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The jet electrodeposition technology was used to prepare nano-Al_2O_3 nanocomposites. Effect of the additive amount of nano-Al_2O_3 particles and cathode current density on the nanoparticle content in composites was studied. The scanning electron microscope and X-ray diffractometer were adopted to analyze the micromorphology of the composites, research the effect of nanoparticle content in composites on the microhardness, bonding strength, and corrosion resistance. The results show that nickel deposited layer has the nanocrystalline microstructure, with the average grain size of about 40 nm; the content of nano-Al_2O_3 particles in the deposited layer can reach 2.5 wt%; the composite coating prepared are all face-centered cubic structure and represent a (200) preferential orientation. With the increase of Al_2O_3 content, the microhardness of coating will increase gradually and the bonding strength and corrosion resistance will first increase and then decrease.

Keywords: electrodeposition; nanocomposite; current density; bonding strength; corrosion resistance

1. Introduction

Electrodeposition of nanocomposite coatings, based on second phase hard particles dispersed in a metallic matrix, is gaining importance for potential engineering applications, however, the very low depositing rate of the conventional electrodeposition has limited the practical application of electrodeposition as a mean to prepare the composite materials [1,2].

Jet electrodeposition changes mass transfer process of deposition reaction by means of electrolyte high-speed flow on cathode surface, thus greatly increasing its limiting current density and enabling electrodeposition reaction to be performed continuously under very high current density, resulting in greatly refining crystalline grain in deposit layer and improving electrodepositing rate. The articles [3] reported that the deposit layer have crystalline microstructure. Till date, the Ni–Al_2O_3 composite coatings fabricated by jet electrodeposition have not been reported.

In this present work, we prepared Ni–Al_2O_3 nanocomposite coatings by jet electrodeposition technology. The effect of the concentration of Al_2O_3 in the electrolyte and cathode current density on the amount of Al_2O_3 codeposited in the composites was systematically studied. Microhardness and bonding strength and corrosion resistance of the Ni–Al_2O_3 nanocomposites were also investigated.

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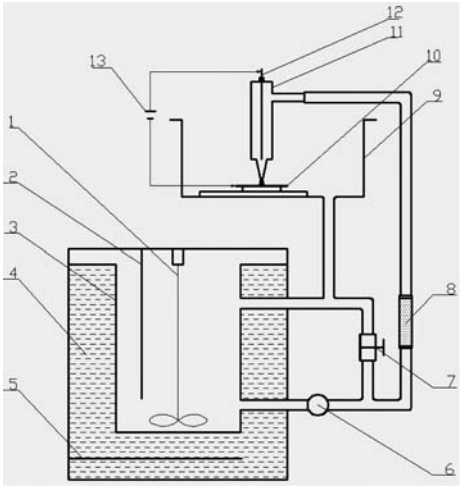

Figure 1. Diagram of jet electrodeposition equipments. (1) agitator (2) temperature transductor (3) vessel with electrolyte (4) distilled water (5) heater (6) centrifugal pump (7) valve (8) flowmeter (9) electrodepositing room (10) cathode (11) nozzle (12) anode and (13) current power.

2. Experimental details

2.1. Experimental equipments

The schematic representation of jet electrodeposite equipments are shown in Figure 1. The electrolyte was pumped from the vessel with invariable temperature electrolyte, and then reflowed to the vessel from the output of electrodeposting room via the bump of filter, and the flowmeter. The electrolyte temperature was measured by the heater and temperature transducer. The jet speed was adjusted by flowmeter.

During the jet electrodeposition process, the electrolyte is jetted on a cathode surface directly because of the existence of electric field between the cathode and anode located in the jet nozzle, as the electric current travels along the jet stream to the cathode, the deposition takes place only on the local cathode surface area where the jet impinges on. Thus, jet electrodeposition provide high depositing rate. In addition, the grain size refining effect of jet electrodeposition is more efficient.

2.2. Composition of electrolyte and processing parameters

The electrolyte used was based on a standard nickel Watt solution. The composition and processing parameters are given in Table 1. Al_2O_3 particles with a mean diameter of 50 nm were used. Each electrolyte was mixed by magnetic stirring for 24 h, and subsequently by ultrasonic agitation for 30 min just prior to electrodeposition. Electrodeposition was carried out on vertical electrodes, and the electrolyte was agitated during electrodeposition with a magnetic stirrer.

Table 1. Composition of the electrolyte and processing parameters.

Composition of electrolyte	Processing parameter
$NiSO_4 \cdot 6H_2O$/250 g L^{-1}	pH/4.0
$NiCl_2 \cdot 6H_2O$/60 g L^{-1}	Temperature of electrolyte/50 °C
H_3BO_3/40 g L^{-1}	Electrodepositing time/20 min
Additive/0.2 g L^{-1}	Jet speed of electrolyte/1 m·s^{-1}

2.3. Composition and properties analysis

The surface morphology and the components of the deposits were studied by using a field emission scanning electron microscope (FESEM, LEO-1530VP) with energy dispersive analyzer system (EDX). The weight fraction of aluminum was determined by using the aluminum to oxygen ratio 2:3 determined by the chemical formula Al_2O_3. The phase constitution of the deposits was characterized via X-ray diffraction (XRD). It was carried out by powder diffraction method at room temperature using a D/MAXRC X-ray diffractometer.

Vickers microhardness tests were conducted on an HXS-1000A microhardness tester using a load of 50 g applied for 10 s. Each hardness value was an average of five measurements.

The bonding strengthened between the composite and substrate was measured on SANSI-028A type universal tensile machine under the following conditions: loading speed 1.0 mm/min and load 0.1 KN. Specimens first, with the diameter of 20 mm and thickness of 100 μm on the low-carbon steel substrate was prepared, then jointed to another piece of low-carbon steel with inorganic glue. Finally, the test was carried out after full solidification.

The corrosion behavior of composite coatings was evaluated by weight-loss method in a 4% HCl solution, which is given by equation as $V = \Delta W/s.t$, where V is the corrosion rate; ΔW is lose weight; s is exposed surface area in the corrosive liquid; and t is the corrosion time. Specimens with area of 30×20 mm were prepared. The mass of the change of the specimens was measured by the analytical balance with precision of 0.1 mg. Before weighing, the specimens were cleaned by ultrasonic cleaning machine.

3. Result and discussion

3.1. Composition of nanocomposites

Figure 2 represents that wt% of Al_2O_3 in the composite varies with different contents (10–40 g/L) of Al_2O_3 particles in the electrolyte. The result shows that the incorporation of nanoparticles has a proportional relation with the content of particles suspended in the electrolyte. This phenomenon can be explained that, the more particulates in suspension within electrolyte, the more particulates travel to around the cathode surface through stirring and the more ones embedded in metal matrix, resulting an increase in the incorporation of Al_2O_3.

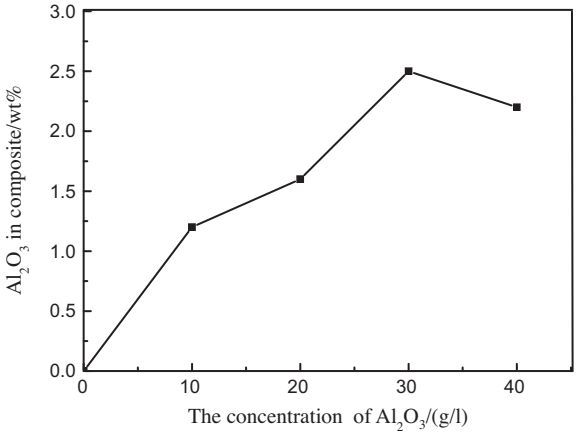

Figure 2. Effect of concentration on the wt% of Al_2O_3 in the composite coatings.

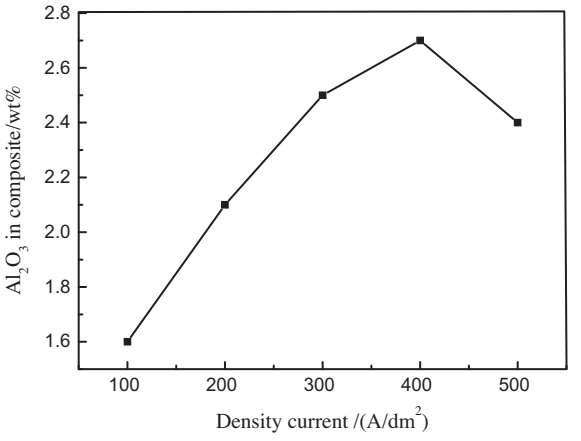

Figure 3. Effect of current density on the wt% of Al_2O_3 in the composite coatings.

However, when the content of Al_2O_3 in electrolyte surpassed 30 g/L, the Al_2O_3 wt% began to decrease. It can be attributed that, on the one hand, the metal matrix has not been able to take so many adsorbed particulates at this point any more, and on the other hand, particulates themselves, due to colliding each other in electrolyte, are agglomerated and result in the decrease of degree of charge at particle surface.

Another reason may be related to those surplus particles dispersed in electrolyte, which scour and seep away the ones not fully embedded on the cathode. Therefore, the particles should not be excessively added into electrolyte and a proper addition of strengthening particle is essential [4,5].

Figure 3 represents that wt% of Al_2O_3 in the composite varies with cathode current density (100–500 A/dm^2). It is found that, when the Al_2O_3 particle in the electrolyte is added to certain amount, the current density of Al_2O_3 particle content in the coating will increase first and then decrease. This is because, with the increase of cathode current density, the cathode over potential will increase accordingly, the electric field force increases, the electrostatic attraction of nanoparticles with positive ion increases, playing a certain role in the codeposition of particle and matrix metal. However, when the cathode current density is too high, the deposition velocity of matrix metal is enhanced and the particle is transported near the cathode and the velocity of embedding into coating is slower than the metal deposition velocity, which will also lead to the decrease of Al_2O_3 particle content in the coating. In addition, the particles embedded into the cathode surface cover parts of cathode surface. What's more, the particle conductivity is so poor that the actual area of the cathode decreases, leading to the increase of actual current density and causing a lot of hydrogen. It will also prevent the codeposition of particle and matrix metal [6,7].

3.2. Microstructure analysis

The scanning electron microscope of surface morphologies of Ni–Al_2O_3 nanocomposites is represented in Figure 4. It is observed that the texture of pure nickel coating is uneven. With the increase of nano-Al_2O_3 content, the density and smoothness of coating will be improved significantly. The reason for this situation is that small nano-Al_2O_3 particles suspended in electrolyte play a certain role in nucleation objectively, increasing the number of growing nuclear, refining the grain of deposition, restraining the growth of nucleation grain, and making the metal deposition layer relatively compact and smooth [8,9]. The measured grain size

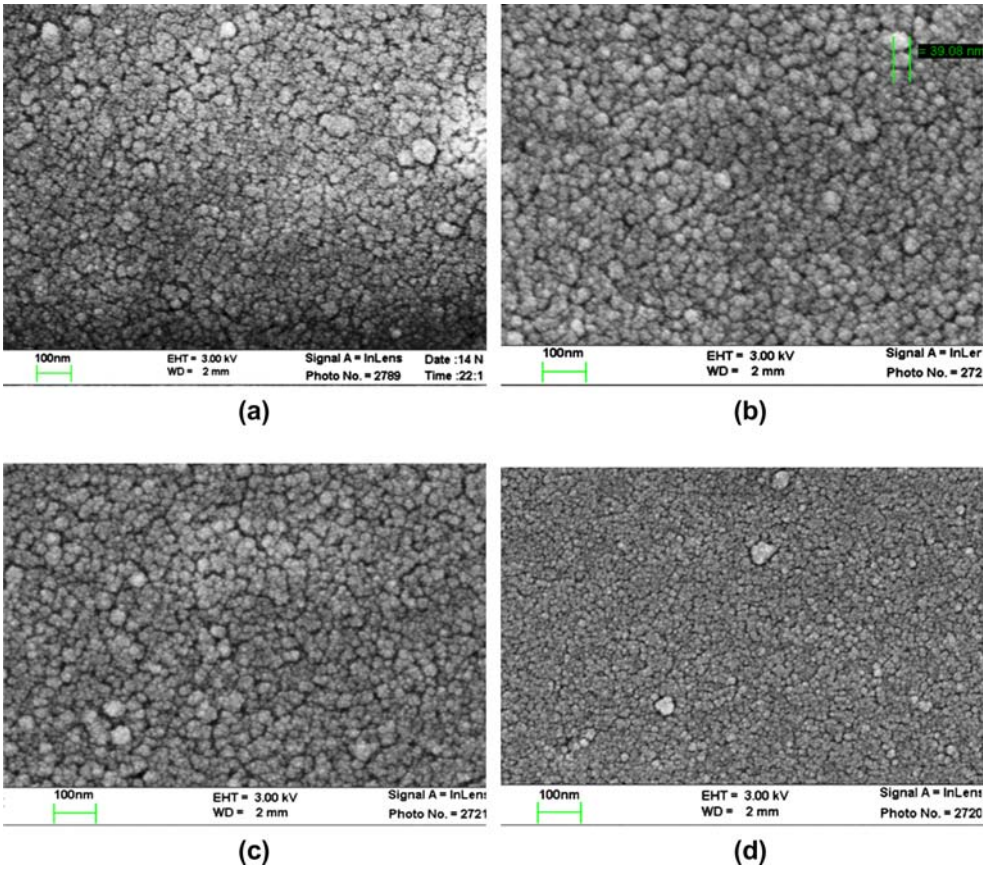

Figure 4. Microstructures of composites, (a) pure nickel (b) 1.2 wt% Al_2O_3 (c) 1.6 wt% Al_2O_3 and (d) 2.5 wt% Al_2O_3.

of coating texture in Figure 4(b) is about 40 nm. Although, the nano-Al_2O_3 distribution condition in coating cannot be clearly distinguished, it can be identified that Ni–Al_2O_3 composite deposition layer has 'double nanostructure,' i.e. the sizes of base metal grain and additive grain are all within the nanorange. This is because the high current density of jet electrodeposition enhances the cathode overpotential directly, decreases the critical crystal nucleus radius of nucleation, increases the nucleation number, restrains the epitaxial growth trend of grain, and avoids the production of bulky grain and refines the grain, making the jet electrodeposition technology to obtain nanocrystalline coating in the DC condition directly.

The XRD patterns and preferential orientation of the several specimens indicate changes in texture of such coatings which are dependent on the Al_2O_3 content of the coatings (Figure 5). It can be found that the crystal planes corresponding to each diffraction peak are (1 1 1), (2 0 0), and (2 2 0) in turn. Both specimens are face-centered cubic structure and represent a (2 0 0) preferential orientation. With the increase in the Al_2O_3 content of the composites, the orientation index of (1 1 1) decrease and that of (2 0 0) increase. A change in preferred orientation would lead to the difference between the coatings; it is possible that the disturbing of the particles affects the growth of crystallites which leads to the evolution of surface diffraction density and orientation and orientation.

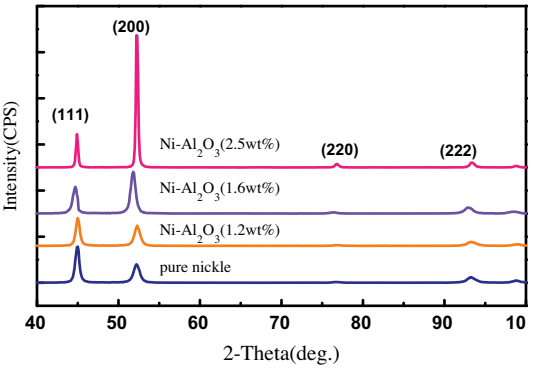

Figure 5. X-ray patterns of composite.

3.3. *Microhardness*

Figure 6 shows the relationship between Al_2O_3 content and coating microhardness. It can be seen that the coating microhardness of pure nickel is 307 HV and the microhardness of coating with the content of 2.5 wt% is 511 HV. Thus, it can be seen that the hardness of composite coating is higher than pure Ni coating and the microhardness of coating increases with the increase of Al_2O_3 content. The more the Al_2O_3 content, the more obvious the strengthening effect. The increase of coating hardness is due to: (1) the Al_2O_3-nanoparticles are distributed in the coating evenly, playing a dispersion-strengthening role in greatly increasing the number of dislocation, twin crystal and various defects in coating; (2) the Al_2O_3-nanoparticles restrain the grain growth and result in the compaction of coating texture in the process of deposition.

3.4. *Bonding strength*

Figure 7 shows the tensile fracture of the nanocomposite after bonding strength test. It is obvious that fracture occurs at the junction surface between coating and substrate, where there is supposed to be the weak position on the entire coating.

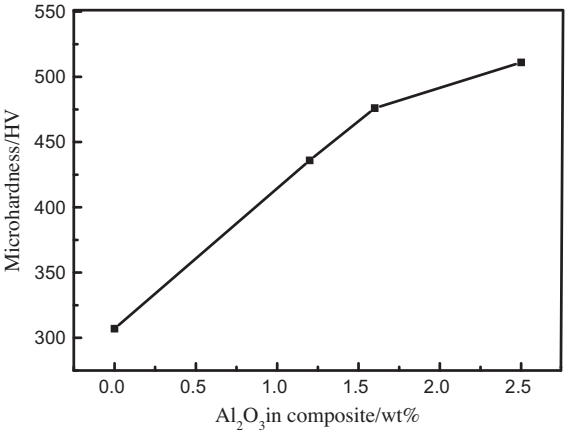

Figure 6. Effect of wt% of Al_2O_3 in the composite on microhardness.

Figure 7. Cross-sectional morphology of the breaking example.

Test results indicate that, when the specimen thickness reached about 100 μm, the bonding strengths were 8.5, 12.3, and 9.9 MPa, respectively, on the coating of pure nickel, composite with 1.6 wt% Al_2O_3 and the one with 2.5wt% Al_2O_3. It reveals that, if Al_2O_3 content is relatively low, bonding strength is better than pure nickel, but will get worse along with the increase of the Al_2O_3 content. The reason is that the combination between the coating and substrate mainly depends on the bonding of substrate and metal matrix. The nanoparticles embedded in coating can refine grain, which indirectly extends the bonding area between metal matrix and substrate, thus effectively improving the bonding strength. As the amount of Al_2O_3 in the coating increases, the interface of metal matrix and substrate correspondingly contains more Al_2O_3 particles resulting in smaller effective bonding area. When the effect of decreasing bonding area due to increasing incoming particulates is more significant than that of metal grain refining which help extend bonding surface, the bonding strength begins to gradually decline as the Al_2O_3 content increases.

3.5. Corrosion behavior

According to the data obtained from the coating static test in 4% HCl solution for 48 h, the average corrosion rate of the coating is as shown in Table 2. When the content is low (1.6 wt%), the nanoparticles cannot play the dispersion role but reduce the corrosion resistance of coating making it worse than nickel coating. When the content is high (2.5 wt%), the nanoparticles will easily produce agglomeration, leading that the structure of composite coating is not compact, the corrosion resistance is bad and relatively lower, but better than pure nickel coating. All this shows that it is important to select appropriate nanocontent to improve the corrosion resistance of coating. The high or low content is bad for its corrosion resistance [10]. Through 48h corrosion test, we found that the surface of pure nickel coating had a lot of corrosion pits and the surface of coating with nano-Al_2O_3 content of 1.6 wt% is smooth and the corrosion pits are not obvious. This further states that the composite coating with a certain content of nano-Al_2O_3 can really improve the corrosion resistance of the coating.

Table 2. Average corrosion rate of the different composite coatings.

	The Al_2O_3 content/wt%			
Corrosion rate	0	1.2	1.6	2.5
$g\,m^{-2}\,h^{-1}$	1.72	1.90	0.70	0.92

4. Conclusions

The nanocomposite coatings with different Al_2O_3 content were prepared by jet electrodeposition and the related composition and structure was investigated.

The Al_2O_3 content in the composites first increase then decrease with the increase in the concentrations of Al_2O_3, current density as well as jet speed. The maximum wt% of Al_2O_3 in the composite is high up to 12.2. The higher the Al_2O_3 content , the composite becomes more smooth and impact. The composite coating is face-centered cubic structure and represented a (2 0 0) preferential orientation. Microhardness of the coating increase, bonding strength and corrosion resistance of the coatings first increase then decrease with increase of Al_2O_3 content in coatings.

Acknowledgments

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