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REGULAR ARTICLE

Emerging Trends in Nanostructured Coatings: Unraveling Processing Techniques, Corrosion Mechanisms, and Tribological Performance

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Surface corrosion and wear significantly limit the lifetimes of industrial components, resulting in high economic and safety costs. However, as surface-level phenomena, these degradation mechanisms can potentially be mitigated through surface modifications alone, without altering bulk properties. Recent advances in nanotechnology have made possible a range of nanostructured protective coatings for surfaces. By incorporating nanomaterials like ceramics and metals, these coatings provide enhanced resistance to chemical corrosion and physical wear. This review discusses the current state of research on nanostructured coatings for surface protection. It summarizes the synthesis techniques for producing nanostructured coatings such as sol-gel and electrochemical deposition methods. The corrosion and tribological behaviors of various coating materials like metal oxides and nitrides are compared. Composite polymer-metal coatings are highlighted for their superior crack resistance compared to traditional ceramic coatings. In addition, bio-inspired self-healing and lubricating coatings are described. Finally, current technical challenges and future research directions are outlined such as improving coating adhesion strength and scale-up for mass production and commercialization.

Keywords: Nanostructured coatings, Cladding, Microstructure, Temperature, Nanofluids, Heat Transfer.

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1. INTRODUCTION

Nanotechnology involves materials less than 100 nm in size and has expanded exponentially since the 1980s. Nanomaterials have at least one dimension in the nanoscale, resulting in high surface area-to-volume ratios. This imparts unique chemical, physical, optical, thermal, and mechanical properties not seen in larger-scale materials [1]. Consequently, nanomaterials now enable innovations in fields from energy conversion to biomedicine. However, industrial systems still face major limitations like corrosion, wear, and friction causing safety risks, efficiency losses, and economic impacts [2].

Surface protection presents a key strategy to mitigate these issues. Surface enhancement through nanocoatings has become a major area of interest due to the vast array of attainable functionality. By engineering coatings at the nanoscale, the properties of the underlying surface can be tuned to achieve targeted performance objectives [3-5]. Common capabilities provided by nanocoatings include the introduction of hydrophobicity or oleophobicity to resist water and oils, lending anticorrosion barriers, altering electrical conductivity, minimizing friction, and preventing biofouling.

Additional specialized functionality may also be imparted through nanocoatings such as self-cleaning behavior, antistatic attributes, scratch resistance, antireflectivity, and UV blocking [6]. The tailored chemical and physical nature of nanocoatings thus allows customizable activation of surfaces to exhibit desired resistive, conductive, optical, wetting, and interfacial traits as demanded by the application at hand. The possibilities for novel surface property enhancement are therefore extensive with the engineering granularity afforded through nanocoatings. Nanostructured coatings uniquely leverage nanomaterials' benefits to enhance surface properties [7]. However, optimizing key coating parameters including thickness, adhesion strength, hardness, and more to meet application-specific demands has proven highly challenging [8]. During machining, stresses can degrade coatings, limiting component lifetimes across industries from automotive to aerospace.

Organic nanocomposite coatings utilizing SiO_2 nanofillers have emerged as an innovative corrosion protection method, offering improved durability and mechanical performance compared to conventional organic coatings alone. The enhanced properties were achieved by incorporating inorganic silicon dioxide nanoparticles into organic polymer matrices to generate hybrid coatings [9]. With its inorganic composition and nanoscale size, SiO_2 proved effective at enhancing coating properties. The inorganic properties provide improved barrier protection while the high surface area at the nanoscale allows improved interaction with the organic phase. Together,

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these factors enable nanocomposite coatings to exhibit superior properties compared to traditional organic coatings alone. Optimization of factors such as nanofiller dispersion, interfacial compatibility, and curing procedures present opportunities to further enhance the protectiveness of SiO_2 – organic nanocomposite coatings.

The hardness of nanocoatings can be enhanced through proper control of their elemental and phase composition, nanostructure, growth-induced macrostress, and/or strong covalent bonds between atoms. Fig. 1 demonstrates the key parameters affecting nanostructured coatings. Nanocoatings fall into three categories: crystalline, nanocomposite (nc), and amorphous (a). Two-phase nc coatings, the basis for multiphase coatings, are further divided based on phase content into: (1) nc coatings with low a phase and high nc phase content ($a \leq$ nc) and (2) nc coatings with high a phase and low nc phase content ($a >$ nc). Nanocoating properties strongly depend on grain size, inter-grain separation, grain composition and crystallographic orientation, and bonding between atoms within and between phases.

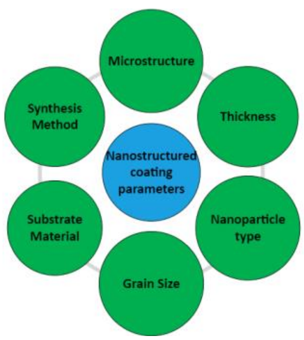

Fig. 1 – Parameters affecting nanostructured coatings

Metal oxides, graphene, carbon nanotubes and other coatings have shown promise for enhancing boiling heat transfer, yet practical challenges remain before widespread adoption. Nano-CuO and porous Al_2O_3 layers demonstrate up to 30% and boiling heat transfer coefficient (HTC) improvements respectively [10]. However, issues with thermal or mechanical integrity, including atomic defects and inadequate adhesion, hinder real-world viability. Ideal coatings must synergize scaffolded micro/nanostructures with tuned surface properties like wettability. Tailoring both physicochemical characteristics and topological features appears crucial for optimizing nucleate boiling while ensuring coating durability and heat transfer efficiency. But identifying optimal materials that harmonize enhanced heat transfer with robustness remains an open challenge. While metal oxides indicate boiling improvements through introduced surface porosity, graphene and nanotubes must better balance the change of thermal properties with mechanical resilience and anticorrosion barriers needed for practical operation. Coating developments show potential, but more research is essential to unify coating composition and hierarchical structures for truly customizable, defect-resistant, and high-performance boiling heat transfer surfaces.

While metal oxides have shown boiling heat transfer improvements, atomic-level defects undermine real-world viability by impairing thermal conductivity, mechanical resilience and anticorrosion barriers needed for robust operation [11]. Insufficient adhesion also plagues metal oxide coatings, necessitating materials advancements that interweave enhanced physicochemical properties with durable micro/nanostructuring. Optimized coatings must harmonize scaffolding topological features like porosity and wettability with superior thermal and anticorrosion properties for defect-resistant, high-performance boiling surfaces.

Graphene presents one nanomaterial solution, leveraging excellent thermal conductivity and mechanical properties to boost boiling heat transfer through nanostructured coatings [11]. However, tedious fabrication and integration has hindered widespread adoption. Streamlined preparation methods for graphene-metal oxide composite coatings have greater viability by simplifying scaling while uniting the advantages of both components. The facile integration of carbon and metal oxides on surfaces could enable customizable, durable and efficient boiling enhancement. Further research into rapidly prototyping optimized carbon-metal oxide composites provides a promising development path for thermal management advancements.

The practical application of metal oxide coatings in thermal management [12] is limited by insufficient thermal conductivity, mechanical strength, and anticorrosion properties stemming from atomic defects and weak physical adsorption, necessitating further research into ideal surface coating materials that can simultaneously tailor physicochemical characteristics and hierarchical micro/nanostructural features for optimized performance.

Nanostructured coatings on prosthetic implants are of great interest for biomedical applications. The prosthetic main body is typically a metal alloy that articulates against a polymer or ceramic surface [12]. Excellent tribocorrosion resistance and biocompatibility can be achieved by coating the surface with nanomaterials like whiskers, nanotubes, graphite, diamond, titanium, or tantalum. Anti-friction nanobiomaterial coatings can also provide antimicrobial functionality by incorporating nanoparticles like silver or tin to prevent infections. For example, nanostructured hydroxyapatite coatings on titanium alloys can increase biocompatibility while reducing graft-host rejection and infections for orthopedic implants. Silver fluoride hydroxyapatite nanopowder coatings have shown excellent antibacterial effects against various pathogens. Additionally, coating nanohydroxyapatite with a phospholipid bilayer can improve implant longevity. In summary, nanostructured coatings enable multifunctional prosthetic surfaces with tailored tribological, biocompatibility, and antimicrobial properties.

This review discusses recent advances in nanostructured coatings for next-generation surface protection. It summarizes nanoparticle-enabled coating synthesis techniques as well as corrosion and wear resistances of ceramic, metallic, and hybrid polymer-metal coatings. Biomimetic and self-healing coatings are highlighted as futuristic directions. Finally, scaling up nanostructured coatings is outlined as a central challenge for commercialization. With progress in understanding and production, nanoengineered coatings can reach their full potential in extending component lifetimes, system efficiencies, and reducing costs across critical engineering domains.

2. METHODOLOGY AND OBSERVATION

Scopus, a database owned by Elsevier B.V., and Web of Science are two premier sources for systematic and scientific literature. Both databases were utilized extensively in this study to compile basic bibliographic records for the literature review. Specifically, a search has been done in Scopus using the keyword "nanocoatings" in publications worldwide from 1997 through 2023.

The search spanned several fields related to nanofluids including chemical engineering, biomedical engineering, mechanical engineering, solar energy, wastewater treatment, transportation, and industrial cooling applications. By searching Scopus across these disciplines, analysis has been done on nanofluid use in heat exchangers over the past few decades and is represented in Fig. 2. From Fig. 2, it is evident that nanofluid in heat exchangers has been an area of interest for many researchers over the years. Increasing product functionality demands across diverse applications coupled with environmental sustainability benefits are driving global nanocoatings adoption.

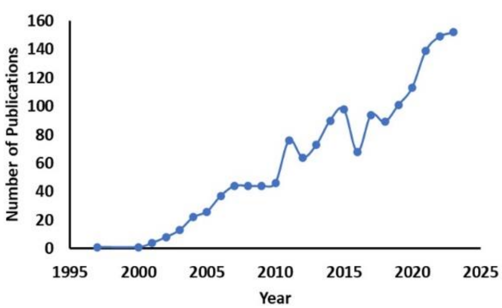

Fig. 2 – Number of articles published per year

3. SYNTHESIS OF NANOSTRUCTURED COATINGS

Nanostructured coatings can be fabricated through a range of methods tailored to the intended application [13]. In addition to conventional techniques like physical and chemical vapor deposition, novel approaches continue to emerge for nanocoating synthesis including laser cladding, sol-gel processing, and more. The choice of optimal technique depends on factors such as nanostructured morphology, adhesion requirements, and substrate compatibility. Fig. 3 provides an overview of nanostructured coating fabrication techniques ranging from vapor deposition methods to electrochemical processing to bio-inspired assembly approaches, enabling versatile nanoscale engineering of surface properties like corrosion and wear resistance.

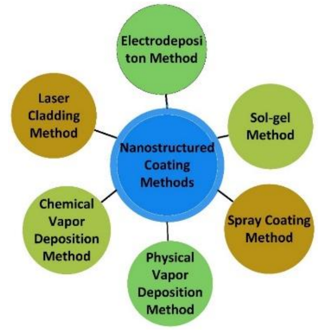

Fig. 3 – Overview of nanostructured coating fabrication techniques

Some of the most popular techniques employed to prepare nanocoatings and the controlling process parameters are summarized in Table 1. Atomic layer deposition offers the best control and conformality given its atomic layer precision, while sol-gel is the most economical method. Physical vapour deposition and Chemical vapour deposition provide good middle ground options balancing cost, throughput, and uniformity. The optimal method depends on the specific nanocoating properties and application requirements.

Table 1 – Insights into Coating Preparation: Techniques and Essential Process Parameters [13]

Method	Process Overview	Key Parameters	Materials Deposited
Chemical Vapor Deposition (CVD)	Precursor gases react and deposit material on heated substrates	Temperature, pressure, gas flowrates	Ceramics, metals, carbides, nitrides
Physical Vapor Deposition (PVD)	Material evaporated or sputtered and condenses on substrates	Power, chamber pressure, deposition rate	Metals, alloys, hard coatings
Thermal Spraying	Molten or semi-molten particles sprayed onto surfaces	Particle velocity, temperature, angle	Composites
Laser Cladding	Powder injected into laser melt pool on substrate	Laser power, scan speed	Metals, alloys, ceramics
Electrodeposition	Substrate biased to deposit metals from electrolyte	Applied potential, current, temperature	Alloys, composites, multilayers
Sol-Gel Processing	Multistep reactions transform precursor solutions into coatings	pH, temperature, catalysts	Ceramics, ceramic-polymer hybrids

4. CORROSION AND TRIBOLOGICAL BEHAVIOR

Ceramic nanostructured coatings [14] made from materials like nitrides, carbides, or oxides stand out for their high hardness, heat resistance, and wear resistance, albeit with a tradeoff in brittleness. Their low friction coefficients also make them suitable for applications requiring minimal friction losses. Metallic nanostructured coatings utilizing metals like copper, nickel, and silver are on the other end of the spectrum - they tend to be quite ductile and tough, with generally good corrosion resistance as well [15, 16]. The friction and wear properties of metallic nanostructured coatings can also be readily tuned through careful engineering of parameters like coating composition and microstructure.

Metal Nanocomposite coatings [17] aim to bridge the gap between the two, incorporating a synergetic blend of distinct phases like a ceramic or metal matrix infused with nano-sized particulate matter. This enables nanocomposite coatings to exhibit a versatile mix of enhanced mechanical and tribological attributes from both phases, including superior hardness, fracture toughness, and abrasion resistance compared to their constituent materials alone. The tunable nature of nanocomposite coatings enables multifaceted property customization to precisely fit application demands. By providing independent control points across factors like formulation, nanostructural structuring, and processing conditions, nanocomposite platforms facilitate intricate engineering of surface feature combinations. This expansive design flexibility allows specialized optimization of friction, wear resistance and other interfacial interactions to excel under diverse operating environments.

Bio-inspired self-healing and lubricating nanocoatings [18] have gathered significant attention in recent research due to their potential applications in various fields. Drawing inspiration from nature, these coatings aim to replicate biological processes that enable organisms to repair and protect themselves. Self-healing capabilities in these coatings involve the incorporation of microcapsules, vascular networks, or other mechanisms that can autonomously mend damage caused by wear and tear.

5. CHALLENGES IN DEVELOPING THE NANOSTRUCTURED COATINGS

Achieving uniform morphology and thickness across large surface areas during the process is difficult [19]. It is hard to prevent undesirable reactions between the nanostructured coating and the substrate and to ensure adhesion and limit delamination, especially for thick nanostructured coatings [19, 20]. Improving coating adhesion strength and scale-up for mass production and commercialization are a few difficulties found in this area.

6. CONCLUSION

This paper offers a comprehensive review of recently developed nanostructured coatings designed to provide improved protection against both corrosion and tribological challenges. Nanostructured and nanocomposite coatings offer promising corrosion protection and friction reduction properties arising from their nanoscale constitution. Various materials from ceramic and metallic to polymer matrices create unique multifunctional films when deposited with reinforcing nanofillers. However, effectively translating laboratory-scale innovation to industrial implementations remains challenging. Biologically inspired surface solutions are gaining attention to advance self-healing capacities. Additive manufacturing promises to unlock novel application-specific nanostructured coatings too. Future research initiatives in this field may involve the following aspects.

- High-throughput computational modeling to accelerate discovery of optimal nanostructures.
- Advanced characterization down to the nanoscale to enable better performance correlations.
- Exploration of phase transformations and other structural changes to dynamically tune tribological performance.
- Integration of multi-functional capabilities beyond wear/friction reduction, such as self-lubrication or self-healing.

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Нові тенденції в наноструктурованих покриттях: розгадка методів обробки, механізми корозії та трибологічні характеристики

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Поверхнева корозія та знос значно обмежують термін служби промислових компонентів, що призводить до високих економічних витрат і витрат на безпеку. Однак, як явища на поверхневому рівні, ці механізми деградації потенційно можуть бути пом'якшені лише за допомогою модифікації поверхні, не змінюючи об'ємних властивостей. Останні досягнення в області нанотехнологій зробили можливим ряд наноструктурованих захисних покриттів для поверхонь. Завдяки використанню таких наноматеріалів, як кераміка та метали, ці покриття забезпечують підвищену стійкість до хімічної корозії та фізичного зношування. У цьому огляді обговорюється поточний стан досліджень наноструктурних покриттів для захисту поверхні. Він узагальнює методи синтезу для отримання наноструктурованих покриттів, такі як методи золь-гель та електрохімічного осадження. Порівнюється корозійна та трибологічна поведінка різних матеріалів покриття, таких як оксиди та нітриди металів. Композитні полімерно-металічні покриття виділяються своєю кращою стійкістю до розтріскування порівняно з традиційними керамічними покриттями. Крім того, описуються самовідновлювальні та змащувальні покриття, створені за біологічним принципом. Нарешті, окреслено поточні технічні виклики та напрямки майбутніх досліджень, такі як покращення міцності адгезії покриття та масштабування для масового виробництва та комерціалізації.

Ключові слова: Наноструктурні покриття, Оболонки, Мікроструктура, Температура, Нанофлюїди, Теплопередача.