structural, optical, and morphological properties of TiO_x films deposited using reactive direct-current magnetron sputtering was studied. DC magnetron sputtering grown films observe a sub-stoichiometric behavior below 14 sccm, and over-stoichiometric behavior after this value of QO_2 flow rate. DC magnetron sputtering deposited films showed single-phase pure anatase. Through the analysis of grain size, the films-based DC magnetron sputtering technique showed higher grains. The average transmittance value of thin TiO_x films was around 87%, and the absorption edge exhibited a blue shift with increasing the oxygen flow rate in work gas. Importantly, optical band gap values were lower in the case of DC magnetron sputtering grown films, and their values were decreasing as a function of oxygen flow rate. SEM images reveal a continuous and crack-free surface morphology for TiO_2 films and confirm the higher crystal grains in the case of DC magnetron sputtering deposited films.

RF magnetron sputtering. Radiofrequency (RF) sputtering is a vacuum technique designed to prevent charge buildup that can occur with certain target materials, as seen in DC sputtering. Accumulated charge can disrupt the sputtering process and compromise film quality, making RF sputtering a preferred method for depositing insulating or dielectric materials [28].

The process consists of two key steps: ionization of the sputtering gas and the subsequent sputtering of material from the target onto the substrate. Unlike DC sputtering, RF sputtering utilizes a high-voltage RF power source to alternate the electrical potential in the vacuum environment. This alternating current prevents the accumulation of charged plasma particles

by continuously reversing the polarity, effectively neutralizing excess charge at the end of each cycle [29].

During the first cycle, if the target material carries a negative charge, ionized gas particles remain at the anode, stabilizing the environment for deposition. In the next cycle, reverse polarization switches the charge on both the target and substrate, causing positively charged sputtering gas atoms to move toward the now negatively charged substrate. This process ensures a steady deposition rate while avoiding electrical imbalances.

The primary limitation of RF sputtering is its lower deposition rate compared to pulsed DC sputtering and its significantly higher power consumption. Although introducing a strong magnetic field along the power source can improve deposition efficiency by keeping the plasma discharge closer to the target surface, RF sputtering remains more energy-intensive than other sputtering techniques.

For example, in [30], thin films of titanium dioxide (TiO_2), with thicknesses ranging from 105 to 231 nm, were deposited on glass substrates using radio-frequency (RF) magnetron sputtering in an argon atmosphere at four distinct RF power levels: 40, 70, 100, and 130 W, with the deposition time, kept constant. The crystallinity of the films improves with increasing RF power, corresponding to an increase in film thickness. Consequently, the samples transition from a poorly crystalline or amorphous structure to a monocrystalline rutile phase with a (110) texture. However, at the highest RF power studied, this texture is partially disrupted by the formation of nanocrystals with different orientations. The surface roughness exhibited multifractal characteristics, with complexity systematically decreasing and surface stiffness reducing as RF power increased. The films exhibited a notable increase in the refractive index and a decrease in the optical band gap, from 3.81 eV to 3.52 eV, as the RF power was increased. This underscores the influence of RF power on the optical and semiconductor properties of TiO_2 films.

4. Methods based on physical processes

Thermal spraying method. The essence of thermal coating application processes lies in the formation of a directed flow of dispersed particles of the spraying material, ensuring their transfer to the surface of the product and the formation of a coating layer. The coating is created due to

adhesion that occurs when the particles collide with the substrate surface. The spraying particles are in the form of a powder or can be obtained by melting and gas fragmentation of the initial material – wire, rods, plasticized mass, etc. Various high-temperature gas environments are used for particle acceleration. Heating the spraying material is carried out to increase the plasticity and adhesion ability of the particles [31].

The formation of thermal coatings occurs in multiple stages. The first stage involves the spraying particle and substrate being approached to the distance of interatomic interaction. In the second stage, a chemical bond is formed between the atoms due to electron exchange. The third stage involves volumetric interaction, which is limited by the time the contact zone maintains high temperatures. The chemical and thermal processes occurring in all three stages of particle interaction with the sample or the deposited layer determine the adhesion strength between the coating material and the substrate.

Thermal coatings are applied to protect surfaces from wear and high temperatures. They are also widely used to restore the geometry of products that have been damaged during production or operation.

Studies have shown [31] that coatings obtained by this method on AISI 321 steel can restore the appearance of an automobile engine cylinder body and have been used in some industrial manufacturing processes. However, the coating is highly prone to cracking due to internal stress during deposition, making parameter control challenging for practical applications.

The advantages of gas-thermal spraying coatings include:

- Relatively high process productivity (up to 8-10 kg/min of self-fluxing alloy powders) with a high material utilization coefficient (over 95%);
- Relatively low noise and light emissions, allowing operators to work without additional protective equipment;
- Low cost and mobility of the equipment, enabling on-site application without dismantling the products.
- The main disadvantages of the gas-thermal spraying method for powder coatings are:
 - Limitations on the spraying materials due to melting temperature (not exceeding 300°C);
 - Insufficient adhesion strength of the coatings to the substrate;

- High coating porosity, which prevents their use in corrosive environments without additional treatment;
- Relatively high equipment cost.

Laser bonding method. An equally relevant method today is laser bonding, which is based on the process of surfacing a coating layer onto the surface of metal or alloy using a laser to ensure the corrosion resistance of the material [32]. It is known [33] that during laser heating of metals in an oxygen or air environment, oxide layers form on their surface, growing even under very short laser pulse exposure (around 100 ns). The process of surface isometric oxidation of metals occurs in several stages, including oxygen adsorption on the surface, binding of its free electrons to metal or oxide, diffusion formation, and electro-migration of metal and oxygen ions through reaction product defects at grain boundaries, as well as the actual oxidation chemical reaction. The key factor determining the oxidation kinetics of metal is the thermal interaction of laser radiation with the metal and the metal-oxide system.

According to [32], the introduction of a rare-earth oxide such as Y_2O_3 into the WC coating composition on AISI 304 steel increases corrosion resistance. However, an excessive amount of the modifying substance significantly reduces the material hardness, making these coatings unsuitable for wear-resistant applications. Additional disadvantages include the presence of transverse cold microcracks in the surfaced layers, which result from the relaxation of high internal tensile stresses, as well as the high cost of the process due to the expensive laser equipment. The advantages of this method include the formation of coatings with a dense microstructure and strong metallurgical bonding with the substrate [33].

Method of intensive plastic deformation of the surface layer, ultrasonic interaction is based on the synthesis of high-strength metal-oxide coatings, particularly by introducing reinforcing particles into the surface layers of the matrix material. In [34], AISI 316 steel was subjected to this type of treatment to improve its surface properties, resulting in a nanostructured surface layer with a thickness of 15 μm . The stainless steel demonstrated increased hardness and wear resistance, as well as a reduction in surface roughness compared to the untreated sample. The nanostructured surface layer exhibited high hardness, allowing it to withstand severe abrasive wear.

This method has several significant advantages:

- Simple technical implementation, as it allows for strengthening already manufactured parts and products;
- Simultaneous formation of metal-oxide coatings and deformation strengthening of the matrix material;
- Prevention of sample heating during the process.

Thus, an analysis of the existing methods for obtaining metal-oxide coatings shows that the most appropriate approach is the electrochemical oxidation method, as it is economically less costly and offers virtually unlimited possibilities for controlling coating properties, thickness, and composite material composition.

4. Conclusions

The comparative analysis of various deposition techniques for metal-oxide coatings demonstrates that each method offers distinct advantages and limitations, making them suitable for different industrial and technological applications. Chemical methods, such as chemical vapor deposition (CVD) and sol-gel techniques, provide precise control over the chemical composition and microstructure of coatings, allowing for high uniformity and tailored functional properties. However, their reliance on high processing temperatures and specialized precursors limits their cost-effectiveness and scalability for large-scale industrial use.

Electrochemical oxidation emerges as a highly effective and scalable technique for forming metal-oxide coatings, particularly due to its ability to control coating thickness, composition, and morphology through electrolyte composition and applied voltage. The adaptability of electrochemical oxidation makes it an attractive choice for industries requiring high-performance coatings with enhanced corrosion resistance, mechanical durability, and adhesion to substrates. Despite some limitations, such as the potential for porosity in oxide layers, advancements in electrolyte formulations and post-treatment processes continue to improve the quality and functionality of electrochemically deposited coatings.

Physical deposition methods, including thermal spraying, magnetron sputtering, and laser-assisted deposition, provide significant benefits in terms of coating density, adhesion strength, and wear resistance. Vacuum-based deposition techniques, such as magnetron sputtering, allow for the fabrication of coatings with superior structural integrity and tailored physical

properties, making them ideal for applications in aerospace, biomedical engineering, and energy storage devices. However, these techniques often require complex and costly equipment, limiting their accessibility for certain industrial applications.

The selection of an optimal deposition method depends on several factors, including the intended application, substrate material, required coating thickness, and economic feasibility. Electrochemical oxidation remains the most viable technique for large-scale applications due to its cost-effectiveness and process versatility, while advanced vacuum-based methods offer superior performance characteristics for high-tech industries.

Future research should focus on optimizing deposition parameters to enhance coating performance, developing hybrid deposition techniques that combine the advantages of different methods, and exploring new materials with improved functional properties. Additionally, advancements in environmentally friendly deposition processes will play a crucial role in minimizing the ecological impact of coating technologies while maintaining high performance and durability.

This study provides a comprehensive evaluation of metal-oxide coating technologies, offering practical recommendations for selecting appropriate deposition methods based on specific application requirements. The insights gained from this research contribute to the further development of high-performance coatings, improving their efficiency and expanding their applicability across various engineering sectors.

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