

# Microstructure of Co-Ni-Al<sub>2</sub>O<sub>3</sub> Composite Coatings by Electroforming

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The metal matrix composite coatings of Co-Ni-Al<sub>2</sub>O<sub>3</sub> were studied by electrolytic codeposition of Co-Ni alloys and Al<sub>2</sub>O<sub>3</sub> on a Cu substrate from a sulfamate electrolyte containing Al<sub>2</sub>O<sub>3</sub> particles. It was illustrated from the examined results of SEM, AFM and XRD that surface morphology and microstructure of Co-Ni-Al<sub>2</sub>O<sub>3</sub> coatings appear to be mainly influenced by variations in Co content. The high Co content coatings with hcp lattice structure have a more uniform and fine structure than that of low Co content coatings with fcc lattice structure. The codeposition of Al<sub>2</sub>O<sub>3</sub> particles in Co-Ni alloys can not change the phase structure of solid solution, only affects the growth and orientation of crystal planes and mostly increase the *d* value of lattice.

**KEY WORDS:** Electroforming, Composite coatings, Cobalt-Ni alloys, Alumina

## 1. Introduction

Composite coatings that oxide, nitride, carbide particles disperse into metal or alloy matrix offer major improvements in mechanical, physical and chemical properties such as stiffness, strength<sup>[1]</sup>, wear resistance<sup>[2]</sup>, elevated temperature<sup>[3]</sup>, magnetic<sup>[4]</sup> and catalytic property<sup>[5]</sup>. Electrodeposition has great potentialities, comparing to conventional routes including co-spraying, internal oxidation, infiltration and high pressure bonding when produce the metal matrix composite materials<sup>[6]</sup>. An outstanding feature of this method is the precision with which the concentration and spacing of the particles can be controlled. Besides, the technique involving no high temperature or high pressure processing steps has obvious advantages. Co-Ni-Al<sub>2</sub>O<sub>3</sub> composites coating has very good mechanical and physical performance by our former investigation. The purpose of this work was to investigate the surface morphology and microstructure of Co-Ni-Al<sub>2</sub>O<sub>3</sub> coating by codeposition from sulfamate electrolyte. This work was undertaken in view of the potential value of Co-Ni-Al<sub>2</sub>O<sub>3</sub> alloys prepared by electroforming for technical and engineering applications.

## 2. Experimental

In order to obtain electrolytic composite Co-Ni-Al<sub>2</sub>O<sub>3</sub> coatings, an electrolyte was prepared having the following composition: 200~300 g/l Co sulfamate, 300~350 g/l Ni sulfamate and 20 ml/l formamide, to which 20~150 g/l  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> particles was added. Reagents of analytical purity and distilled water were used for preparing the solution. Using an optical microscope, the mean size of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> particles was estimated to be 0.5  $\mu$ m. The Al<sub>2</sub>O<sub>3</sub> particles were pre-treated with acetone and warm 5% HNO<sub>3</sub> to remove residual organic and impurities, then washed with distilled water and dried. In addition, an ultrasonic generator was used to minimize Al<sub>2</sub>O<sub>3</sub> particles agglomeration in the suspension. To investigate surface morphology, microstructure and composition of Co-Ni-Al<sub>2</sub>O<sub>3</sub> alloy deposits, SEM, EDS, AFM, and XRD methods were applied.

## 3. Results and Discussion

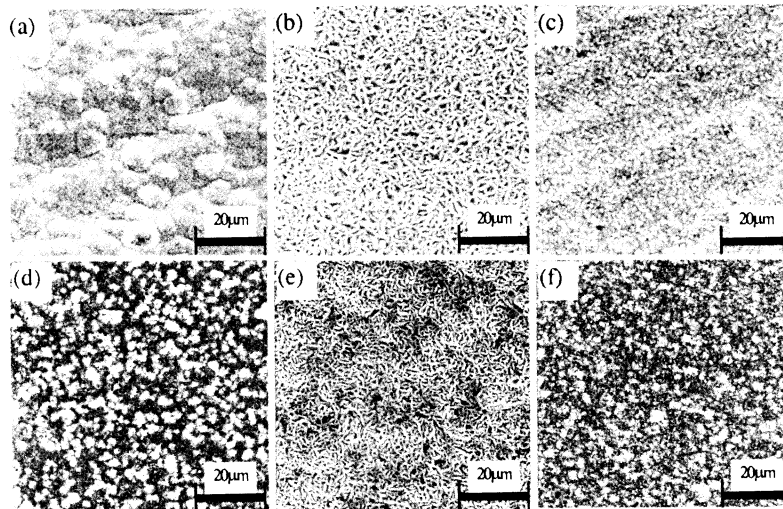
Figure 1 compares the SEM morphology of Co-Ni

coatings and Co-Ni-Al<sub>2</sub>O<sub>3</sub> composite coatings. It can be seen that the Co-Ni deposit has a rather regular surface, whereas the Co-Ni-Al<sub>2</sub>O<sub>3</sub> composite coating develops a nodular distributed surface structure. Al<sub>2</sub>O<sub>3</sub> particles are uniformly distributed in the Co-Ni matrix. A smaller Co-Ni grain size is observed in the composite coating compared to the Co-Ni coating. The adsorption of Al<sub>2</sub>O<sub>3</sub> on the cathode surface increases cathodic polarization and contributes to developing fine grains<sup>[7]</sup>. As the Co contents in the Co-Ni and Co-Ni-Al<sub>2</sub>O<sub>3</sub> coatings increases from 16 to 42%, there is a decrease in grain size and the morphology changes from a nodular aspect which are related to low Co content coating to a fibril one, associated with medium Co content coating. At the mean time, the structure becomes less compact. Nevertheless, more compact and fine granular morphology is observed in the Co-rich alloy (>78%). The structure of the Co-Ni and Co-Ni-Al<sub>2</sub>O<sub>3</sub> coatings all become more homogeneous as the Co content increases.

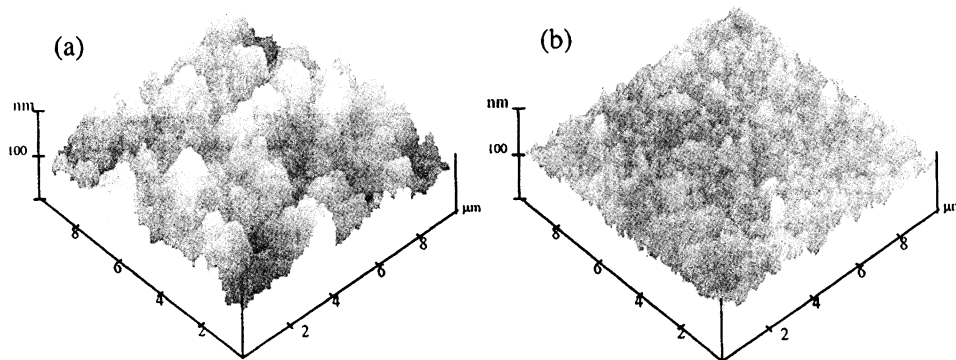
In order to investigate the microstructure of Co-Ni-Al<sub>2</sub>O<sub>3</sub> composite coating, scanning analysis and measurements were conducted using atomic force microscopy (AFM) method. The results are shown in Fig.2. Spherical growth is clearly visible on the surfaces of the composite coatings. The microstructure of Co-Ni-Al<sub>2</sub>O<sub>3</sub> appears to be influenced by variations in Co contents in the composite coating. The microstructure of Ni-80Co-8.7 vol. pct Al<sub>2</sub>O<sub>3</sub> coating has a more uniform and fine structure than that of Ni-20Co-8.5 vol. pct Al<sub>2</sub>O<sub>3</sub>.

The phase composition and structure of Co-Ni alloys and Co-Ni-Al<sub>2</sub>O<sub>3</sub> coatings with different Co contents was investigated using X-ray diffraction. As can be seen from Fig.3, the crystal structures both Co-Ni coatings and Co-Ni-Al<sub>2</sub>O<sub>3</sub> composite coatings were mainly dependent on the Co contents in deposits. It is confirmed for Co-Ni and Co-Ni-Al<sub>2</sub>O<sub>3</sub> coatings that a single-phase solid solution of Co in Ni with a face-centered cubic (fcc) lattice for the lower Co contents and a solid solution of Ni in Co with a hexagonal close packed (hcp) lattice for the higher Co contents are obtained. The Co-Ni and Co-Ni-Al<sub>2</sub>O<sub>3</sub> coatings with the lower Co contents all exhibit fcc Ni (111) growth orientation with significant (200), (220) and (311) reflections as well. Nevertheless, at higher Co contents, the Co-Ni coating shows very strong hcp Co (200) growth orientation, while Co-Ni-Al<sub>2</sub>O<sub>3</sub> composite coating forms strong hcp Co (100) texture. Therefore, it can be concluded that the phase structure of Co-Ni alloy solid solution is not changed by the codeposition of Al<sub>2</sub>O<sub>3</sub> particles, but it influences the growth of crystal planes and increases the lattice *d* value apparently.

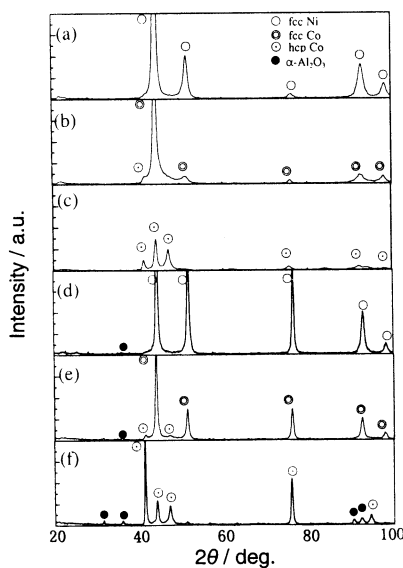
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**Fig.1** SEM micrographs of Co-Ni and Co-Ni-Al<sub>2</sub>O<sub>3</sub> coatings (a) Ni-16Co, (b) Ni-40Co, (c) Ni-78Co, (d) Ni-20Co-8.5 vol. pct Al<sub>2</sub>O<sub>3</sub>, (e) Ni-42Co-8.7 vol. pct Al<sub>2</sub>O<sub>3</sub>, (f) Ni-80Co-8.7 vol. pct Al<sub>2</sub>O<sub>3</sub>



**Fig.2** AFM analysis results of Co-Ni-Al<sub>2</sub>O<sub>3</sub> composite coatings (a) Ni-20Co-8.5 vol. pct Al<sub>2</sub>O<sub>3</sub>, (b) Ni-80Co-8.7 vol. pct Al<sub>2</sub>O<sub>3</sub>



**Fig.3** XRD pattern of Co-Ni-Al<sub>2</sub>O<sub>3</sub> composite coatings (a) Ni-16Co, (b) Ni-40Co, (c) Ni-78Co, (d) Ni-20Co-8.5 vol. pct Al<sub>2</sub>O<sub>3</sub>, (e) Ni-42Co-8.7 vol. pct Al<sub>2</sub>O<sub>3</sub>, (f) Ni-80Co-8.7 vol. pct Al<sub>2</sub>O<sub>3</sub>

#### 4. Conclusions

(1) Surface morphology and microstructure of Co-Ni-

Al<sub>2</sub>O<sub>3</sub> coating appear to be mainly influenced by variations in Co content. As the Co content of the Co-Ni and Co-Ni-Al<sub>2</sub>O<sub>3</sub> coatings increased, there was a decrease in grain size and the morphology change from a nodular aspect to a fibril one, and then to more compact and fine granular morphology.

(2) By AFM, the high Co content Co-Ni-Al<sub>2</sub>O<sub>3</sub> composite coatings with hcp lattice structure have a more uniform and fine surface structure than that of low Co content coatings with fcc lattice structure.

(3) The codeposition of Al<sub>2</sub>O<sub>3</sub> particles into Co-Ni alloys can not change the phase structure of solid solution, only affects the growth and orientation of crystal planes and mostly increase the *d* value of lattice.

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