ELECTRODEPOSITION OF NICKEL-COBALT / ALUMINA (Ni-Co/Al2O3) COMPOSITE COATINGS: A CURRENT APPROACH

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ABSTRACT
This paper provides a review of the electrodeposition process that is used to produce nickel-cobalt / alumina (Ni-Co/Al2O3) composite coatings. The electrodeposition techniques, consisting of direct current, pulse current and pulse reverse current, sediment electrodeposition, and CO2 bath, are described. The effects of electrodeposition variables, including applied current density, deposition time, particle concentration and use of surfactants, are also explained. The paper then discusses the limitations of previous studies, such as lack of focus on the effectiveness of this coating in corrosive and erosive environments, and the effects of alumina particles on coating microstructures. It also suggests longer exposure to corrosive media for more significant corrosion study. Further research needs to be conducted in order to improve the corrosion and erosion resistance of Ni-Co/Al2O3 in harsh environments, such as marine conditions.

Keywords: nickel-cobalt / alumina composite coatings, electrodeposition, corrosion and erosion resistance, micro hardness and wear rate, particle concentration.

INTRODUCTION
Electrodeposition is a process of incorporating metals to the substrates by using the electrochemical method. The electrodeposition technique offers several advantages, such as precisely controlled near room temperature operation, low energy requirements, capability to coat complex component geometries, low cost, and simple scale-up [1]. The ability of the technique to coat various types of materials, such as oxide, nitride, carbide and metallic, in a metal matrix allows it to provide coatings for multiple applications [2]. The advantages of this technique has encouraged researchers to further explore its potentials.

In recent years, there have been increasing interests focused on electrodeposited nickel-cobalt (Ni-Co) and Ni-Co based metal matrix composite (MMC) coatings due to their superior properties, such as higher hardness [3]–[6], improved anti-wear, better corrosion resistance and oxidation resistance [7], as compared with pure Ni and Ni based composite coatings. The properties of Ni-Co or Ni-Co based composite coatings are mainly dependent on the incorporated particles and microstructures of the Ni-Co matrix [7]–[11]. Based on these studies, it was found that the highest nanoparticle concentration in the coating was reported to be less than 30%vol. The average %vol was reported to be just around 10%vol regardless of particle type and matrix. The low concentration of ceramic particles in the coatings have limited their mechanical performances as compared to ceramic coatings.

Among the various inert particles, alumina (Al2O3) particles have many superior properties, such as low price, good chemical stability, and high micro hardness and wear resistance at high temperatures. Hence, Al2O3 coatings are widely used for shipboards and submarines, textile industry and machinery to give protection and support to their structures [12]. The presence of Al2O3 particles in Ni-Co based metal matrix could increase the micro hardness of the coating. These hard ceramic particles provide greater hardness through dispersion strengthening of the coating [13], [14]. However, a lot of factors should be considered to obtain superior coating properties, such as particle characteristics, electrolyte composition including additives, temperature, pH, surfactant type and concentration, current density, hydrodynamics (laminar, mixed and turbulent regimes), and electrode geometry [10].

This paper reviews the electrodeposition techniques that are used to produce Ni-Co/Al2O3 coatings, and the electrodeposition variables that influence the coating performance. It then discusses further research that needs to be conducted in order to improve the corrosion and erosion resistance of Ni-Co/Al2O3 coating in harsh environments, such as marine conditions.

ELECTRODEPOSITION TECHNIQUES
The most commonly used electrodeposition technique is the direct current (DC) technique. This technique uses an electrochemical cell as shown in Figure-1, which consists of anode and cathode electrodes, electrolyte, and DC power supply. The currents flow from the anode to the cathode through the electrolyte. During the process, free metal ions in the electrolyte will transfer to the cathode to gain the electrons and form a solid metal [15]. The simple setup of this technique has encouraged researchers to conduct various researches related to this technique as shown in Figure-1.
Some studies have also been conducted on the electrode arrangement in the bath. The conventional electrodeposition technique positions the electrodes vertically. However, a few researchers have suggested positioning the electrodes horizontally, with the cathode placed below to the anode. This type of arrangement is known as the sediment electrodepositing technique [16]. This technique would allow the particles to settle down easily as sediment on the cathode surface with the support of gravitational and electrophoretic forces. Figure-2 shows a schematic image of the applied force during the deposition process. The gravitational and electrophoretic forces act vertically in the same direction, while the in conventional technique, the electrophoretic force is disturbed by the gravitational force in the perpendicular direction. Working with Ni-SiC coating, they found that the percentage of SiC content in the coating increased as compared to the conventional technique. Feng et al. [17] reported that Ni-Al₂O₃ coatings produced using this technique provide better micro hardness and lower wear rate than Ni-Al₂O₃ coatings produced using the conventional technique. Bakhit et al.[18], who investigated the effect of the electrodeposition technique on micro hardness and corrosion properties, also found that sediment electrodeposition increases the SiC content in the Ni-Co matrix and improves the micro hardness of nanocomposite coatings [19].

Other techniques frequently used for the electrodeposition process include pulse current and reverse pulse current. In the pulse current technique, the current supply or potential alternates between two different values, while the pulse reverse current technique uses an alternating current between the anodic and cathodic current densities. These techniques are used to control the electron transfer through the electrolyte by controlling the current distribution. Regulating the current would remove the negatively charged layer that is constructed during the plating process [20]. Chang et al. [21] found that Ni-Co/Al₂O₃ coatings produced using this technique are uniform, compact and possess finer grain. Similar findings were reported by Mohan et al. [22] for Ni/nanoAl₂O₃ coatings and Nemes et al. [23] for Zn/CeO₂ coatings. In addition, Bakhrololoom & Sani [24] reported that pulse current provides better mechanical properties to Ni-Al coatings. They also investigated the relationship between frequency and duty cycle of pulse currents with the micro hardness and wear behaviour of the coatings. They found the hardness of the coating increased when low duty cycle and frequency were used. These results are in good agreement with the findings of studies conducted using Zn-TiO₂ coatings [25], [26].

Zheng & An [27] fabricated Zn-Ni/Al₂O₃ coatings using an ultrasound horn in the electrolyte to produce ultrasonic streaming and cavitation bubbles. They found that increasing the ultrasonic power from 0 to 0.7 W/cm² would increase the Al₂O₃ content in the coating from 4.5 to 8.9 wt.% and could reduce the agglomeration of the Al₂O₃ particles. The presence of ultrasonic streaming is believed to catalyse the movement of the Al₂O₃ nanoparticles towards the cathode, while the cavitation bubbles deagglomerate the nanoparticle. However, as the ultrasonic power is further increased, the coating performance reduces, with high porosity and reduced Al₂O₃ content. Bakhit & Akbari [2] also used this method in their research involving deposition of Ni-Co/SiC composite coatings. Other researchers also agree with the advantages provided by the ultrasonic method [8], [28]–[30].

Another technique that been discussed among the researchers is the addition of CO₂ in the electrolyte. CO₂ is emulsified in the electrolyte with pressure of more than 10 MPa to increase the solubility of H₂ produced during the electrodeposition process. The presence of CO₂ in the water forms carbonic acid, which increases the H⁺ content in the solution [31]. As a result, the coatings produced have better hardness and low porosity, as reported by Chung et al.[32] and Chiu et al.[33].
ELECTRODEPOSITION VARIABLES

In addition to the electrodeposition techniques, the mechanical properties of the produced coatings are influenced by several deposition variables, which include applied current density, deposition duration, particle concentrations and particle type [14].

Current density

Wu et al. [34] studied the effect of current density on Ni-Co/Al2O3 coatings. The highest volume percentage of Al2O3 was obtained at current density of 3 A/dm2. The study on Ni-Al2O3 coatings conducted by Goral et al. [35] found that microhardness increases when current density is increased from 2 to 6 A/dm2. Simultaneously, this parameter also provides more uniform particle distribution. Current density also gives the same effect to Ni-SiC coatings, as reported by Bakhit et al. [18]. The optimum current density used to obtain the highest particle content in the coating was 3 A/dm2. In contrast, Sun et al. [36] reported that the lowest current density used (6.5 A/dm2) provided a slightly higher Al content as compared to current density of 34 A/dm2, but the difference was less than 1%.

Deposition period

Farrokhzad et al. [14] studied the effect of deposition time on the coating characteristics of Ni/Al2O3-TiO2. They found that the coating prepared at 120 min of deposition time was thicker than the coating prepared at 90 min of deposition time. However, duration time had no significant effect on the microhardness of the coatings. While not many papers discuss the effect of deposition time, some researchers prefer to vary the duration in order to get the suitable thickness of coatings for their studies [2], [18], [28].

Particle concentration

Another approach used to improve coating properties is by varying the ceramic particle concentration in the electrolyte. Farrokhzad et al. [14] reported that molarities of Al2O3 and TiO2 particles is proportional to the particle volume in the coating. However, Gul et al. [37] found that the increase of volume of Al2O3 in the coating is not comparable to the increase of concentration of Al2O3 particles in the electrolyte; a six times increment of Al2O3 in the electrolyte only increased the Al2O3 concentration in the coating by less than three times. Nguyen et al. [38] also reported similar results; by increasing the fly ash concentration in the electrolyte from 20 to 50 g/l, it could produce coatings with 2.5% higher particle concentration. The concentration of matrix particles in the electrolyte also influences the ceramic particles in the coatings. Kuo et al. [8] increased the concentration of Ni2+ (by changing the concentration of Ni(NH2SO3)2) in the electrolyte. As result, they managed to increase the Al2O3 particles in the coating from 8.4 to 26.8 vol%. Conversely, low Ni2+ concentrations would encourage H+ reduction, which produces coatings with high porosity.

Additive

The presence of a surfactant could develop positive charges on the particle surface to prevent agglomeration and improve particle stability in the electrolyte. Chen et al. [39] used hexadecylpyridinium bromide (HPB) as a surfactant in Ni-Al2O3 coatings. The increase of HBP to 300 mg/l enhanced Al2O3 content by up to 14.7 vol%. Similar results were also reported by Gul et al. [37] and Narasimman et al. [16] by using SiC particles. Surfactants are also used in the sediment electrodeposition technique to decrease electrolyte viscosity and thus, gravitational force and diffusion coefficient improve the deposition process [29]. Chiu et al. [33] used an octa (ethylene oxide) dodecyl ether (C12EO8) surfactant to emulsify the electrolyte in presence of CO2. The emulsified electrolyte increases the solubility of H2. Hence, the formation of H2 gas bubble could be minimised to produce a smoother surface [31]. Commonly used surfactants are hexadecylpyridinium bromide (HPB) [29], [37], [39], [42], tetramethyl ammonium hydroxide (TMAH) [16], polyglycol [40], H(CH2=CH2)O–(CH2)12H [32], cetyltrimethyl ammonium bromide (CTAB) [8] and sodium dodecyl sulfate (SDS) [2], [41].

pH

Electrodeposition composite coatings usually deposited from acidic bath. The pH range from 3 to 5 commonly used due to the optimum parameters of Ni-Co coating [7], [42] which shows a high current efficiency, bright and smooth deposit with fine grain size [43], [44]. In contrast, the alkaline bath had reported gave higher alumina concentration in the coating [45]. Bund & Thieming [45] also describe that surface charge of alumina particle was dependence to pH of the bath. In the acidic bath, surface charge of the alumina particle is positive while in the alkaline bath it would be negative. The magnitude of the surface charge of particle in contact with the electrolyte affect the stability of the particle dispersions and ability to adsorb ion from the solution [46].

DISCUSSION

Composite coating performance has improved over time in terms of mechanical properties and corrosion resistance. However, some improvements are needed with the intention of making this coating reliable for harsh environments. Applications in marine environments expose materials to corrosive conditions and erosive medium. Thus, the use of materials that combine erosion and corrosion resistance with high mechanical strength is a requirement in industrials applications [47].

While the improvement of Ni-Co/Al2O3 coating properties has shown good achievement to proof its ability as a protective coating, there is a lack of studies on the effectiveness of this coating in erosive environments. Most
researches conducted separate between corrosion and erosion effects. Rayes et al. [47] describe the erosion-corrosion as an acceleration of the deterioration rate of metal due to the combined effect of erosion and electrochemical attacks. The combined effect could enhance the damages not only to the coating, but also to the substrate through the combined interaction between the two processes. Erosion could strip the coating and catalyse the corrosion attack. On the other hand, corrosion occurs first to catalyse the erosion process. This mechanism leads the greater damage to the coating and substrate [47]–[49].

The presence of ceramic particles in the metal matrix also gives different results among the researchers in terms of their corrosion behaviour. Some of the researchers claim that ceramic particles could enhance the corrosion resistance of the coatings [18], while others report different findings [33], [36]. They verified that the corrosion behaviour of the coatings is not only influenced by the embedded particles, but also other factors. The coating microstructure plays a big role in providing corrosion protection [50]. The presence of permeable defects, such as pores, cracks and grain boundary gaps, could allow the electrolyte to penetrate and interact with the metal surface, which catalyses the corrosion attack [51]. The interaction between the electrolyte and substrate exhibits galvanic corrosion either to the coating or to the substrate itself depending on nobility of the materials. That is the reason why several researchers have tried to reduce the porosity in their coatings [52]–[54]. However, previous studies on Ni-Co/Al2O3 coatings did not discuss this effect very well.

The penetration of the electrolyte through the permeable defects is sluggish due to the small space or capillary. As a result, the electrochemistry impedance spectroscopy (EIS) tests for corrosion could give different values over the time and require a longer testing period. Nevertheless, most of the corrosion studies were conducted in a day or two, which believed not be sufficient to model the real process.

Another issue rising from the literature is the low concentration of the ceramic particles in the coatings. Kuo et al. [8] found that lower electrolyte concentrations tend to decrease the agglomerated Al2O3 particle size. The Al2O3 particles would disperse effectively in the electrolyte solution. As a result, it would create more opportunity for loose Al2O3 particles to attach onto the electrodes or substrate [8]. The increase of Al2O3 particles could provide better mechanical performance, especially micro hardness and wear resistance [55]. Kuo et al. [8] also changed the Ni2+ concentration in order to control the electrolyte concentration, as compared to researchers who used Al2O3 concentration as the focus of their study [14], [28], [30]. However, the effect of Ni2+ concentration with the presence other metallic elements, such as Co2+, and inert particle, such as Al2O3, has not been studied. Other than that, Al2O3 nanoparticle could adsorb Ni2+ well as reported by Srivastava et al. [56]. They were using Al2O3 as an adsorbent in the aqueous solution to remove the heavy metal. The adsorption of Ni2+ to the Al2O3 seems can be use as a carrier in order to deposit the nanoparticle in the coating. However, further studies need to identify the right pH value and the effect of the other anion or cation to the Al2O3 surface charge.

CONCLUSIONS

This paper has reviewed several electrodeposition techniques that have been used to produce Ni-Co/Al2O3 composite coatings. Direct current is the most commonly used technique due to its simple setup. Other techniques that can be used are pulse current and pulse reverse current, sediment electrodeposition, and CO2 bath. All the techniques discussed have their own advantages to improve the coating properties. In addition, process variables, including applied current density, deposition time, particle concentration and use of surfactants, also give great effect to the coating performance.

Although the electrodeposition of composite coatings has been established, some improvements are still needed with the intention of making this coating reliable for severe environments. For this purpose, a corrosion-erosion study for Ni-Co/Al2O3 coatings should be conducted. Furthermore, increase of Al2O3 content is a key to produce coatings with excellence performance.

REFERENCES


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