Research Article

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Characterization of Co–Ni–TiO₂ coatings prepared by combined sol-enhanced and pulse current electrodeposition methods

Abstract: This research comprehensively explores the synthesis of Co–Ni–TiO₂ coatings employing a hybrid methodology that integrates sol-enhanced and pulse current electrodeposition techniques. The investigation examined the surface morphology and intrinsic properties of Co–Ni–TiO₂ coatings, revealing the significant influence of pulse duty cycle variations on the characteristics of coatings. A detailed analysis indicates that a pulse duty cycle of 0.4 optimized the coating’s performance, offering superior attributes compared to other duty cycle settings. The study elucidates that lower duty cycles foster hydrogen evolution reactions on the cathode surface, culminating in the formation of a porous, needle-like coating structure. Conversely, higher duty cycles are found to mitigate the effects of material replenishment, thereby affecting the coating’s quality and performance. The findings of this investigation not only shed light on the critical relationship between the pulse duty cycle and the properties of Co–Ni–TiO₂ coatings but also lay a foundational framework for the further refinement and optimization of these coatings for advanced applications.

Keywords: Co–Ni, pulse electrodeposition, nanoparticles, duty cycle

1 Introduction

Cobalt-nickel (Co–Ni) coatings [1–3] are extensively utilized across various industries owing to their remarkable physical and chemical advantages, alongside notable mechanical characteristics. These coatings are renowned for possessing low internal stress, elevated hardness, and superior wear resistance, making them promising protective decorative layers. The fabrication of Co–Ni coatings with desirable properties can be achieved through several established methods, including but not limited to chemical plating [4–6], electroplating [7–9], pulsed electrodeposition, chemical vapor deposition [10–13], plasma spraying [14–17], and electroless plating [18–20].

Recent advancements in the field of electrodeposited Co–Ni coating research have highlighted enhancing their performance through nanoparticle reinforcement [21–24] and the adoption of pulse electrodeposition techniques [25,26]. Pulse electrodeposition [27], in particular, has been shown to significantly improve electrochemical polarization, ensure the timely replenishment of metal ions and nanoparticles near the cathode, and mitigate issues related to concentration polarization and internal stress compared to traditional direct current electrodeposition methods. Furthermore, the introduction of nanoparticles within the coating matrix has been identified as a viable strategy to enhance overall coating performance by facilitating the even distribution of these particles. Despite these advantages, the propensity of nanoparticles to aggregate due to their high-energy surfaces poses a substantial challenge.

Addressing this concern, our research group has made significant strides by developing a novel chemical synthesis approach for producing titanium dioxide (TiO₂) sol [28–30] characterized by its excellent dispersibility and stability. The introduction of this TiO₂ sol into the sol-enhanced electrodeposition process enables the in situ generation and co-deposition of nanoparticles alongside metal ions, effectively circumventing the issue of aggregation and ensuring the uniform distribution of nanoparticles within the coatings.
In this study, we explore the synergistic effects of combining pulse current electrodeposition with sol-enhanced electrodeposition techniques to fabricate Co–Ni–TiO₂ coatings of superior quality. Our investigation delves into how varying concentrations of TiO₂ sol influence the coatings’ microstructure, phase composition, hardness, wear resistance, and corrosion resistance. The outcomes of this research underscore the potential of sol-enhanced and pulse electrodeposition methods in augmenting the mechanical properties and corrosion resistance of Co–Ni–TiO₂ coatings, thereby presenting a promising pathway for the development of advanced coating technologies.

2 Experimental

2.1 Pulse current electrodeposition of Co–Ni–TiO₂ coatings

The preparation of TiO₂ sol was accurately conducted following specific methodologies outlined in our previously published work [28,29]: 8.68 mL of tetrabutylorthotitanate [Ti(OBu)₄] was dissolved in a mixture solution of 35 mL ethanol and 2.82 mL diethanolamine. After magnetic stirring for 2 h, it was hydrolyzed by adding a mixture of 0.45 mL deionized water and 4.5 mL ethanol dropwise under magnetic stirring.

In the current study, Co–Ni–TiO₂ coatings were synthesized utilizing a pulse current electrodeposition technique. This method was applied to a copper sheet substrate, which served as the cathode. Simultaneously, a high-purity cobalt plate was employed as the anode to facilitate the deposition process. To achieve precise control over the electrodeposition process, an adjustable pulse power supply was utilized. This setup allowed for the adjustment of current densities in the electrodeposition process, an adjustable pulse power supply was utilized. This setup allowed for the adjustment of current densities in the range of 25–225 mA cm⁻². The electrodeposition was conducted at a temperature of 50°C.

For this experiment, a current density of 25 mA cm⁻² was maintained. Moreover, the solution was stirred at a speed of 300 rpm for 30 min. The process parameters, including different duty cycles, were varied to investigate their effects on the morphology and properties of the resulting coatings.

2.2 Characterization of the coatings

Co–Ni–TiO₂ coatings were characterized to assess their microstructural, mechanical, and electrochemical properties. Surface and wear track morphologies were examined using a scanning electron microscope (SEM, Hitachi SU-8010) and an energy-dispersive X-ray spectroscope (Horiba, X-Max 50).

The phase composition of the coatings was meticulously determined using a D8 Advance-Bruker AXS X-ray diffractometer (XRD). This analysis was critical for identifying the crystalline structures present in the coatings, which directly impact their mechanical properties. The microhardness of the coatings was measured using a sclerometer. Wear properties were evaluated using a friction instrument (MSR-2T, Lanzhou, China). For these tests, zirconia balls of 4 mm diameter were employed under a load of 5 N at a wear rate of 10 mm s⁻¹. For each sample, the tested hardness was the average of five tests conducted randomly on the sample surface.

Electrochemical measurements were performed in a 3.5 wt% sodium chloride (NaCl) solution to evaluate the coatings’ corrosion resistance. These tests were conducted at a scan rate of 1 mV s⁻¹ using an electrochemical workstation (CS2350, Corrtest, Wuhan, China) in a standard three-electrode cell configuration.

3 Results and discussion

3.1 Structural and phase characterization

Various duty cycles of pulse electrodepositions were utilized to fabricate Co–Ni–TiO₂ coatings. Figure 1 illustrates the SEM and XRD analyses of the Co–Ni–5 mL L⁻¹ TiO₂ coatings synthesized at different duty cycles. At a low duty cycle of 0.2, the SEM images reveal that the Co–Ni–TiO₂ coating exhibits a loosely structured needle-like morphology. This can be attributed to the short duty cycle, which induces a higher cathodic overpotential, thereby enhancing the hydrogen evolution reaction at the cathode. This reaction significantly influences
the morphology of the coating’s surface, leading to the formation of a comparatively loose structure. When the duty cycle is increased to 0.4, this modification reduces the cathodic overpotential by lowering the current density applied during the pulse duration, which in turn, diminishes the hydrogen evolution reactions and lowers their effects on the surface.

Figure 1: Surface SEM morphologies of Co–Ni–TiO$_2$ coatings at different duty cycles of (a) 0.2, (b) 0.4, (c) 0.6, and (d) 0.8; (e) X-ray diffraction patterns of Co–Ni–TiO$_2$ coatings at different duty cycles.
structures. Nonetheless, the cathodic overpotential remains sufficiently high to favor the nucleation rate of the Co–Ni–TiO₂ coating. In this scenario, the nucleation predominate over grain growth, resulting in a more refined surface morphology characterized by smaller grain sizes. As the duty cycle increases to 0.6 and 0.8, the cathodic overpotential decreases further, leading to a slowdown in the nucleation process. Under these conditions, the grain growth process takes precedence over nucleation. Additionally, the decrease in the pulse current turn-off time restricts the supply of metal ions near the cathode surface and reduces the number of nucleation sites, both of which favor grain growth and lead to grain coarsening.

Figure 1e shows the XRD patterns of the Co–Ni–TiO₂ coatings prepared under various duty cycles. The diffraction peaks are observed at (111), (200), and (220) planes at a duty cycle of 0.2. The hydrogen evolution reactions at lower duty cycles could alter the textures of the XRD diffractograms, resulting in prominent peaks at (111) and (200). The incorporation of Ni atoms into the Co lattice structure shifts the characteristic peak of Co from the standard peak positions. As the duty cycle is increased, the diffraction peaks at (111) and (200) planes vanish, while the intensity of the peak at (220) plane grows. This pattern shows the necessity of regulating the duty cycle to achieve optimal coating deposition while mitigating the detrimental effects on hydrogen evolution reactions and grain coarsening.

Figure 2 demonstrates the SEM images of Co–Ni–TiO₂ coatings obtained under varying duty cycles. It reveals that at a duty cycle of 0.2, cracking between the coating and substrate is observed. This phenomenon can be attributed to the fact that at lower duty cycles, the elevated cathodic overpotential causes an intense hydrogen evolution reaction. This gas-release process could result in a porous, needle-like structure. Consequently, this leads to a reduction in the adhesion strength of the coating and a decrease in coating thickness due to the consumption of applied current in the side reactions. As the duty cycle is increased to 0.4, the reduced extent of the hydrogen evolution reaction is conducive to the deposition of the coating and enhances the deposition efficiency, leading to a thicker coating. Further increase in the duty cycle results in a

![Figure 2: Cross-sectional morphology of Co–Ni–TiO₂ coatings at different duty cycles of (a) 0.2, (b) 0.4, (c) 0.6, and (d) 0.8.](image-url)
thinner coating thickness. The shortened off-time of the pulse current is detrimental to the replenishment of metal ions at the cathode surface. Therefore, it slows down the deposition of metal ions and reduces the efficiency of deposition on the cathode surface, which in turn leads to a thinner coating.

3.2 Mechanical and corrosion performance

Figure 3 presents the mechanical testing outcomes. Figure 3a elucidates the hardness of Co–Ni–TiO₂ coatings synthesized at varying duty cycles, indicating an initial increase in hardness followed by a decrease as the duty cycle increases. The decrease in hardness at a duty cycle of 0.2 is linked to the loose surface structure formed by the vigorous hydrogen evolution reactions. Elevating the duty cycle to 0.4 mitigates the hydrogen evolution reaction, enhancing the quality of the coating and, consequently, its hardness. This improvement in hardness can be attributed to the effects of fine-grain and dispersion strengthening on the coating’s performance in hardness tests. Under these conditions, the replenishment of TiO₂ nanoparticles resulting from the relaxation time during pulse current could increase the number of nanoparticles incorporated into the composite layer with significant dispersion. The increased nucleation sites and the appropriately increased applied current could help to properly refine the coating surface and give a fine-grain straightening effect. The increased dispersion strengthening by the well-distributed nanoparticles also contributes to better mechanical performance.

However, a reduction in coating hardness is observed at a duty cycle of 0.8, likely due to a decrease in the fine-grain strengthening effect. Figure 3b shows the average friction coefficient of the Co–Ni–TiO₂ coating at various duty cycles, revealing an initial decrease followed by an increase in the friction coefficient with increasing duty cycles. This behavior is corroborated by the wear track width measurements displayed in Figure 3c–f, where the width decreases from 369 μm at a duty cycle of 0.2–255 μm at 0.4 but increases to 375 μm at a duty cycle of 0.8.

The corrosion behavior of the Co–Ni–TiO₂ coating under different duty cycles was also examined. Figure 4 depicts the potentiodynamic polarization curves of the coatings fabricated at varied duty cycles, indicating that the corrosion resistance of the Co–Ni coating initially improves with increasing duty cycle but deteriorates at a duty cycle over 0.6. Table 1 presents the Tafel curve fitting

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**Figure 3:** (a) Microhardness and (b) average friction coefficients of Co–Ni–TiO₂ coatings with different duty cycles. The morphology of the wear track of the Co–Ni–TiO₂ composite coating prepared at duty cycles of (c) 0.2, (d) 0.4, (e) 0.6, and (f) 0.8.
results, indicating a corrosion rate of 0.071 mm·a^{-1} for the Co–Ni–TiO₂ coating at a duty cycle of 0.2. The formation of a loose needle-like structure on the coating’s surface at this duty cycle facilitates the penetration of the corrosive medium, thereby diminishing the coating’s corrosion resistance. Elevating the duty cycle to 0.4 significantly reduces the corrosion rate to 0.034 mm·a^{-1}, signifying improved corrosion resistance at this higher duty cycle. The optimal corrosion resistance observed at a duty cycle of 0.4 can be ascribed to its compact surface, which effectively blocks corrosion attacks. However, further increasing the duty cycle to 0.8 leads to an increase in the corrosion rate to 0.072 mm·a^{-1}, as the coarsened surface lowers the coating’s density and corrosion resistance.

### 4 Conclusions

In this study, Co–Ni–TiO₂ coatings were synthesized via an innovative method that combined pulse current with enhanced electrodeposition techniques, which exhibited superior characteristics. The synthesis of Co–Ni–TiO₂ coatings was conducted across varying pulse duty cycles to ascertain the optimal conditions for achieving a compact surface morphology. It was demonstrated that employing a pulse duty cycle of 0.4 significantly enhanced surface compactness. Furthermore, the application of this specific pulse duty cycle in the fabrication process of Co–Ni–TiO₂ coatings achieved the most diminutive grain size, alongside optimizing mechanical robustness and corrosion resistance. The outcomes of this comprehensive study shed light on the intricate relationship between the duty cycle parameters and the resultant properties of Co–Ni–TiO₂ coatings. This investigation lays a foundational framework for the future optimization and enhancement of these coatings, aiming to maximize their performance and applicability in various industrial sectors.

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### Author contributions

Zihan Liu, Songling Zheng, Zengcheng Miao, Jiaming Liu: Investigation and methodology; Zhen He and Jiajian Guan: Writing, reviewing and Investigation.

### Conflict of interest

Authors state no conflict of interest.

### References


