

# **A Comprehensive Review on Nanocrystalline Coatings: Properties, Challenges and Applications**

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#### **Abstract**

In general, metallic substrates react with their environment and progressively degenerate into a stable state such as oxide or hydroxide. Nanocrystalline metallic coatings are extensively used to protect metallic substrates against corrosion in a variety of industrial and household applications. When compared to conventional polycrystalline metallic coatings, nanocrystalline metallic coatings can signifcantly improve the metallic substrate's corrosion resistance, surface hardness, wear, and scratch resistance. This review has elucidated the infuence of corrosion, nanocoating materials, diferent nanocoating techniques, and challenges associated with nanocoating. The goal is to include existing research on the benefcial impacts of nanocoating material structure, grain size, coating technique, additive concentration, and pH value on corrosive behaviour.

**Keywords** Nanocoatings · Corrosion resistance · Physicochemical properties · Metallic substrate · And nanocrystalline

## **1 Introduction**

Corrosion seems to have been a prominent research problem for the past 150 years, piqueing the research community's interest. In an extensive range of industrial and household systems, it's recognised as a primary cause of catastrophic failure, deterioration, and the existence of fatal accidents [\[1](#page-18-0)]. Corrosion can be produced by a number of factors, including the existence of chloride, fuorine, sulphur dioxide, carbon dioxide, oxygen and other elements [[2](#page-18-1)]. In terms of economic repercussions, corrosion-related efects include the system maintenance expenses, waste of materials, equipment breakdown, a decline in productivity, and a reduction in usable life. Furthermore, material corrosion difficulties have a wide range of societal repercussions, including safety (the formation of hazardous compounds and explosions), natural resource depletion, and severe health issues. According to research conducted by the National Association of Corrosion

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Engineers (NACE) in 2013, the global Cost of Corrosion (COC) is estimated to be \$2505 billion, accounting for 3.4% of the total Global gross Domestic Product (GDP). Corrosion-related overhead expenses inside the United States (US) sector are expected to reach \$552 billion every year, contributing to 6% of the country's entire GDP [[3,](#page-18-2) [4](#page-18-3)]. This is the cost of attempting to control and repair corrosion issues in various sectors/applications such as petroleum industries, water recycling unit, bridges, automobiles, as well as domestic appliances, which are just very few examples of prime economic consequences. Other corrosion expenses are also essential such as lost productivity due to delays, malfunctions, service interruptions, operational costs as well as taxes [\[5](#page-18-4)]. The projected cost of corrosion in several fnancial divisions was acquired and analysed, as shown the total percentage cost of corrosion of individual economic regions in USD Billion are in Fig. [1.](#page-1-0) According to one study, corrosion costs in the United Kingdom, the United States, and Japan were linked to modernised industrial and services economies, but farming and the oil sector economy were signifcant contributors in Kuwait and India, respectively. According to the literature, anticorrosive preventative measures, monitoring, and the application of safety norms and procedures are critical in reducing the range of 15–35% of loss caused by corrosion [[6,](#page-18-5) [7\]](#page-18-6).

The total COC for each country and its individual sectors was determined using the COC of the economic region and



<span id="page-1-0"></span>**Fig. 1** Total percentage cost of corrosion in USD Billion



<span id="page-1-1"></span>**Fig. 2** Total GDP percentage of economic regions in USD billion

the GDP of a particular region. The total GDP % of individual regions in USD billion is illustrated in Fig. [2.](#page-1-1) The worldwide cost of corrosion is then calculated by aggregating the countries in each economic area by sector (Table [1](#page-1-2)). According to a 2013 NACA study, the overall predicted global COC is 2,505 billion USD, or 3.4% of total GDP value [\[8](#page-18-7)]. Furthermore, these expenses do not usually cover individual safety or environmental impacts. However, it may be a challenge to incorporate costs associated with safety and environmental impacts for a single country or global cost of corrosion study. These costs should be factored into an overall COC to make judgements and prioritise projects to be completed within an organisation [[9,](#page-18-8) [10\]](#page-18-9).

When a substance is subjected to a hostile environment, corrosion is a usual activity that makes it disintegrate. The type of substrate (material) employed, and the outdoor area are the two most important factors that impact corrosion development [[13](#page-18-10)]. If the two dissimilar metals are exposed to a corrosive environment it corrodes and results in the dissolution of the substrate. The corrosion susceptibility of a material is afected by environmental temperature, acidic condition, dissolved gases as well as stress and strain [\[14](#page-18-11)]. Corrosion can express itself in a variety of ways depending on the corrosion process  $[15]$ . These forms of corrosion consist of homogeneous galvanic, pitting, cracks and delamination. In general, uniform corrosion has been the most common type of corrosion to be found in nature since it occurs most frequently and results in the highest amount of material damage and lost. Whereas, the corrosion process does not ingest a great quantity of material, it is hard to esti-mate and manage, which might result in an early failure [[16](#page-18-13)]. As presented in Fig. [3,](#page-2-0) corrosion in all its forms can produce catastrophic defect in required component of practically any

<span id="page-1-2"></span>**Table 1** Global cost of corrosion by individual economic region (in billion USD) [[7](#page-18-6), [11,](#page-18-14) [12\]](#page-18-15)

Economic regions	COC study region	Year of study	<b>Total GDP</b> USD billion	Industry COC USD billion	COC of agri- culture in USD billion	COC of ser- vices in USD billion	COC of total in USD bil- lion	COC% in GDP
<b>United States</b>	<b>United States</b>	1998	16,720	303.2	2.0	146.0	451.3	2.7
India	India	2011	1670	20.3	17.7	32.3	70.3	4.2
European Region	United King- dom	1970	18,331	401	3.5	297	701.5	3.8
Arab World	Kuwait	1987	2789	34.2	13.3	92.6	140.1	5.0
China	China	2011	9330	192.5	56.2	146.2	394.9	4.2
Russia	Russia	2011	2113	37.2	5.4	41.9	84.5	4.0
Japan	Japan	1997	5002	45.9	0.6	5.1	51.6	1.0
Asia	India and Japan	1997-2011	2302	29.9	1.5	27.3	58.6	2.5
Rest of the World	Average	2016	16,057	382.5	52.4	117.6	552.5	3.4
Global			74,314	1446.7	152.7	906.0	2505.4	3.4



**Fig. 3** Corrosion effect on bolt, flange and pipes [[17](#page-18-16)]

<span id="page-2-0"></span>process, including fanges, pipelines, bolts, and so on, if dependable and helpful practises are not followed [[10,](#page-18-9) [17\]](#page-18-16).

To prevent corrosion, a number of treatments are now used, and determining the most appropriate one demands enhancing the correlation between processing cost, performance improvement, and corrosion efects. Corrosion could be controlled by using the following methods:

- Materials that look unreactive, mostly in electrochemical series or can create an oxide coating (passivate) in a specific region are preferred [\[11](#page-18-14), [18\]](#page-18-17).
- Incorporating inhibitors, altering the temperature and pH level of a particular environment, lowering the velocity of fuid fow, removing sand and silt from the hydraulic system, and so on are examples of changes in environmental conditions [[19,](#page-18-18) [20\]](#page-18-19).
- To minimise fractures and cracks, material coatings and thin flms are used to modify the surface (often referred to as physical barriers) [[21\]](#page-18-20).
- In cathodic protection, the corrosive current is stopped as well as urged to pass towards the coated metal. The material to be safeguarded can be connected with anodic material or a power source [\[22](#page-18-21)].

Every method of corrosion management does have its individual benefts and drawbacks, and the optimal solution is determined by the necessities of the system as well as the conditions under which it is functioning. The utmost prevalent strategy for avoiding or minimising the corrosion has been coating. This is due to the enormous number of coating materials and coating techniques that are available for use in applications and environmental circumstances [\[23\]](#page-18-22). Based on the application, coating thickness, material, temperature, size, and structure are varied. Additionally, coatings can provide fat and smoother surfaces to enhance the interfacial efficiency and the flow of fluids above the coating surface [[24](#page-18-23)]. However, adding a coating appears to require a signifcant initial investment, it is also considered to become more sustainable, economical and suitable for a variety of applications. Surface coating technologies are frequently advised for preventing corrosion because they provide either active or passive protection against the elements. It is possible to achieve active corrosion protection when corrosion inhibitors (chemicals) are introduced to severe conditions in order to control or prevent corrosion [\[25\]](#page-18-24). Inhibitors are used to limit the rate of corrosion via form a tiny protective coating on top of the metallic substrate with chemical inhibitors. Inhibitors reduce the rate of corrosion by forming a thin protective coating over it, or by reacting with the corrosive element in the aqueous medium. Passive protection can be obtained when a coating provides a physically impenetrable oxide barrier between the substrate and the immediate environment [[26](#page-18-25)]. It has recently been hypothesised that nanomaterial coatings could be used as a corrosion prevention technique. Nano-scale (less than 100 nm) materials are defned as those that have at minimum one of its morphological characteristics (size of grain, crystal lattice size, particle form, etc.) [[27](#page-18-26)]. They can be classifed as 0D, 1D, or 2D depending on their size and shape. Compared to conventional materials, nanomaterials possess superior physical and thermal properties. Their tiny size allows them to have greater surface volume ratios, thus providing greater contact areas compared to other materials [\[28\]](#page-19-0). It is considered that materials' surface modifcation with a wide range of coating processes is utilised in order to reduce corrosion rate. Figure [4](#page-3-0) illustrates the various corrosion protection/ control techniques based on their processing techniques and source of the coating material [[13](#page-18-10), [29](#page-19-1)].

In this review article, the corrosion behaviour of various NC materials, corrosion testing, and their testing environments are briefy discussed. Each corrosion test can aid in the measurement of essential corrosion data as well as the interpretation of the corrosion process for understanding [[31\]](#page-19-2). Based on the constant time with an aqueous solution, the weight loss of immersed test specimens was determined by the immersion test. It's intended for use in protracted corrosion investigations and in cases where the homogeneity corrosion process has occurred. [[32\]](#page-19-3). The penetration rate is supported to represent the corrosion rate, which is the reduction in material thickness over a unit of time. The coating material, environment, NC composition, particle size, etc., these are the prime factors which afect the behaviour of coatings [[17](#page-18-16), [33](#page-19-4)]. The sections that follow go through these elements in depth for various types of NCs, which are divided into three categories based on the material on which they are nanocoated: nanocomposite coatings, ceramic coatings, and metallic coatings [[34\]](#page-19-5).



<span id="page-3-0"></span>**Fig. 4** Corrosion protection techniques [\[13,](#page-18-10) [21](#page-18-20), [29](#page-19-1), [30\]](#page-19-6)



<span id="page-3-1"></span>**Fig. 5** Published research articles in the area of corrosion resistance NCs on metallic substrates

The corrosion behaviour of nanomaterial-coated metallic surfaces has been studied thus far, but a more independent experimental investigation is required in this area. As per the Science Direct Journal's statistical data, nanomaterial coating-based corrosion resistance research began to gain traction between 2003 and 2010. However, the maximum number of articles (approximately 50% of articles) have been published in the last fve years. As presented in Fig. [5](#page-3-1), the number of published articles associated with nanomaterial



<span id="page-3-2"></span>**Fig. 6** Research article distribution of nanocoating and corrosion resistance

coating and corrosion has increased, but only in a limited manner. From the aforementioned statistical data, experimental research articles (397 articles) have the largest number of published articles, followed by review articles (119 articles) and others (292 articles). In this research area, the Progress in Organic Coatings journal has the largest percentage of published articles, followed by Surface and Coating Technology, Ceramics International, Applied Surface Sci-ence, and others (Fig. [6\)](#page-3-2).

According to the structure of this article, the remaining part of the article is divided into four sections. The second section of this article explains the nanocoating materials,

diferent types of coating methods, morphology analysis and their applications. The third section is explained about the physiochemical properties, efect of environmental pH value and additives concentration of the nanomaterial coated metallic substrates, as shown in the Fig. [7](#page-4-0) [\[35](#page-19-7)]. The section four examines the difficulties in performing corrosion resistance behaviour investigations of the NCs, as well as future research potential based on research gaps identifed in the previous sections. At the end, the ffth chapter presents the conclusion of this work.

# **2 Metallic Nanocoating on Metallic Substrates**

A NC material has a complete nanoscale microstructure in which all of the elements and generally, crystals are smaller than 100 nm in size. Coatings with layers thinner than 100 nm can also be made [[36](#page-19-8)]. Grain, interphase barriers, misalignment, and other characteristics are numerous. As a result, nanostructured coatings difer from larger-grained, standard coatings, allowing them to endure the mechanical and corrosion characteristics of their rivals. Metallic and ceramic NCs are two diferent forms of NCs that are distinguished by their component materials. Nanocomposite coatings, for example, can be made up of two or more nanosized components [[37\]](#page-19-9).

Since the NC particles are so small, they will be more efective at sealing gaps and preventing contaminants from migrating into the substrate's surfaces. In addition, the grain boundaries of NCs have a high density, which improves adhesion and extends the coating's lifespan [\[38](#page-19-10)]. In corrosive environments, NCs have excellent mechanical and electrical properties, making them stronger, harder, and more corrosion and wear-resistant [\[29\]](#page-19-1). NC technology has had a significant infuence on the development of paints, with qualities



<span id="page-4-0"></span>Fig. 7 Factors affecting the corrosion behaviour of nanomaterial coating [[35](#page-19-7)]

such as self-healing, superior scratch and wear resistance, and self-cleaning. It also allowed for the development of safer alternatives to chromium-based toxic coatings [\[39](#page-19-11)].

#### **2.1 Methods of Nanocrystalline Coatings**

Due to their amazing qualities, NCs are employed in practical life situations. Garments, computers, mobile phones, spectacles, and so on are just a few examples. In the construction sector, they are used in mosaics, window frames, foorboards, sidewalls, paints, and air purifers, among many other things. They are photovoltaic materials with high clarity and adhesion properties [\[40\]](#page-19-12). Metallic NCs are utilised in the biomedical area to increase surface qualities as needed. They're frequently employed in pharma frms for etching treatment, interface covering, and anti-corrosion qualities, as well as in secondary industries such as drug delivery and bio-compatibility [\[41](#page-19-13)]. Due to the aforementioned characteristics, NCs are used in a range of industries, including defence, automotive, energy efficiency, environmental protection, and so on. Chemical coating, physical coating, and mechanical coating are three basic deposition techniques that could be employed to make NCs, as shown in Fig. [8](#page-5-0) [[42\]](#page-19-14). Mechanical deposition, which may be done by spincoating, spraying, painting, or dip-coating, is the best and cheapest approach. Physical deposition procedures include sputtering, condensation and bonding processes. Physical difused bonding necessitates a sensible temperature and pressure, whereas brazing bonding needs higher temperatures in order to give enhanced properties. At low temperatures and pressures, surface-activated bonding (SAB) is used to bind the fat-polished surfaces. Physical vapour deposition (PVD) is often carried out in a vacuum; however liquid phase epitaxy (LPE) can be carried out at standard pressure as an alternative [[16](#page-18-13), [43](#page-19-15)]. Selective laser sintering (SLS) has a somewhat 3-D printing process that uses additive manufacturing, a unique manufacturing approach, to build a layer-by-layer construction [\[20](#page-18-19)]. Sputtering procedures have provided superior epitaxial growth with deep bonds while also having lower growth rates, but they are signifcantly more expensive than other methods. Sputtering could be performed with a molecular beam epitaxy (MBE) system, a pulsed laser deposition (PLD) system, or a radio frequency (RF) system. Chemical bonding methods (CBM), such as atomic layer deposition (ALD), sol–gel, and Langmuir, are typically cheaper in price, although they need costly precursors [\[36](#page-19-8), [37](#page-19-9), [44\]](#page-19-16).

Each of the abovementioned flm deposition procedures afects the homogeneity and surface characteristics of the substrate's interface, including tensile, fatigue strength, and ductility [\[39\]](#page-19-11). The technology, like traditional coatings, should be used under optimal conditions to ensure that the NC has fne surface coverage in terms of uniformity,

<span id="page-5-0"></span>



adhesion, softness and the absence of cracks on the surfaces coated with it [[45\]](#page-19-17). Considering the dip coating as an example, it is both cost-efective and efective coating intricate structures, however it can lag from mismatching thermal expansion coefficients and requires high temperatures to be efective. The limits of pulsed laser deposition and hot embossing are the same as dip-coating. In some cases, rapid cooling might result in an amorphous structure [\[31](#page-19-2), [46\]](#page-19-18). The sol–gel method is popular because it requires low processing temperatures and is a low-cost coating. Although, this processing technique requires expensive raw materials as well as a strictly regulated processing environment [[47\]](#page-19-19).

The coating procedure used to apply a NC has an impact on its corrosion resistance. Figure [9](#page-5-1) shows how thin flm deposition can be utilised to make NCs. The coating technique determines the surface topography, which has an



<span id="page-5-1"></span>**Fig. 9 a**–**d** AFM image of Zn under varied current densities [[50](#page-19-20)]

impact on NC qualities. The most common method for depositing metallic NCs comprises electrodeposition [\[42,](#page-19-14) [48](#page-19-21)]. Electrodeposition is the process of depositing a thin layer of conducting material on a conducting substrate by the use of electrolysis. Unlike all the other methods, which result in grain boundaries as well as porosity, the electrodeposition process results in a dense, pores-free surface treatment. For electrodeposition, a DC or possibly a circulating current source could be utilised instead. Porosity, hardness, surface roughness, and ductility have all been proven to improve by pulse electrodeposition [\[49](#page-19-22)]. Compared to direct current electrodeposition, pulse electrodeposited nanocrystalline zinc deposits showed a fner grain surface and more lattice defects. Because of the higher current density throughout pulse deposition, the nucleation rate has risen, reducing the number grains. The dc source produced huge grains with encapsulated crystals, but the current density of 200 mA/ cm<sup>2</sup> produced the smallest grains having enclosed crystals. Moreover, pulse self-automated of nanocrystalline Nickel–Copper alloy flms exceeded straight electrodeposition across both oxygenated as well as pertinent or relevant conditions [[42](#page-19-14), [50](#page-19-20)].

#### **2.2 Metallic Materials for Nanocrystalline Coatings**

Cadmium (Cd), tungsten (W), iron (Fe), nickel (Ni), phosphorous (P), zinc (Zn), cobalt (Co), copper (Cu), and other pure metals have been used metallic NC [\[32](#page-19-3), [38](#page-19-10), [51](#page-19-23), [52](#page-19-24)]. NCs could be manufactured from pure metal or alloyed to improve the properties of metallic substrates. Nanomaterials behave diferently than micromaterials, hence, nanosized coatings can improve performance even more. Metallic NCs may be made using several processes, including sputtering, as well as multi-arc ion plating methods are used along with electrodeposition, which has been developed as the most extensively used metal deposition technique [[53\]](#page-19-25). NC produce a wide range of applications in a variety of disciplines, including automobiles and aeronautics, energy generation, marine condensers with tubes, electronic companies, water electrolysis, and others [[41](#page-19-13), [54\]](#page-19-26). Figure [10](#page-6-0) presents the various NC techniques, coating mechanism, NC materials, advantages and disadvantages of the metallic NC on diferent metallic substrates.

It has been demonstrated that incorporating metals into a NC facilitates the physical characteristics, thermal characteristics, mechanical, and chemical characteristics of the coating [\[56\]](#page-19-27). Creating the nanosized metallic coating over the metallic substrates has protected the substrate or a signifcant enhancement in coating properties. For instance, the much more fragile zinc NC can overcome both weldability plus surface polish problems arising when the Zn coating thickness must be raised to provide the vital protection. Whenever exposed to extreme temperature and high oxidising



<span id="page-6-0"></span>**Fig. 10** NC techniques, coating mechanism, NC materials, advantages and disadvantages of the metallic NCs [[42](#page-19-14), [48](#page-19-21), [55\]](#page-19-30)

conditions, pure zinc has low corrosion resistance; hence, it is combined with other metals to improve corrosion resistance. It has been established that the toughness of Zn–Ni alloy coatings is larger than the corresponding toughness of Zn and Cd [\[57](#page-19-28)]. Moreover, zinc-nickel alloys are one of the most potential alternatives for cadmium in space applications, because both of its inadequate sticky wear and low corrosion resistance. Another instance of a highly efective NC is Co and its alloys. In terms of wear and corrosion resistance, they have been shown to be a cost-efective alternate for toxic Cr [[58\]](#page-19-29).

In terms of mechanical and electrical characteristics, even in the form of nanoscale the alloyed metal revealed better properties over pure metals. The nanocrystal structured nickel–tungsten alloy has a greater hardness and scratch resistance than nanocrystal structured pure tungsten. Nickel alloyed with copper lowers saltwater pitting and improves Ni corrosion resistance in a reducing environment [\[59](#page-20-0)]. Furthermore, nickel alloyed with phosphorous kinds it easier to passivate the coat when exposed to acidic environments than pure Ni  $[57, 60]$  $[57, 60]$  $[57, 60]$ .

The corrosion resistance of an electrodeposited nanocrystalline Zn–Ni nanocoating in NaCl solution was examined, and it was discovered that 26 nm grain size (13.31 wt%) and 37 nm grain size (17.62 wt%) of Ni content provided the best corrosion resistance [[61](#page-20-2)]. An electrodeposited (both pulse and direct current) Co–Ni alloy NC in a 3.5 wt% NaCl solution, the inclusion of phosphorous (P) increases the corrosion resistance. The maximum corrosive resistance properties were achieved by direct deposition of P at an ideal concentration of 9 wt%, as indicated in Fig. [11](#page-7-0) [\[62](#page-20-3)].

<span id="page-7-0"></span>**Fig. 11** pulse deposited Co-P by Nyquist and Bode plot: **a** and **b** Co–7 wt% of P, **c** and **d** Co–9 wt% of P and **e**, **f** Co–10 wt% of P  $[66]$  $[66]$  $[66]$ 



According to impedance spectra obtained from Nyquist plots, the resistance of a flm increases as its P content increases. The double-layer capacitance (Qdl) and coating capacitance (Qcoat) calculated by Bode plots revealed that P concentrations were less than 9 wt% indicating enhanced surface homogeneity. Although a greater proportion of P improved flm resistance, it resulted in protrusions that tends to reduce the overall coating resistance. According to literature, varying the phosphorous proportion in nickel–phosphorous NC from 5 to 15 wt% transitions the alloy structure from crystal to amorphous [[63](#page-20-4), [64\]](#page-20-5). In neutral or acidic conditions, raising the phosphorus fulflled of the Ni–P NC enhances corrosion resistance, but not in alkaline media. The homogeneous amorphous structure of phosphorous showed higher resilience to chloride ion assault as relative to the crystallised phosphorous material [[51,](#page-19-23) [65](#page-20-6)]. This is why in neutral or acidic solutions, only the amorphous material passivates. However, the addition of 1.1 wt% phosphorous used

to have a greater impact on the coarse grain size in acidic circumstances. The nanocrystal structured Co-1.1 wt% of P alloy coated (10 nm of crystallite size) reduced the corrosion potentiality around 60 mV for the top side when EIS research was executed in a 0.1-M  $H_2SO_4$  solution. This increased potential of 60 mV is greater than nanocrystal structured Co (20 nm of mean grain size) with microcrystalline Cobalt [[66\]](#page-20-7). Table [2](#page-8-0) presents the advantages and disadvantages of anticorrosion coating methods.

#### **2.3 Morphology Analysis of Nanocoating**

There are numerous approaches available for the characterization of NCs in terms of structure, chemical, and physical properties, which are all discussed below. This section examines and evaluates the most commonly used approaches and procedures for analyzing commercially available NCs. As a result, most of the characterization approaches presented



<span id="page-8-0"></span>

in this segment for describing unique physical or chemical properties of NCs, such as SEM, TEM, AFM, XRD, EDS, and FTIR. These characterization techniques are integrated to thoroughly explore the properties and mechanisms of NCs [\[76\]](#page-20-8). Figure [12](#page-8-1) is a flow chart illustrating the various characterization techniques for NCs [[49,](#page-19-22) [77](#page-20-9)].

Transmission electron microscopy (TEM) is an extremely strong tool for deciphering the surface morphology of NCs.

<span id="page-8-1"></span>**Fig. 12** Characterization techniques for nanocoating's [\[66,](#page-20-7)

[69,](#page-20-13) [77](#page-20-9)]

Because the imaging signals employed in this method are stronger, the images obtained from TEM have a higher resolution than those obtained using other methods [[78](#page-20-10)]. High resolution TEM (HRTEM) is commonly used surface characterization techniques that enables atomic-scale imaging. HRTEM can achieve a maximum resolution of 0.05 nm. Atoms and faws in a crystalline substance can be identifed at such a microscopic scale. Pictures are captured



from various angles to create 3D photographs of a material's crystal structure [\[79](#page-20-20)]. Atomic force microscope (AFM) is one of the most advanced scanning probe microscopes available, which compare to other optical techniques AFM images have higher resolution. An AFM is used to analyse samples in the absence of a vacuum, and it possesses three critical capabilities, including image capture, manipulation, and measurement of force. The imaging mode generates a high-resolution 3D image  $($   $\sim$  10 nm in resolution) from the surface topography  $[80]$ . It is feasible to test nanoscratch resistance and nanohardness. Scanning electron microscopy (SEM) is a technique for obtaining 2D and 3D images of the structure and composition of a NC surface. Secondary electrons (SE) are frequently employed to develop an elemental histogram of a NC surface, whereas backscattered electrons (BSE) are utilised to examine the composition of NC sample surfaces. SEM techniques have a resolution of less than 1 nm. Unlike SEM, AFM, TEM and XRD system frequently needs a vacuum atmosphere in order to examine a NC specimen [[76](#page-20-8), [81\]](#page-20-22). Figure [13](#page-9-0) presents the various morphological analysis techniques and their features.

Surface microstructure seems to be a crucial element which has a signifcant direct impact on a surface's corrosion resistance. In fact, it is related to the majority of the aforementioned factors. For instance, the coating processes predict the morphology of surfaces, the size of the grain, and any desirable coating orientation. The Zn–13Ni and Zn–17Ni alloys were electrodeposited over the stainless steel with a direct current of varying current densities ranging from  $0.5$  to  $8$  A/cm<sup>2</sup> [\[82](#page-20-23)]. To develop a more coherent and compact surface deposition a higher range of direct current was employed. For the development of clear boundaries, the deposition size is larger and homogeneous in nature, which delivers much better performance in the Zn–17Ni nanocrystalline coatings. In the morphological examination of nanocrystalline Zinc coating, a similar phenomenon

# **3 Physiochemical Properties of Metallic Nanocoating**

#### **3.1 Structure Size of Coating Materials**

The corrosion test was carried out in a NaOH solution. Microcrystalline electrogalvanised metal specimens (EG) had a 60% higher corrosion rate than nanocrystalline zinc electrodeposited with the use of pulse-current approach. The nanocrystalline zinc protective coating was entirely covered, according to examinations. This was owing to the nanocrystalline shape, which improved the kinetics and stability of the passive flm [[89,](#page-20-25) [90\]](#page-20-26). As per past studies on a nanocrystalline Ni–Cu alloy NC, the nanocrystalline structure has a systematic methodology of signifcantly larger corrosion resistance than the microcrystalline structure subsequently the high-density grain boundary of the NC structure starts to move the creation of a stable as well as preventative oxide layer. Figure [14](#page-10-1) depicts how the results obtained by pulsedepositing Fe onto low-carbon steel samples and then analysing them in alkaline conditions. Compared to microcrystalline heated (50 nm grain size) with cast (20 nm grain size) iron samples, nanocrystalline size samples showed higher corrosion resistance [[89,](#page-20-25) [91\]](#page-20-27).

In alkaline conditions with increased corrosion current density, Alinezhadfar et al. [[92\]](#page-21-0) found that nanocrystalline

<span id="page-9-0"></span>

[[76](#page-20-8), [81](#page-20-22)]

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<span id="page-10-0"></span> $\overline{\phantom{a}}$ 

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<span id="page-10-1"></span>**Fig. 14** Impact of structure size on nano- and micro-coating [\[92\]](#page-21-0)

cobalt (67 nm) had superior corrosion resistance (100 nm) than polycrystalline cobalt NC. As a result, fner grain coatings may cause defect spots at grain boundaries, increasing the likelihood of corrosion in these active locations. A greater volume of intercrystalline elements are present in nanocrystalline structures compared to polycrystalline structures, and the nanocrystalline structure contains a greater number of active sites [\[93\]](#page-21-1).

#### **3.2 Grain Size of Nanocoating**

The impact of material particle sizes was investigated further for various sizes deep inside that nanoscale. Since a fner nanograin size did not have the best corrosion resistance in all of the studies, it is not necessary for the grain size of the nanomaterial to be low or high to get the same corrosion protection [[94\]](#page-21-2). Figure [15](#page-11-0)c shows that electrodeposited nanocrystalline nickel displayed improved corrosion resistance across 16 nm grain sizes, 56 nm grain sizes, and 250 nm grain sizes for the lowest particle size [[95\]](#page-21-3). The 6.6 nm particle size nanocrystalline Ni–Cu alloy NC had a higher current density than that of the 12.7 nm grain size nanocrystalline Ni–Cu alloy coating in a 3 wt% of NaCl solution (35.8 wt% of Cu) [[96\]](#page-21-4).

Meng et al. found the same results of greater enhancement with increasing nanograin size. With a grain size of 50 nm, the impedance and phase value of a Q235 steel coating were greater than those with a grain size of 10 nm [\[99\]](#page-21-5). On the 50-nm coating, this implies that a more stable passive flm was obtained. (Fig. [15a](#page-11-0), b). Moreover, difraction patterns acquired from TEM pictures of a 50-nm coating revealed the presence of growing twins. These growing twins create a unique boundary with low free energy, which considerably reduces the adsorption of aggressive ions through the passive flm's surface [[97,](#page-21-6) [98](#page-21-7)]. In addition, nanocrystalline Zn–17Ni with an intermediate grain size had the highest corrosion resistance compared to the other Zn–Ni alloys.

<span id="page-11-0"></span>**Fig. 15** The infuence of grain size on the nanocrystalline Zn– Ni alloy NC; **a** Nyquist plots, **b** bode plots with diferent grain sizes, and **c** variation in polarization resistance of Zn–Ni alloy NC with respect to grain size (nm) [[97](#page-21-6), [98\]](#page-21-7)





This suggests that the NC's composition can surpass the efect of smaller grain size. For another type of alloy, such as the Ni–W alloy, the acidity of the test media had a greater impact on the corrosion resistance of the nanocoating than the nanocoating's grain size [\[98\]](#page-21-7).

 $Z''(\Omega \text{ cm}^2)$ 

#### **3.3 Characterization of Physiochemical Properties**

#### **3.3.1 Physical Property Analysis of Nanocoating**

Microhardness is a property of NCs that indicates the coatings' microscale resistance to deformation caused by applied pressures. Vickers microhardness measurements are generally used to determine the microhardness of NCs. The increased microhardness can be studied with the microstructure modifcation of NCs. Wear resistance, which is used to determine coating erosion resistance, is frequently investigated in conjunction with microhardness [[100](#page-21-8), [101](#page-21-9)]. The microstructural elements of the NCs, including the particles' quantity, size, and shape, are critical elements afecting their wear resistance. Hardness and wear are both critical constraints in defning the industrial and domestic application of NCs. There are also other physical properties of NCs that are crucial to understand, such as tensile and fexural properties, toughness, and surface roughness. When it comes to industrial applications, the physical properties of NCs have a signifcant efect on their overall performance and lifespan [[102\]](#page-21-10). Figure [16](#page-11-1) illustrates the various physical properties for nanomaterial coated substrates.

#### **3.3.2 Chemical Property Analysis of Nanocoating**

The elemental composition of NCs can be determined with a technique called energy-dispersive X-ray spectroscopy (EDS). Typically, the EDS device is utilised in conjunction with the SEM equipment, as the EDS device makes use of the X-ray radiation created during SEM examination. Each element has a unique X-ray difraction pattern, which



<span id="page-11-1"></span>**Fig. 16** Various physical properties for nanomaterial coated substrate [[101,](#page-21-9) [102\]](#page-21-10)

enables their detection using EDS analysis [\[103\]](#page-21-11). X-ray difraction can be used to determine the phase structure of a crystalline substance (XRD). Additionally, XRD can be used to determine the orientation and size of the individual phase, and the distance between two NC layers [[104\]](#page-21-12). Threedimensional Fourier transform infrared spectroscopy (FTIR) has been employed frequently for evaluating the chemical composition of NCs on diferent substrates. It can also be used to obtain spectrum of absorption or emission from NCs. Furthermore, it is possible to demonstrate the production of coatings and provide evidence of chemical interaction between distinct phases. Additionally, the chemical composition of the nanomaterial can be investigated [[105\]](#page-21-13). Nuclear magnetic resonance (NMR) can also be used to characterise the chemical structure. NMR is utilised to detect the atomic nucleus's unique quantum mechanical magnetic properties. The term "NMR" refers to electromagnetic resonance. When compared to FTIR, NMR has the ability to give additional information about the structure of certain components as well as the degree to which molecules condense. FTIR and NMR are often employed to characterise the structure of NC's, furthermore, these techniques can confrm the success of production of NCs [\[103](#page-21-11), [106\]](#page-21-14). Figure [17](#page-12-0) shows the various chemical property characterization techniques and its superior features.

#### **3.3.3 Electrochemical Characterization of Nanocoating**

When it comes to corrosion resistance, electrochemical characterization methods are frequently employed to estimate the corrosion behaviour and performance of NCs. "Electrochemical impedance spectroscopy (EIS), linear polarisation resistance (LPR), potentiodynamic polarisation (PDP), cyclic voltammetry (CV), scanning kelvin probe (SKP), scanning electrochemical microscopy (SECM), and scanning vibrating electrode technique (SVET)" these are the commonly utilized methods for corrosion study. Corrosion can manifest itself in two ways: as localised or as general

corrosion, thus, EIS, LPR, PDP, and CV are frequently employed to investigate general corrosion, while SKP, SECM, and SVET are frequently employed to investigate localised corrosion [\[96](#page-21-4)[–99](#page-21-5), [107,](#page-21-15) [108\]](#page-21-16). Figure [18](#page-13-0) illustrates the diferent electrochemical characterization techniques which are generally used for electrochemical property analysis and its special features over other.

EIS is a non-destructive technique for investigating and estimating the endurance of coatings that reveals fundamental aspects of interfaces. Along with current density and corrosion rate, the EIS can provide information on the corrosion state of NCs, allowing for the determination of rate of corrosion [\[108\]](#page-21-16). In electrochemical corrosion studies, LPR is a commonly used approach for evaluating the performance of NCs. LPR analysis, similar to EIS, delivers data on current density and corrosion rate. While LPR is a much faster process and easier to analyse than EIS, it is less reliable than EIS in terms of accuracy. The corrosion current in LPR data is derived from the polarisation resistance data using the Stearn–Geary relationship. LPR is one of the most widely used methods for evaluating the performance of metallic NCs in electrochemical corrosion studies. Figure [19](#page-13-1) depicts the polarisation curves of specimens immersed in a 3.5% NaCl solution with and without a nanocrystalline Ni–P coating. Even at elevated temperatures, this graph depicts a consistent rise in corrosion resistance between Ni–P coated and uncoated specimens. At the corrosion potential, the coated samples had a lower current density than the uncoated substrate. The invention of a Ni–P nanostructured coating increased the corrosion resistance of the coating layer of the Ni–P phase, preventing the migration of corrosive ions to the metal surface [\[112\]](#page-21-17).

Another technique for determining the electrochemical behaviour of nanocomposite coatings is CV. The Nernst equation is used to calculate the expected value of voltage, causing an electrochemical cell to create current, and this is measured using this instrument. The CV technique is used to examine the electroactivity, stability, and redox

<span id="page-12-0"></span>

<span id="page-13-0"></span>



<span id="page-13-1"></span>**Fig. 19** Polarization curves for samples without coating and with coating in 3.5 wt% NaCl solution [[112\]](#page-21-17)

behaviour of NCs [[109](#page-21-18)]. PDP quantifcations yield data on corrosion potential and corrosion current. From the connection of the anode and cathode twigs, the aforementioned pieces of information are determined. It is extensively utilized to examine the properties of NCs. The SKP has uses for determining the cathodic protection of NCs over the substrate surface by calculating the potential difference between the electrode and specimen, it is a noncontact method. The SKP method has been widely used to test the corrosion resistance of coatings. To fnd out how a coating on a surface protects itself from corrosion, SECM can be used to look at how current and voltage change when metal dissolves or oxygen is used at the interface [[110](#page-21-19)]. This is a very good way to look at localised corrosion. The SVET is a novel electrochemical method for determining the anti-corrosion features of coatings. It has three electrodes and a vibrating microelectrode. The rate of vibration and wave amplitude are measured above the NC surface. SVET is used to measure localised corrosion behaviour at the NC and substrate material interfaces in terms of the current density at that point [\[111\]](#page-21-20).

## **3.4 Impact of Environmental pH Value on Nanocoating**

In all of the above-mentioned aspects, it was important to specify the test media. The environmental pH value is afected by the test solution, which represents the material's ability to withstand corrosion attacks. Whenever nanocrystalline oriented cobalt was studied in various sodium hydroxide solutions (NaOH), Hydrochloric acid (HCl), sodium chloride (NaCl), and Sulfuric Acid  $(H_2SO_4)$ , varied corrosion current density values were achieved [[113\]](#page-21-21). However, in a solution of NaOH, excellent corrosion resistance was reported to nanocrystalline zinc (pH 13.6) as well as nanocrystalline iron formations. Mahalingam et al. reported an increase in the corrosion rates for nanocrystalline Ni–W alloy in pH 3 (acidic media) better than in the pH 10 (alkaline media) of 3.5 wt% NaCl solutions [\[114](#page-21-22), [115\]](#page-21-23). In addition, it was discovered that the corrosion behaviour of a similar alloy was afected by the pH value of the test media, which was investigated further. Figure [20](#page-14-0)a and b demonstrates that in the corrosion rate increased with grain size reduction (rises in W content) in alkaline media, whereas it improved with grain increased size (decreases in W content) in acidic medium [[116](#page-21-24)].



<span id="page-14-0"></span>**Fig. 20** Impact of pH on nanocrystalline Ni–W alloy coating **a** Ni–W alloys at pH 3; **b** at pH 10 [[116\]](#page-21-24)

#### **3.5 Concentration of Additives in Nanocoating**

The addition of ingredients to the NC material that aid in the creation of a fatter, highly polished fnish. The additive absorbed particles infuence energy for activation and also the charge transfer speed during electrodeposition and prevent the surface and decrease the formation of surface-active sites of a metal substrate [[117\]](#page-21-25). The proportion of additive material used in the development of improved NC substrates is critical. The nanocrystal structured Nickel–Tungsten alloy NC was done by electrodeposition on a mild steel substrate with a citrate bath  $(C_6H_5O_7-3)$  including salicylaldehyde  $(C_7H_6O_2)$  additive [\[118\]](#page-21-26). A better resistance rate of corrosion has been observed at an additive concentration of 100 ppm, which provides a fne-grained NC with a homogeneous nanocrystalline structure. However, according to the literature fndings further, an increment in the volume concentration of additive material of more than 100 ppm leads to an increase in the additive-to-additive bonding [[119](#page-21-27)]. This additive adhesion affects the corrosion resistance and homogeneity of the NC. Figure [21](#page-14-1)a and b illustrates the polarization curve of the nanocrystalline structured nickel–cobalt alloy coated on a steel substrate with 10 wt% of sodium hydroxide (NaOH) and saccharin  $(C_7H_5NO_3S)$ , which improves the corrosion resistance property [[120](#page-21-28)]. This enhancement in corrosion and tribocorrosion resistance are correlated to the smoother surface morphology and reduction in grain size (Fig. [21c](#page-14-1)). While NC nanocrystal structured nickel–cobalt alloy, the addition of sodium lauryl sulphate led to its lower hardness value, it boosted corrosion resistance while decreasing tribocorrosion resistance [[117,](#page-21-25) [121](#page-21-29)]. Table [4](#page-15-0) summarized the experimental work associated with metallic NC, as well as the important factors of NCs and corrosion resistance that have been reported. Table [5](#page-16-0)

<span id="page-14-1"></span>





<span id="page-15-0"></span> $\underline{\textcircled{\tiny 2}}$  Springer

<span id="page-16-0"></span>

shows an overview of mechanism of action, advantages, and disadvantages of various anticorrosion coatings.

### **4 Challenges and Future Directions**

Generally, material properties such as durability and stability are determined based on the corrosion resistance of the material, and it's critical to examine, as it defnes the overall performance of the material. The corrosion process based experimental investigation reveals the fundamental mechanisms and kinetics that govern. Nanocoating includes ultimately fne elements that may have an impact on the fnal surface in terms of the structure of crystalline lattice, state of surface, grain size, porous, distribution of intermetallic particles, etc., These elements have higher density grain boundaries and are very smaller in size that's challenges the development of novel corrosion concepts. For instance, surface smoothing enhances the integrity, homogeneity, and fatigue, reducing the chance of pit development on the surfaces for the long run. At the same time, the nanoparticles covered the substrate surface gives excessive smoothness, which may decrease the coating's adherence and induce detachment of portions of the NC. In addition, decreasing the surface roughness may raise the potential of preferred intergranular corrosion, which may allow the formation of a more defective and permeable coating at the triple-junction grain boundaries. This duality of interactions allows the nanomaterials to interact with the surface in two opposing orientations, making it difficult to determine which approach is appropriate. Furthermore, the presence of such nanoparticles on the surface of the substrate has afected the development of oxides; hence, the transition mechanism of the surface state is altered, making it difficult to identify. The surface state transition from passivation to pit initiation and ultimately to flm breakdown has been controlled by the composition of the flm. It was determined that the state of the uncoated surface would be dependent on the initial conditions and the cleanliness of the fnal coated surface. This new state will have an impact on the overall surface corrosion. Due to the heterogeneous dispersion of the NC particles over the coated substrates surface, ions may accumulate and produce weak areas of a greater possibility that cause pit nucleation. On the other hand, aggregated nanocoating materials may physically insulate the base substrate surface from the electrolyte. Therefore, it is difficult to predict the changeover mechanism, and it demands more corrosion research.

This review found that the use of various nanocrystalline metallic particles as coating materials ofered the best enhancement of corrosion resistance properties. In the future perspective, a combination of nanocrystalline anticorrosion and superhydrophobic metallic nanocoating could create synergistic effects. This dual behaviour of the nanocoating surface protects the metallic substrates from various environmental conditions. For instance, in the marine environment, anticorrosion coating could offer protection against corrosion attack as well as superhydrophobic nanocoating to control biofouling. This could greatly reduce the maintenance costs and increase the performance of marine vehicles. The enhanced biocompatibility and lower toxicity of metallic nanocoating materials would allow them to be used in a large range of applications, including food and medical industries.

# **5 Conclusion**

This review study presented an in-depth analysis of metallic nanocoatings over metallic substrates. Nanocoatings have a greater potential for increasing corrosion behaviour than macro- and micro-sized material coatings. Nano-crystalline microstructures have exceptional corrosion resistance due to their small grain size and large flling space. A nanocoated metallic substrate surface becomes tougher, stifer, and more adhesive. The coating's thickness and shape should be tailored to optimise its protection against destructive and eroding factors. Aside from increasing corrosion resistance, nanocoatings have been shown to have adverse side efects in some circumstances. Due to their small size, nanocoatings generate a homogeneous thin layer over metallic surfaces. Notably, nanoparticles have a high density between grain boundaries, increasing their host substrate's corrosion resistance. As a result of the agglomeration of small particles into larger ones, the substrate material becomes more susceptible to corrosion assault. Thus, to achieve optimal corrosion protection, it is necessary to consider all environmental factors afecting nanocoatings and their substrates.

It is crucial to consider that there is no one aspect that infuences corrosion resistance solely. Meanwhile, all the other factors contribute to the corrosion resistance of the nanocoating. Nanocrystalline structured Nickel and its alloys have a lot of prospects as a promising metallic nanocoatings, primarily in the state of nanocrystalline Ni–P alloy. Furthermore, Zn–Ni alloys containing 14–17 wt% of nickel revealed high-corrosion resistance behaviour. To improve the corrosion resistance behaviour of nanocoating in neutral and acidic conditions, 9–11 wt% of nanocrystalline phosphorus is added to the metallic coating material. There was no clear correlation between corrosion behaviour and particle size for the various sizes of nanoparticles reported in the nanocoating. Conversely, the composition of the nanocoating and the acidity of the medium may have a stronger impact on the grain size. Due to the fner surface created by PED compared to DCE, it has been revealed that PED has superior corrosion resistance properties than DCE. To acquire the best corrosion resistance property, the concentration of the additive used in the nanocoating process must be optimised. In this review, several factors which infuence the corrosion behaviour of nanocrystalline metallic nanocoating have been addressed.

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**Data Availability** The raw/processed data required to reproduce these fndings cannot be shared at this time due to legal or ethical reasons.

#### **Declarations**

**Conflict of interest** The authors declare that they have no known competing fnancial interests or personal relationships that could have appeared to infuence the work reported in this paper.

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