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Chemical and electrocatalytical interaction: influence of non-electroactive ceramic nanoparticles on nickel electrodeposition and composite coating

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Abstract This article focuses on the nanoparticle electrocatalytical action on electrodeposition of nickel and the chemical combination state between nanoparticles and matrix metal in composite coating. The electrochemical behavior, from common and composite brush electroplating solution, is investigated by cyclic voltammetry. The interaction between nanoparticles and matrix metal nickel is researched by X-Ray Photoelectron Spectrometry (XPS). The microstructure and morphology of coating are observed with Transmission Electron Microscope (TEM) and Scanning Electron Microscope (SEM). The results show that nanoparticles not only can obviously induce the increasing of the current efficiency and decreasing of overpotential, but also can distinctly refine the metal crystal grains of composite coating. The experimental results demonstrate that nanoparticles take part in the electrode reaction and can evidently catalyze nickel electrodeposition. Part of the unsaturated oxygen atoms on nanoparticles surface can combine with some of the absorbed nickel atoms and form nickel-oxygen chemical bonds. There is chemical binding interaction at the interface between nanoparticles' surface and matrix metal nickel.

Introduction

Nanometer composite brush electroplating is a kind of new type surface repairing technology, which can prepare excellent surface coating. In the last several years, this technology has been invented to apply in practice. But in general, it is still in the developing stage. Most of investigation work has been concerned with preparing coating, testing performance, and developing new brush electroplating solution. Relatively little effort has been devoted to the study on nanoparticles' behavior during electrodeposition process and interaction between nanoparticles' and matrix [1–6]. In fact, the structure and performance of composite coating are closely related to nanoparticles which play an important role in coating [7–9]. In the case of viewpoint about interface interaction, the combination of matrix metal and composite particles has been popularly considered as mechanical connection without chemical binding [9, 10]. In this article, special attention is paid to the influence of nanoparticle on the metal electrodeposition process and composite coating structure. The binding state between nanoparticles and matrix nickel in coating is studied by the X-ray Photoelectron Spectrometry. The microstructure and morphology of coating are observed with Transmission Electron Microscope and Scanning Electron Microscope. The cyclic voltammetry is used for determining the electrochemical response from n-SiO_2/Ni, n-Al_2O_3/Ni composite brush electroplating solution and common nickel-based brush-plating solution. The electrochemical properties are compared with each other.

Experimental

Coating preparation [8]

The substrate used for preparing the brush electroplating coating is 30CrMnSi steel with 50 × 20 × 1 mm^3. The brush electroplating solution contained 264 g L^{-1}

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$NiSO_4 \cdot 6H_2O$, 56 g L^{-1} ammonium citrate, 23 g L^{-1} ammonium acetate, 105 g L^{-1} ammonia water, and 20 g L^{-1}. The n-SiO_2 with amorphous or n-Al_2O_3 with γ-type crystal is added into brush electroplating solution with the concentration of 20 g L^{-1}. The conglobation phenomenon of these nanoparticles was serious. A method, namely high-energy mechanical chemical method [11] was utilized to disperse these nanoparticles in solution. After the regular processing techniques, such as electrocleaning, activating, preparatory plating and plating, DSD-75-S power unit (Academy of Armored Force Engineering) was used to prepare brush electroplated coating with 0.1 mm in thickness. The other conditions were as follows: voltage 12 V, moving speed of anode 9 m min^{-1}, and operation temperature 20 °C. All coatings were prepared under the same experimental conditions.

Spectrum experimental

The surface morphology and microstructure of coating were observed by Quanta 200 SEM (FEI Company, Holland) and Hitachi H-800 TEM (Japan) respectively.

The coating with proper size was used for XPS and X-diffraction testing. Before experiment, the coating surface was mechanically polished to remove surface oxide and the fresh surface was exposed, then the sample was placed into the vacuum room immediately to measure.

XPS measurement was preformed by using ESCA LAB220I-XL(VG SCIENTIFIC). X-ray diffraction was measured by using D8 ADVANCE (German Blucker Co.). In XPS experiment, position sensitive detector (PSD) and Al anode target with photon energy 1,486.6 eV were used. The pressure in vacuum room was kept at 4×10^{-9} Pa. The C1s (284.6 eV) was used to calibrating spectral series displacement.

Electrochemical experiment

The electrochemical cell was designed as a three-electrode cell. The nickel micro-disk electrode sealed in a glass tube was used as the working electrode with 1 mm diameter, and the platinum plate was used as the counter electrode with 8×15 mm^2, the saturation calomel electrode (SCE) was selected as the reference electrode. Potential was measured and quoted relative to SCE.

Before each measurement, the nickel micro-disk electrode was polished with metallurgical coated abrasive paper and alumina powder down to 0.3 μm to obtain a mirror surface, then ultrasonicated and thoroughly rinsed with distilled water, acetone, distilled water successively, and at last transferred to the brushplating solution without being dried.

Electrochemical measurement was performed with Potentiostat/Galvanostat Model 273A (EG&G Instrumental Inc.). The computer was used in recording cyclic voltammograms. The working electrode was held at potential 0.0 mV for 2 min before each measurement to ensure reproducible initial state at its surface. All experiments were performed at room temperature (about 20 °C).

Results and discussion

Coating microstructure and interaction between nanoparticles and matrix metal

The microstructure of n-Al_2O_3/Ni and n-SiO_2/Ni composite coating is depicted in Figs. 1 and 2. In composite coating, the size of nanoparticles distributes in the range of 30–50 nm and their content by weight was about 1% [8]. Nanoparticles are evenly dispersed in the matrix nickel. Compact binding interface between nanoparticle and matrix nickel is observed. The surface morphologies of common nickel coating, n-Al_2O_3/Ni composite coating, and n-SiO_2/Ni composite coating are respectively depicted in Fig. 3a–c. By comparing these figures, it is clear that the three kinds of coating show the typical cluster crystal with cauliflower shape. Every cluster crystal is composed of many fine crystal cells. The surface crystal grains of the composite coating are finer, evener, and smoother. These results demonstrate that the nanoparticles can distinctly refine the crystal grains of composite coating and improve coating structure.

The XRD results from common nickel, n-Al_2O_3/Ni and n-SiO_2/Ni coating show that (111) and (200) faces are their main crystal faces. The lattice constants of (111) crystal

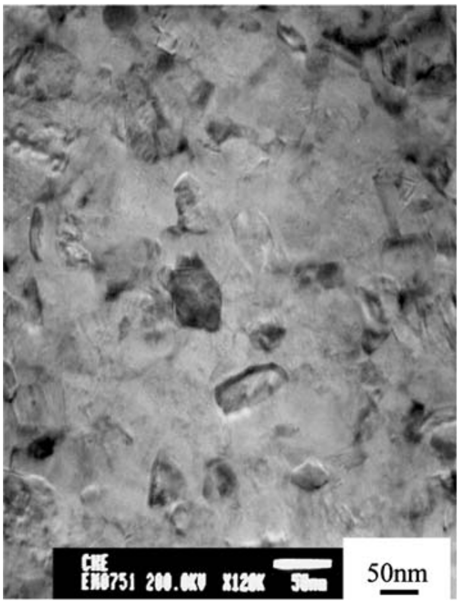

Fig. 1 Microstructure of n-Al_2O_3/Ni composite coating

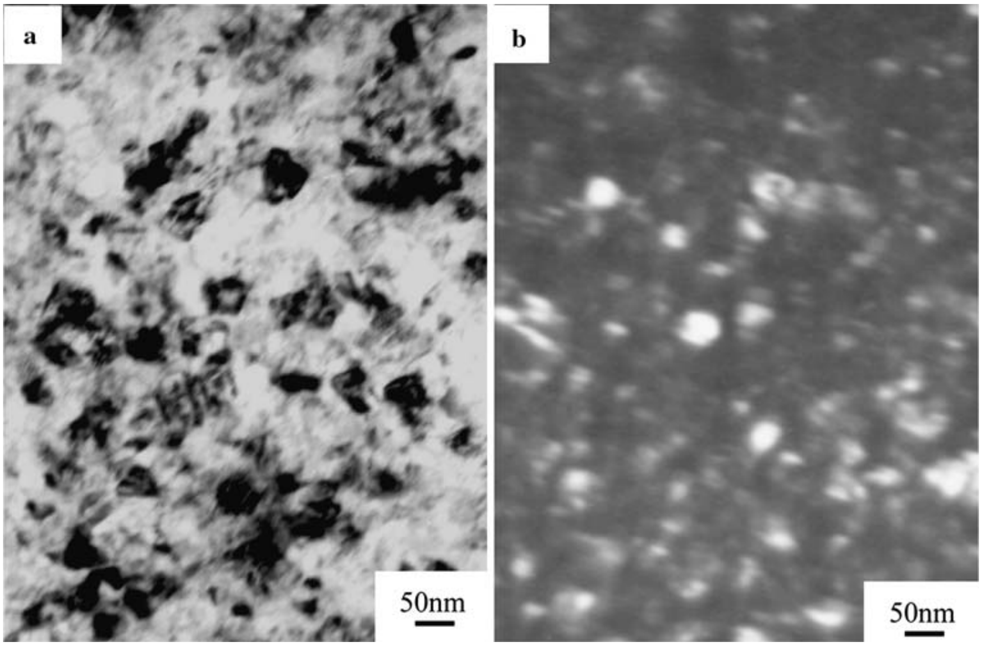

Fig. 2 Microstructure of n-SiO_2/Ni composite coating, (**a**): bright field image; (**b**): dark field image

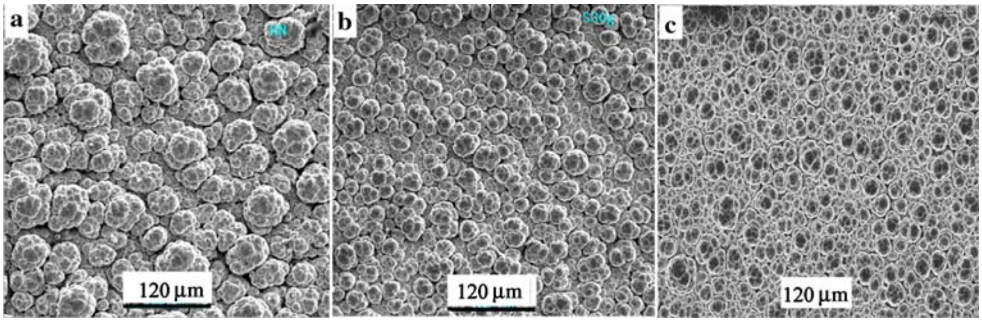

Fig. 3 Surface morphology of coating, (**a**): common nickel coating; (**b**): n-Al_2O_3/Ni composite coating; (**c**): n-SiO_2/Ni composite coating

face are 0.353118, 0.350856, and 0.351596 nm respectively, and that of (200) crystal face are 0.352662, 0.351068, and 0.351664 nm. This further indicates that nanoparticles in composite coating can reduce the crystal grain size [12].

If nano-Al_2O_3 and nano-SiO_2 were mixed mechanically with matrix metal, the size of crystal grains would be independent of nanoparticles. It suggests that there is not only mechanical, but also chemical interaction between nanoparticles and nickel matrix.

Interaction at the interface between nanoparticles and matrix nickel in composite coating

The XPS measure is used for deciding the binding state, chemical binding, or mechanical mixing, at the interface between nanoparticle and matrix nickel in the composite coating. The experimental results are depicted in Figs. 4–6. All data are corrected for physical drift.

The binding energy of Si2s in composite coating and in n-SiO_2 powder is 152.9 eV and 153.9 eV respectively (Fig. 4). The binding energy of Al2p in composite coating is 0.7 eV lower than that in n-Al_2O_3 powder (Fig. 5). These facts elucidates that there is a chemical bond between nanoparticles and matrix nickel. Aluminum or Silicon in composite coating is inclined to acquire electron. Since the chemical shifts are not more than 1 eV, the binding way is situated between ionic bond and covalent bond.

The XPS peak of Ni–Al or Ni–Si does not exist, which demonstrates that Al or Si atom does not directly react with Ni atom. In addition, considering the electronegativity of nickel, oxygen, aluminium, and silicon, it is impossible that aluminium atom or silicon atom directly captures electron from oxygen. The binding energy of Al2p and Si2s seems not be decreased. Actually, the surface atoms of

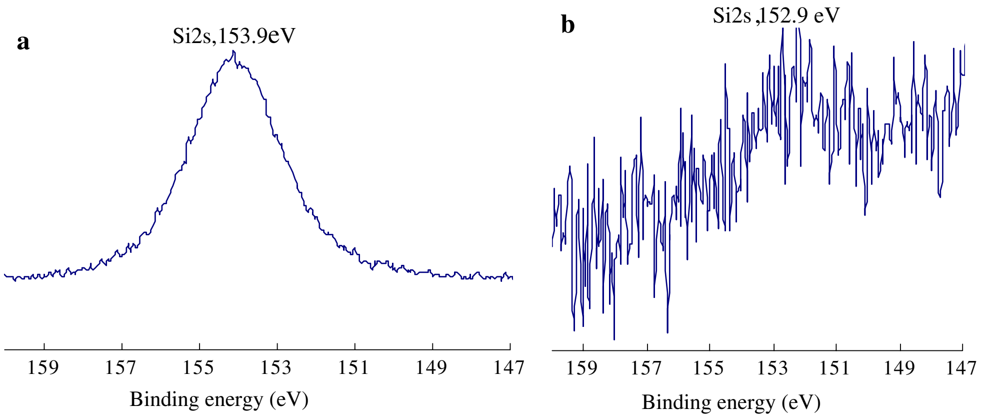

Fig. 4 XPS spectra of silicon, (**a**): n-SiO_2 powder; (**b**): n-SiO_2/Ni composite coating

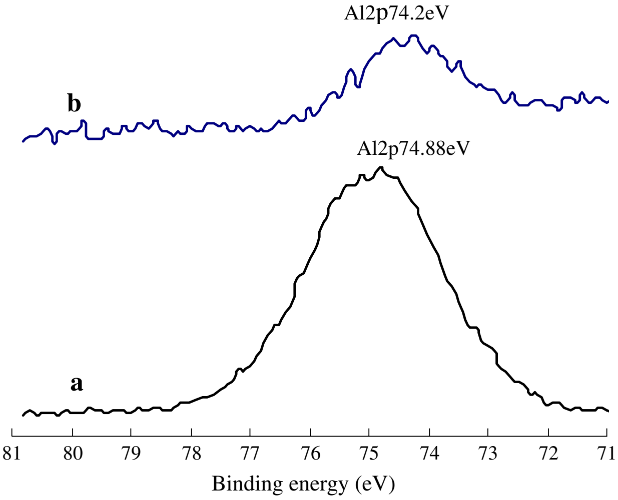

Fig. 5 XPS spectra of aluminum, (**a**): n-Al_2O_3 powder; (**b**): n-Al_2O_3/Ni composite coating

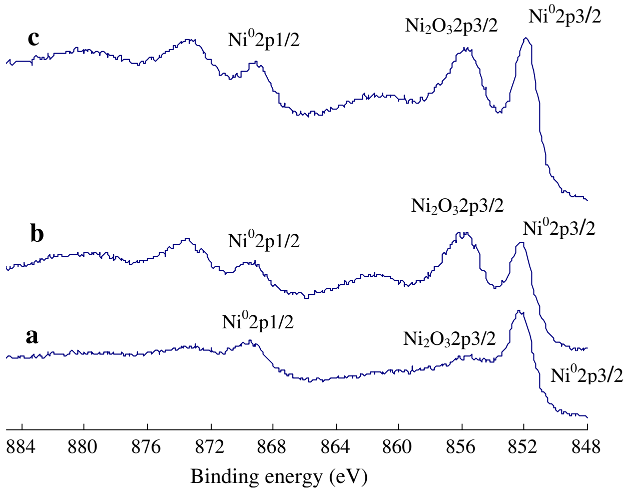

Fig. 6 XPS spectra of nickel, (**a**): common Ni coating; (**b**): n-SiO_2/Ni composite coating; (**c**): n-Al_2O_3/Ni composite coating

nanoparticle stay in unbalanced force field which is different from that of inner atoms [13]. In the case of n-Al_2O_3 or n-SiO_2, many oxygen atoms on surface have unsaturated chemical bonds, which may react with adsorbed nickel atoms by means of chemical combination. The experimental results from XPS can be reasonably explained as follows: the unsaturated chemical bonds of oxygen atoms on nano-Al_2O_3 or nano-SiO_2 surface combine with adsorbed nickel atoms, acquire electron, and lead to the increase in the electron cloud density outside of oxygen atom nucleus, the part of the electron cloud can be transferred outside of aluminium or silicon atom nucleus near this oxygen atom, so the electron cloud density outside of Si or Al atomic nucleus increases and electron binding energy decreases.

The electrons of $Ni^02p_{3/2}$ and $Ni_2O_32p_{3/2}$ in coating contribute two low energy peaks in Fig. 6.

It can be seen that the XPS peaks of nickel appear at same binding energy but the proportion of peak area. The experimental data of binding energy are 852.05 eV and 855.4 eV with common nickel coating. The corresponding values are 852.20 eV and 855.60 eV with n-SiO_2/Ni composite coating, 851.89 eV and 855.58 eV with n-Al_2O_3/Ni coating. According to the results, it can be decided that three kinds of nickel-based coatings consist of Ni^0 and Ni_2O_3. The nickel oxide in common nickel coating is mainly from the surface oxide removed incompletely. If nano-Al_2O_3 and nano-SiO_2 were mixed mechanically with matrix nickel and there were no chemical interaction at their interface, the proportion of nickel oxide to Ni^0 in composite coating would be close to that in common nickel coating. In fact, the ratio of nickel oxide in the composite coating is much higher than that in common nickel coating (Fig. 6). The reason is that the unsaturated chemical bond of oxygen on nanoparticles surface can bind with nickel atom in matrix metal and form Ni–O chemical bond. The nickel oxide in composite coating consists of surface oxide and interior oxide. The later one is composed of the compound of nickel atom and oxygen atom on the nano-Al_2O_3 and nano-SiO_2 surface in the matrix [14, 15].

In the interior of coating, there is little nickel oxide derived from oxidized growth surface of matrix metal during plating process. Under the same preparation conditions, the relative content of oxide should be approximative to each other in three kinds of coatings. So the oxide from the preparation process is not the key factor for bringing about the different proportions of peak area between nickel oxide and Ni^0 in Fig. 6.

The chemical bonds between oxygen atom and nickel atom lead to compact binding between nanoparticles and matrix nickel, which can profitably contribute to improvement of composite coating performance.

Electrocatalysis of non-electroactive nanoparticles on nickel electrodeposition

Under the same experimental conditions, the cyclic voltammograms (CVs) and steady-state polarization curves were obtained with ϕ1 mm Ni micro-disk electrode in common or composite solution. The typical voltammograms were depicted in Figs. 7–10. The insets in Figs. 9 and 10 are corresponding Tafel plots. By comparing these figures, it is clear that the general shapes of these plots are similar except for the overpotential and current efficiency.

As these curves show, there is a little current response below −0.50 V in Figs. 7 and 8. For composite and common solution, the current increases slowly below −0.85 V or −0.87 V then rises quickly. In reverse scan process, the dissolution peak of nickel is at −0.36 V in common plating solution and shifts slightly positively in composite solution. Underpotential deposition is not found. There are two important differences between common and composite system, one is that the electrode potential of composite system is lower than that of common one with same current, the other is that the current of composite system is higher than that of common one with same potential (Figs. 7–10).

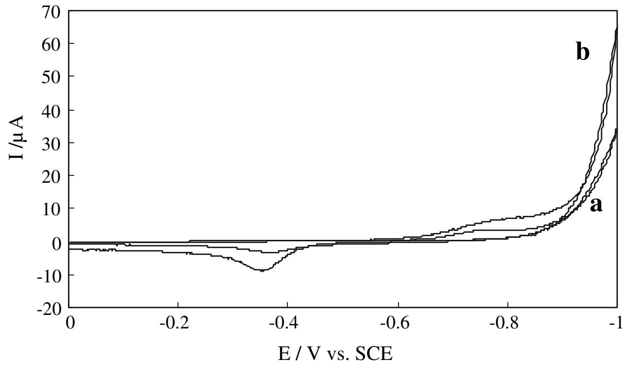

Fig. 7 Cyclic voltammogram: scan velocity 50 mV/s, potential range 0.00 V ~ −1.00 V. (**a**): common nickel electroplating solution; (**b**): n-SiO_2/Ni composite solution

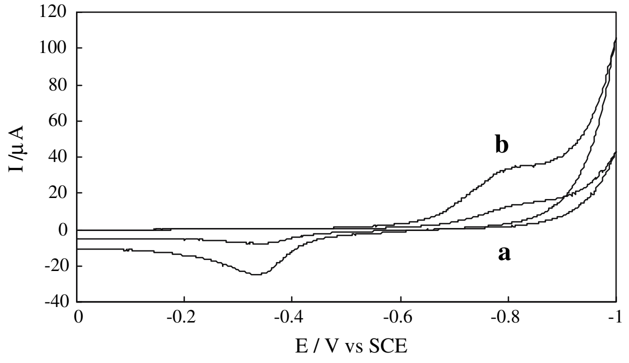

Fig. 8 Cyclic voltammogram: scan velocity 50 mV/s, potential range 0.00 V ~ −1.00 V. (**a**): common nickel electroplating solution; (**b**): n-Al_2O_3/Ni composite solution

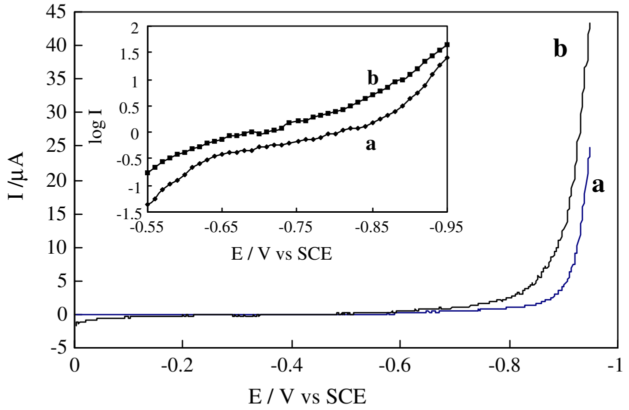

Fig. 9 Steady-state polarization curves of nickel elecrodeposition, the inset is its Tafel plot, scan velocity 1 mV/s, potential range 0.00 V ~ −0.95 V. (**a**): common nickel electroplating solution; (**b**): n-SiO_2/Ni composite solution

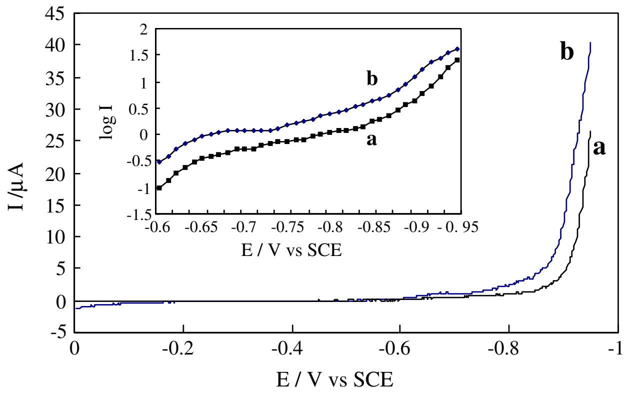

Fig. 10 Steady-state polarization curves of nickel elecrodeposition, the inset is its Tafel plot, scan velocity 1 mV/s, potential range 0.00 V ~ −0.95 V. (**a**): common nickel electroplating solution; (**b**): n-Al_2O_3/Ni composite solution

The main steps of metal electrodeposition involve mass transfer of reactant in liquid, electron transfer, and crystallization at electrode surface. The n-Al_2O_3 and n-SiO_2 have no electrochemical activity themselves. No electron exchange will directly happen between nanoparticles and electrode. Therefore, nanoparticles cannot affect the electron exchange reaction at electrode interface. The effect of nanoparticles should be present to the subsequent crystallization. During composite electrodeposition process, some of nanoparticles may be caught by electrode surface. Therefore, part of electrochemical active area is blocked and available reactive area is decreased. If there were no chemical interaction between nanoparticles and electrode surface, the current response of composite system should be lower than that of common system at same potential. In fact, the experimental results are opposite to this inference.

The electrochemical nucleus process appears in three of types systems (see Figs. 7 and 8). Under the same experimental conditions, the current loop is more distinct in composite system [16–18]. It shows that composite system can form nucleus more easily than common system [19]. During electrodeposition process, the decreasing of overpotential induces the increasing of current density at the same potential. Simultaneously, the increasing of nucleus sites leads to the decreasing of true current density. The nucleus number of composite system is more than that of common system. The distribution coefficient of charge becomes lower in each crystalline grain. As a result, the metallic crystal grain becomes fine, which is consistent with coating microstructure observation.

Above experimental results prove that nano-Al_2O_3 and nano-SiO_2 take part in the electrode reaction and can evidently catalyze nickel electrodeposition.

Co-deposition mechanism of nanoparticles and the essentiality of interaction at interface between nanoparticles and matrix metal

During mass transfer in solution, nanoparticles and Ni^{2+} are firstly carried near the electrode by solution convection, then some of them arrive at electrode surface through fluid boundary layer by electric field and hydromechanical effect. In electrochemical process, Ni^{2+} acquires electrons, becomes absorbed atom, diffuses on surface, forms nucleus or moves to crystal growth site, and finally enters into the metal crystal lattice. Simultaneously, some of nano-Al_2O_3 or nano-SiO_2 are captured by electrode surface. The nanoparticles combining weakly with electrode are carried away by friction effect of brush pen and convection of solution, while the nanoparticles combining strongly with electrode are held in growing metal surface. During crystallization process, the absorbed nickel atoms are diffusing on growing metal surface. Some of adsorbed atoms may arrive at the interface between captured nanoparticles and growing metal surface, and can combine with unsaturated chemical bond of oxygen atom on nano-Al_2O_3 or nano-SiO_2 surface by means of chemical bond. As a result, Ni–O chemical bonds form and these nickel atoms become new nucleation and growing sites. The nano-Al_2O_3 or nano-SiO_2 are gradually embedded in newly deposited nickel atoms. When embedding proceeds to some degree, nanoparticles will be inlayed in the growing metal layer forever, and so the composite coating forms.

In general, the unperfect location on metal surface is considered to be reaction activation site, which has a high reaction activity and become the probable combining site for nanoparticles. The growth, form, and performance of composite coating are closely related to distribution of nanoparticles in composite coating.

In the case of nanoparticles surface, the probable combining position for Ni atoms should be defect site with highly chemical reaction activity, which gather many unsaturated chemical bonds and can combine easily with the other atoms [13, 20], lower active energy is needed for nucleation and growing. This is an important reason why the overpotential of nickel electrodeposition was decreased.

In addition, nanoparticles' concentration is related to the quality of the brush electroplating coating [21].

There are not only mechanical, but also chemical interactions at the interface of nano-Al_2O_3 or nano-SiO_2 and matrix nickel in this composite coating, which is the essentiality of interface interaction.

The experimental results also show that crystalline n-Al_2O_3 or amorphous n-SiO_2 have the similar effect in the composite coating or during electrodeposition process, which are mainly due to the micro-size effect and specific surface characteristics of nanoparticles.

Conclusions

(1) Nano-Al_2O_3 and nano-SiO_2 take part in electrode reaction and can distinctly catalyze nickel electrodeposition.
(2) The unsaturated bond of oxygen on nano-Al_2O_3 and nano-SiO_2 surface can combine with the absorbed nickel atoms by way of chemical bond. There is not only mechanical connection, but also chemical combination at the interface between these nano-Al_2O_3 or nano-SiO_2 surface and matrix nickel in the composite coating.

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