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ARTICLE

Effects of n-Al_2O_3 Particles Content on Structure and Performance of Electro-Brush Plating Ni-Co Alloy Composite Coatings

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Abstract: The composite electronic brush plating technique was used to prepare alloy nanocomposite coatings with different nano-Al_2O_3 particles contents. The effects of nanoparticles content in the electrolyte on the deposition rate, nanoparticles content in coating, microhardness and tribological property of composite coatings were investigated by scanning electron microscopy, microhardness tester and attrition testing machine. It is found that with the increase of nano-Al_2O_3 particles content in the electrolyte, the deposition rate of coatings drops, the surface morphology of the coating becomes flat, the microhardness first increases and then decreases, and wear scar depth and friction coefficient decrease first and then increase. When the nano-Al_2O_3 particles concentration in the electrolyte is 20 g/L, the coating reaches its optimized structure and performance.

Key words: nanocomposite plating technique; nanoparticle; hardness; tribological property

The nanomaterials, due to their small size effect, have unique physical, chemical, electrical, and magnetic properties, and belong to the research field of the materials science leading frontier[1]. The nanocomposite coatings refers to a special metal matrix composite, formed by mixing one or more insoluble nanosized solid particle (s), inert particle (s), fibers, etc., uniformly to the metal deposition layer by the method of electrodeposition[2-4]. The electronic brush plating technique, a significant innovation in the electrodeposition field, is an advanced technique of surface engineering and equipment remanufacturing, and widely applied to equipment surface reinforcement and repairing[5,6]. The nanoparticle composite coatings prepared by the electronic brush plating technique have higher hardness[7,8], excellent abrasion resistance[9,10], corrosion resistance[11] and higher anti-fatigue properties[12,13], which attracts more and more attention. However, the studies are focused more on the nickel base composite plating by the electronic brush plating, and there are fewer studies on the alloy nanocomposite plating, which is far from developing the advantages of the nanocomposite electronic brush plating technology.

In the present investigation the composite electronic brush plating technique was adopted to prepare the alloy nanocomposite coatings using Ni-Co alloy coatings as matrix, nano-Al_2O_3 particles as the reinforcing phase. The effects of nanoparticles content in the electrolyte on the deposition rate, nanoparticles content, microhardness and tribological property of composite coatings were discussed.

1 Experiment

The technical principles of nanocomposite electronic brush plating are basically consistent with the technique of electronic brush plating, employing a dedicated constant voltage DC power device, a plating pen engaging positive electrode of powered source as the anode of brush plating, and a workpiece engaging the negative electrode of the power source as the cathode of brush plating. The anode of the plating pen uses highly pure graphite blocks with the anode

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outside surrounded by lots of cotton immersed in the electrolyte and wearable polyester cotton sleeve. The plating pen moves on workpiece surface at a relative moving speed after the plating pen is fully immersed in the electrolyte upon brushing plating. Under the influence of electrical force, metal ions in the electrolyte obtain the electrons, reducing to give the metal plating on cathode surface, forming a matrix phase of the nanocomposite plating; at the same time, nanoparticles in the electrolyte are carried to co-deposit into the metal coating, forming a nanocomposite coating reinforcing phase, and the nanocomposite electronic brush coatings become thickening gradually as the electronic brush plating time is passing by.

The nano-Al_2O_3 particles were selected as the reinforcing phase in the test with the main specifications as shown in Table 1.

Table 2 lists the main components and the content of the Ni-Co electrolyte employed in the tests. The electrolyte was dark green and would smell acetic acid.

During the process of n-Al_2O_3/Ni-Co composite electronic brush electrolyte prepared by the high energy ball milling, firstly, Ni-Co alloy electrolyte was formulated according to Table 2, and then nano-Al_2O_3 particles were gradually added to the formulated electrolyte, simply stirred with a glass rod, at this time, the agglomerated nanoparticles could not decompose, and the nanoparticles were adsorbed one another. In order to disperse the agglomerated nanoparticles, the electrolyte with the nanoparticles was poured into a high energy ball mill to conduct a sufficient ball milling dispersion (24 h). Hard agate balls in the ball mill will mill and disperse the agglomerated nanoparticles, greatly reducing the grain size of the nanoparticles. The nanoparticles could adsorb metal ions and functional groups in the electrolyte. The metal ions and functional groups mutually generate an electrostatic force resistance effect, so that the nanoparticles cannot be close to each other, and then n-Al_2O_3/Ni-Co composite electronic brush electrolyte was obtained.

The process of electronic brush plating was as follows: preplating surface preparation, electronic cleaning, washing with deionized water, 2# activating with activate fluid, washing with deionized water, 3# activating with activate fluid, washing with deionized water, wiping without electricity, plating the base coating, washing with deionized water, wiping without electricity, brush plating the working plating.

With Nova NanoSEM 450/650-type environmental scanning electron microscope, the surface topography of the coatings was tested, and Feature Max-type X-ray spectrometer was used to test and get the element distribution of the coating surface. The microhardness was measured by HVS-1000 digital display microhardness tester, at load 0.49 N, for loading time 15 s.

The tribological properties of the coatings were tested by CETR-UTM-3-type ultra-functional attrition testing machine. Fig.1 is a schematic diagram of the test principles. The milled sample of the coating test-piece is a Si_3N_4 ball with a diameter of 4 mm, HV hardness of 17 GPa. To ensure the relative property, 1000# abrasive paper was used to polish the coating surface before the test. Before each test, the upper and lower samples must be cleaned with ultrasonic and alcohol and 3 trials were run under the same conditions. After finishing the test, the wear rates were calculated by the wear scar depth recorded by the tester. Dry friction test was conducted at room temperature. Test parameters were as follows: load 10 N, amplitude 5 mm, frequency 5 Hz, and time 20 min.

2 Results and Discussion

2.1 Deposition rate

Fig.2 shows how the addition amount of the nanoparticles in the electrolyte affects the coating deposition rate. As can be seen from the figure, with the increase of nanoparticles in the electrolyte, the coating deposition rate becomes slow, and the dependence of the drop of the coating deposition rate on the increase of the nanoparticles content in the electrolyte approximately exhibits a linear relationship. Ni-Co alloy coating deposition rate is 4.8 μm/min. When the nanoparticles content in the electrolyte is 25 g/L, the deposition rate is reduced to 2.067 μm/min, which is about 43% of Ni-Co alloy coating deposition rate.

There are three reasons for the reducing of the coating deposition rate when the nanoparticles are added to the electrolyte. Firstly, for the added nano-Al_2O_3 particles in the electrolyte are non-conductive particles, they act as a shield, reduce the conductivity of the electrolyte, and thus reduce the deposition rate. Secondly, nano-Al_2O_3 particles are co-deposited

Table 1 Index of nano-Al_2O_3 particles

Nano-particle	Particle size/nm	Specific surface area/m^2 g^{-1}	Purity/ %	Apparent density/ g cm^{-3}
Al_2O_3	50	≤10	≥99	1.6

Table 2 Main components and the content of Ni-Co electrolyte (g/L)

Nickel sulfate	Cobalt sulfate	Nickel chloride	Formic acid	Acetic acid	Hydrochloric acid
100~125	0~50	40~60	18	48	150

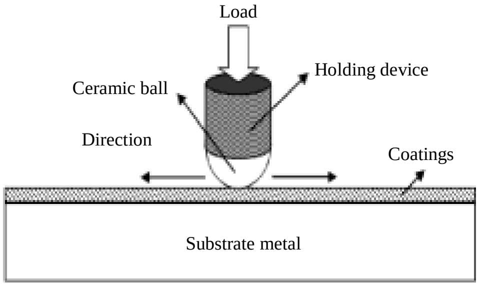

Fig.1 Schematic diagram of CETR test rig

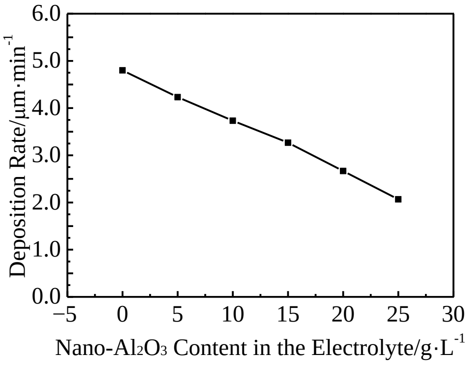

Fig.2 Deposition rates changing with the nanoparticles content in electrolyte

by Ni-Co alloy deposition wrapping. The nanoparticles are insulating ones. It must have nucleation again for continuing the deposition where the nanoparticles are located. The deposition of nanoparticles in the composite coating corresponds to the “Mosaic” of nanoparticles; however, the thickening rate of the nanoparticle’s “Mosaic” is less than the deposition rate of Ni-Co alloy electro crystallization. Thus, with the increase of the addition amount of nanoparticles in the electrolyte, the coating deposition rate decreases significantly. In addition, since the coating thickness was tested with a micrometer in the present test, the alloy coatings surface has higher roughness than the alloy nanocomposite coatings, so that the virtual size is produced during testing, and the test value of the alloy coatings is too large.

The electronic brush plating process was basically conducted manually with relatively large labour intensity. Slow deposition is a disadvantage for nanocomposite electronic brush plating technique. Therefore, in practical applications, the addition amount of nanoparticles is minimized as far as possible under the premise of meeting property requirements.

2.2 Surface topography

Fig.3 shows how different nanoparticles content in the electrolyte affects the coating surface topography. As can be seen from the figure, Ni-Co alloy coating surface is slightly rough. After co-depositing with nanoparticles, the surface morphology of alloy nanocomposite coatings is flatter and more uniform. During the electrodeposition process, the substrate surface is slightly convex, producing a “point effect”, the current density increases, and the deposition rate increases, so that the coating layer surface becomes uneven, and the nanoparticles are co-deposited into the coating, adsorbed to the slight convex on the cathode surface, so that the coating surface becomes flat. As can be seen from Fig.3a~3e, with the nanoparticles content increasing from 0 g/L to 20 g/L in the electrolyte, the coating surface becomes smoother and flatter, but when the nanoparticles content reaches 25 g/L in the electrolyte, the surface smoothness becomes slightly worse. This is because the nanoparticles easily produce agglomeration; the smoothness degree of the coating surface is in reduction. With the nanoparticles increasing in the electrolyte, it is more likely for nanoparticles to re-agglomerate during deposition, leveling effect weakens, and thus the flatness of the coating surface is reduced during the deposition process when the nanoparticles concentration increases in the electrolyte.

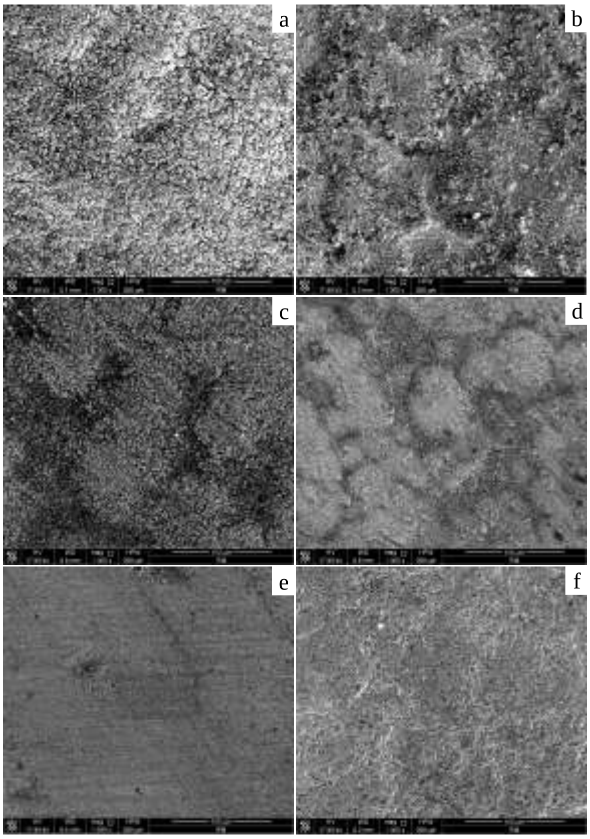

Fig.3 Coating surface topography changing with nanoparticles content in electrolyte: (a) 0 g/L, (b) 5 g/L, (c) 10 g/L, (d) 15 g/L, (e) 20 g/L, and (f) 25 g/L

The coating surface is further electrically deposited cathode surface, directly affecting the behavior of the electrodeposition, and the final properties of coatings will also be influenced. If continuing electrodeposition on a relatively flat cathode surface, the microstructure of the coatings will be more evenly. The uniformity will be increased, and the coating property will be also improved. Thus, in order to have an optimal structure and property, the addition amount of nano-Al_2O_3 particles is selected as 20 g/L in n-Al_2O_3/Ni-Co alloy composite electrolyte.

2.3 Nanoparticles content in coating

Fig.4 shows how the addition amount of nanoparticles in the electrolyte affects the nanoparticles content in the coatings. As can be seen from the figure, with the increase of addition amount of nanoparticles in the electrolyte, the nanoparticles content will increase in the coatings. When the addition amount of nanoparticles is 20 g/L, the nanoparticles content in

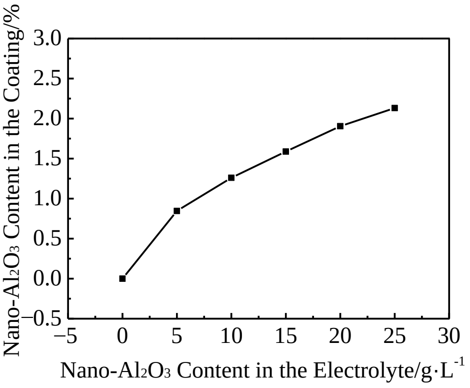

Fig.4 Changes of nanoparticles content in coating with addition amount of nanoparticles in electrolyte

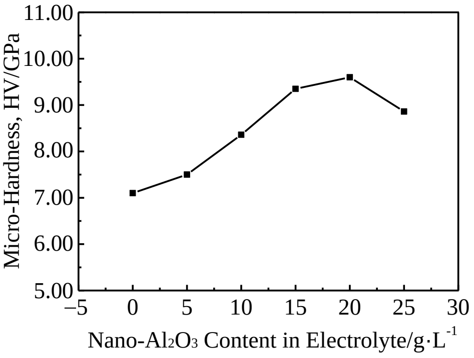

Fig.5 Coatings hardness changing with nanoparticles content in electrolyte

the coating is 1.9 wt%. When the addition amount of nanoparticles is 25 g/L, the nanoparticles content increases to 2.1 wt% in coating. The dependence of the nanoparticles content in the coating on the addition amount of nanoparticles in the electrolyte does not show an absolute linear relationship, but with the increase of addition amount of nanoparticles increasing in the electrolyte, the increasing trend of nanoparticles in the coatings becomes slightly slow.

Since the nano-Al_2O_3 particles are insulating ones, the particles are co-deposited by the wrapping function of Ni-Co alloy. When the nanoparticles concentration in the electrolyte is low, the probability that the nanoparticles are wrapped when co-deposited with Ni-Co alloy increases fast with the increase of concentration, but when the nanoparticles concentration in the electrolyte is higher, the increase of the probability for being wrapped becomes slower. The nanoparticles concentration in the electrolyte is too high, which will produce agglomeration due to a higher surface activity during friction between the plating pen and the substrate. The agglomerated nanoparticles, due to the larger volume, reduce the probability for being wrapped; at the same time, the deposition rate of the alloy nanocomposite coating decreases, and the increasing amplitude for the co-deposition amount of nanoparticles decreases.

2.4 Microhardness

Fig.5 shows how the addition amount of nanoparticles in the electrolyte affects the microhardness. As can be seen from the figure, the coating microhardness increases as the addition amount of nanoparticles increases in the electrolyte. When the addition amount increases to 15 g/L, the coating hardness is 9.35 GPa. Upon increasing to 20 g/L, the n-Al_2O_3/Ni-Co nanocomposite coatings get the largest hardness, reaching 9.60 GPa, increasing by about 35.2% compared with that of the Ni-Co alloy coating hardness 7.10 GPa. When the nanoparticles content increases to 25 g/L in the electrolyte, the coating has a hardness of 8.86 GPa with slight decreasing.

Nanoparticles are wrapped and co-deposited in the Ni-Co alloy matrix metal. During the deposition process, the nanoparticles are non-conductive. It must have nucleation again if the coating continues to grow. The co-deposition of nanoparticles increases the nucleation rate. The nanoparticles co-deposited into the coatings will impede the crystal grains near the nanoparticles to continue to grow, the coating crystal grains are refined, crystal boundary area increases, resulting in difficult deformation of crystal grains, and increasing of coating hardness. When the addition amount of nanoparticles in the electrolyte is below 20 g/L, the strengthening effect increases, coating property such as hardness is improved. When the addition amount of nanoparticles in the electrolyte is over this value, the nanoparticles in the coating agglomerate, the coating microstructure can become loose, the coating property may be reduced, and the hardness may decrease somewhat.

Integrating the effects of nanoparticles on the coating deposition rate, surface morphology and nanoparticles content in the coating and coating hardness, the addition amount of the nanoparticles in the electrolyte is not as more as better from the perspective of the applicability of the process. With excessive addition amount, although the nanoparticles content in the coating increases slightly, but the coating deposition rate, surface morphology and coating hardness are reduced, and thus the nanoparticles should be added moderately. The amount of nanoparticles with 15~20 g/L in n-Al_2O_3/Ni-Co alloy nano-composite electronic brush electrolyte is more reasonable.

2.5 Tribological property

Fig.6 shows how nano-Al_2O_3 particles affect the wear scar depth and the friction coefficient of the n-Al_2O_3/Ni-Co alloy nanocomposite coatings under the conditions of dry friction. From the analysis of Fig.6a, it can be found that the wear scar depth of Ni-Co alloy coating is 33.80 μm. The wear scar depth is slightly reduced with increasing of nanoparticles content, reaching a minimum 21.40 μm at 20 g/L, about 57.4% reduced compared with Ni-Co alloy coating abrasion resistance, thereafter, the wear scar depth slightly increases again. As can be seen from Fig.6b, Ni-Co alloy coating has a friction

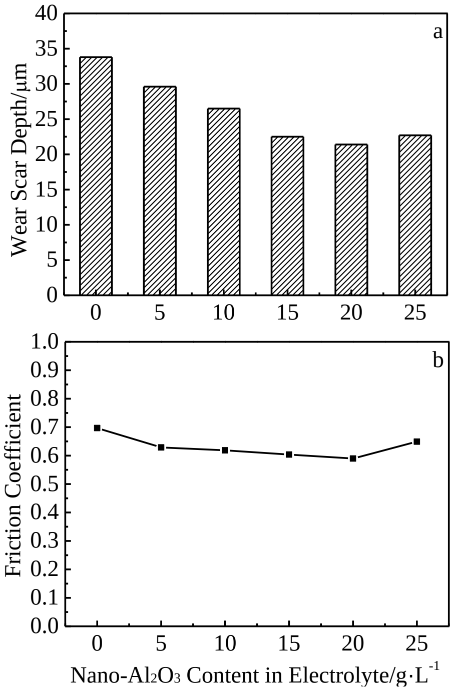

Fig.6 Dry friction coating wear scar depth (a) and friction coefficient (b)

coefficient of 0.70, and the friction coefficient is slightly reduced with increasing nanoparticles content, reaching a minimum 0.59 at 20 g/L, thereafter, the friction coefficient increases slightly. With a comprehensive analysis, when the concentration of nanoparticles is 20 g/L, alloy nanocomposite coating has the best tribological property.

Fig.7 shows the wear topographies of n-Al_2O_3/Ni-Co alloy nanocomposite coatings at the nanoparticles concentration with 20 g/L in electrolyte, wherein, Fig.7a is friction topography of Ni-Co alloy coating, and Fig.7b is wear topography of n-Al_2O_3/Ni-Co nanocomposite coating. As can be seen from Fig.7a, under the same test condition, the wear surface of Ni-Co coating takes on discontinuous sheet-like flaking. Under a heavy stress, the coating exhibits a stronger brittleness, sheets tending to fall off, low alloy coating hardness, low resistance to shear forces, forming more grinding, which exacerbate the wear rate. As can be observed from Fig.7b, the sheet-like flaking on alloy nanocomposite coating surface is significantly reduced compared with that on Ni-Co alloy coating; meanwhile, squamous morphology appears in local coating. This is because the hardness of alloy nanocomposite coating is significantly increased due to the refined crystalline strengthening and dispersion strengthening effect of nano-Al_2O_3 particles, and coating structure is refined, wherein microcrack number is reduced, and density increases. During the process of wear, co-deposited nano-Al_2O_3 particles act as a support, reducing the number of crack producing source in the coating, inhibiting the spread of the crack in the coating, and improving wear resistance of the coating.

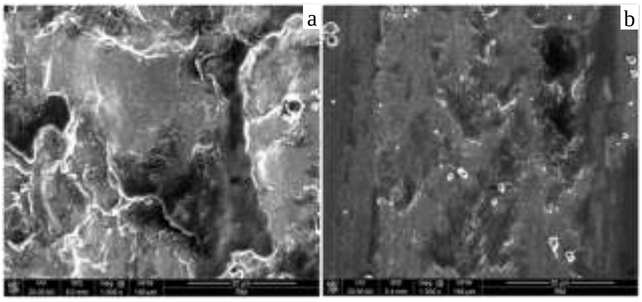

Fig.7 Wear scar morphology comparison of coatings under dry friction: (a) Ni-Co and (b) n-Al_2O_3/Ni-Co

3 Conclusions

1) With the increase of nanoparticles concentration in the electrolyte, the coating deposition rate drops. When the nanoparticles concentration in the electrolyte is 25 g/L, the deposition rate of nanocomposite coating versus Ni-Co alloy coating is reduced by 43%, while nanoparticles content in coating increases to 2.1 wt%.

2) With the increase of nanoparticles concentration in the electrolyte, the coating surface topography becomes flatter, hardness increases, and tribological performance is enhanced. When the nanoparticles concentration in the electrolyte is 20 g/L, alloy nanocomposite coating properties reaches the optimized value, while nanoparticles concentration continues to increase, and properties decrease slightly.

3) Due to the refined crystalline strengthening and dispersion strengthening effect of nano-Al_2O_3 particles, the alloy nanocomposite coating structure is refined and its hardness increases. The wear morphology of coating takes on squamous flaking, and abrasion resistance is improved.

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纳米 Al_2O_3 颗粒含量对 Ni-Co 基纳米复合电刷镀层组织和性能的影响

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摘　要：采用电刷镀技术制备了不同 Al_2O_3 颗粒含量的合金纳米复合电刷镀层，使用扫描电镜、硬度测试仪和摩擦磨损试验机测试了镀液中纳米 Al_2O_3 颗粒含量对镀层的沉积速度、纳米颗粒含量、硬度和摩擦学性能的影响。结果表明，随着镀液中纳米 Al_2O_3 颗粒含量的增加，电刷镀层沉积速度降低、表面形貌平整，显微硬度先提高而后降低，磨痕深度和摩擦系数先减小后增大。当镀液中纳米 Al_2O_3 含量为 20 g/L 时，镀层具有最优的组织和性能。

关键词：纳米复合镀层；纳米颗粒；硬度；摩擦学性能

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