

Residual Stresses on Electro-Deposited NiCo-Al and NiCo-Zr Composite Coatings

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Abstract: This experiment examined the residual stresses on electrodeposited NiCo-Al and NiCo-Zr composite coatings as well as the impact of varying Co²⁺ concentrations on other properties of the coating, namely grain size and texture. To prepare for the experiments, this project employed modified Watt Baths containing NiSO₄·6H₂O (240 g/L), NiCl₂·6H₂O (40 g/L), H₃BO₃ (30 g/L) and C₁₂H₂₅NaSO₄ (0.2 g/L) in order to electrically deposit them on to Aluminum and Zirconium and to produce the two types of aforementioned specimen: NiCo-Al and NiCo-Zr. The amount of Co in the end product is regulated via adjusting the concentration of CoSO₄·7H₂O, providing a range of concentrations from 5 to 40 g/L. Furthermore, structural analyses of the coatings were performed via X-ray diffraction at 40kV and 30mA in standard 2θ-θ mode. The Voigt method was used to calculate grain size and micro-strain of coatings using the integral breadth of the (200) peak. Residual stresses on the as-deposited composite coatings were measured by using stress analyzer and classical sin²ψ method. Peaks of (331)α of Ni were selected to calculate the residual stresses. Results show that, for both NiCo-Al and NiCo-Zr composite coatings, grain size decreases and micro-strain increases with increasing Co contents. Pole figure experiments shown typical fiber texture for composite coatings. Texture coefficient results show that the (111) texture coefficient increases while (111) texture coefficient decreases with increasing Co content. In addition, results show that the residual stress of NiCo-Al and NiCo-Zr composite coatings increases as Co content increases, which could be attributed to decreasing grain size and texture evolution from (200) texture to (111) texture.

Introduction

In recent years, there has been increasing interest focused on the electro-deposited NiCo and NiCo based metal matrix composite (MMCs) coatings due to their combined superior properties, such as higher hardness [1-5], improved anti-wear [2, 4], better corrosion resistance [1, 3, 6] and oxidation resistance [5, 7] as compared with the pure Ni and Ni based composite coatings. The properties of the NiCo or NiCo based composite coatings were mainly dependent on the microstructures of the NiCo matrix and the incorporated particles.

The properties of pure Ni coatings could also be enhanced by alloying with Co element [1, 6]. Meenu Srivastava et al [1] found that the microstructures and properties of the NiCo alloy were dependent on the Co content and the coating attained the maximum hardness at Co content of 50 wt %. Jianqiang Kang et al. [6] pointed out that the presence of Co element increased the thickness of the space charge layer, which enhanced greatly the stability of the passive film than that of the pure Ni coating. Similar to the pure Ni coatings, the particle -reinforced Ni based composite coatings could also be enhanced by alloying with Co [5, 7, 8]. Meenu Srivastava et al. [5] found that the presence of 25 wt % cobalt in the Ni-CeO₂ matrix increased the hardness and improved its wear resistance. Also in Meenu Srivastava's study [7], the NiCo-Al composite coatings were fabricated and addition of 30 wt % Co in the NiCo-Al composite coating exhibited high temperature oxidation

and corrosion resistance. In reference [8], addition of 28 wt % Co content in the Ni-SiC matrix showed a higher hardness than other coatings.

In our early works, the fabrication and characterization of Ni-Al and Ni-Zr were reported [9, 10]. However, the effects of Co on the microstructures and properties, especially the texture, residual stress and corrosion resistance of the NiCo-Al composite coatings need further investigation. In this study, the NiCo-Al and NiCo-Zr composite coatings with different Co contents were prepared. Then, the effects of the Co content on the microstructure, texture, grain size, micro-strain and residual stress of the NiCo-Al and NiCo-Zr composite coatings were investigated in detail.

Experiments

Coating processes

NiCo-Al and NiCo-Zr composite coatings prepared by the electrodeposition method from the modified Watt baths containing NiSO₄·6H₂O (240 g/L), NiCl₂·6H₂O (40 g/L), H₃BO₃ (30 g/L) and C₁₂H₂₅NaSO₄ (0.2 g/L). Co was added as the CoSO₄·7H₂O and the additions ranged from 5 to 40 g/L of Co concentrations. Al and Zr particles with a mean diameter of 1 μm were added into the solutions at concentration of 20 g/L and 10 g/L, respectively. The solution temperature and pH value were maintained at 50 °C and 4.2, respectively. Pure nickel plate and stainless steel plate with an area of 1 × 1 cm² were used as the anode and cathode, respectively. The applied current density was maintained at a constant of 4 A/dm² for 1 hr.

Coating characterization

The chemical composition was examined by using the Energy Dispersive X-ray Spectroscopy (EDX) method attached to the FESEM(FESEM, JSM-7600F). Structure analysis of the coatings was performed by a Rigaku Ultima IV X-ray diffractometer (XRD, Cu Kα radiation, λ = 1.54056 Å) in standard 2θ–θ mode and the voltage and current were 40 kV and 30 mA, respectively. The Voigt method [11] was used to calculate the grain size and microstrain of the coatings using the integral breadth of (200) peak. Residual stress data on the as-deposited Ni-Zr composite coatings were collected on a Proto LXR Residual Stress Analyser and analyzed using the classical sin²ψ method [12]. The voltage and current were 30 kV and 25 mA, respectively. The peaks of (331)α of Ni were selected to calculate the residual stress.

Results and Discussion

Fig. 1 show the chemical contents of the NiCo-Al and NiCo-Zr alloy coating as a function of the CoSO₄·7H₂O concentrations in the bath. It was obvious that the Co contents linearly increased while Ni contents linearly decreased with the increasing CoSO₄·7H₂O concentrations in the bath.

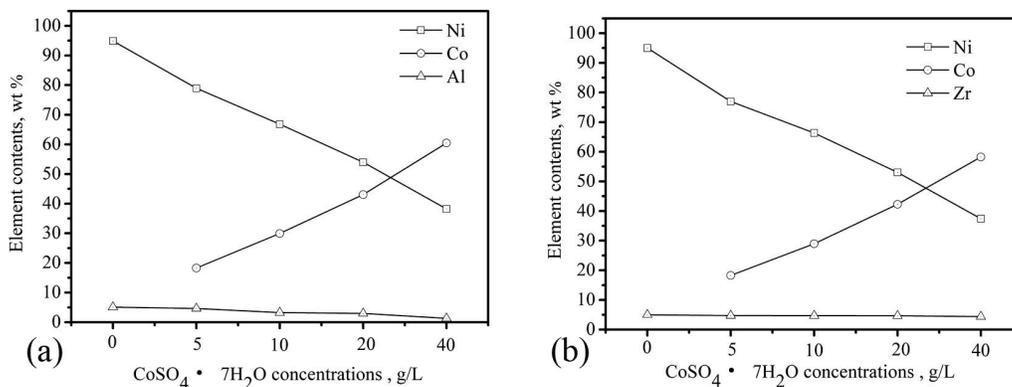


Fig.1 Element content variation of (a) NiCo-Al coatings and (b) NiCo-Zr coatings deposited under different Co²⁺ concentrations

Fig. 2 show the XRD patterns of the NiCo-Al and NiCo-Zr composite coatings with different Co contents. As shown in Fig. 2, the NiCo matrix peaks corresponding to the (111), (200), (220), (311) and (222) planes were detected. It could also be found from the XRD patterns that, as the Co contents reached 60.5 wt%, the hcp Co phase appeared. The similar results were also reported in reference [13].

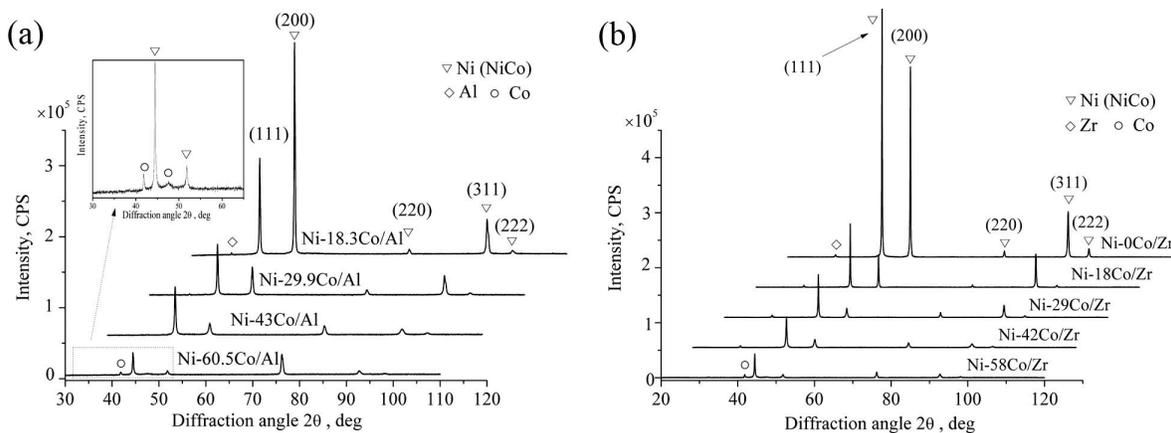


Fig.2 XRD patterns of (a) NiCo-Al coatings and (b) NiCo-Zr coatings with various Co contents

Fig. 3 show the texture coefficients of the NiCo-Al and NiCo-Zr composite coatings. It could be found that, as the Co contents increased, the (200) texture coefficients decreased and (111) texture coefficients increased.

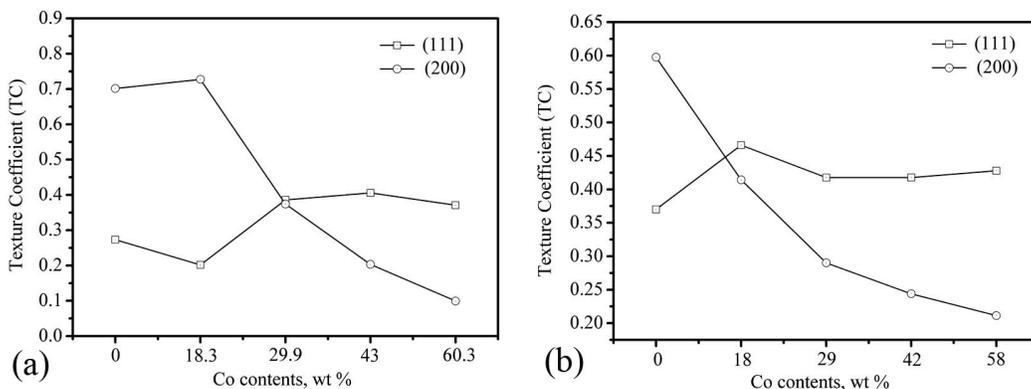


Fig.3 Texture coefficient of (a) NiCo-Al coatings and (b) NiCo-Zr coatings with various Co contents

Fig. 4 demonstrate the calculated grain size and microstrain of the NiCo-Al and NiCo-Zr composite coatings with different Co contents. As seen in Fig. 4, increasing the Co contents led to the decrease in grain size of the composite coatings. From Fig. 4, it could also be found that the microstrain of the composite coating increased with increasing Co contents.

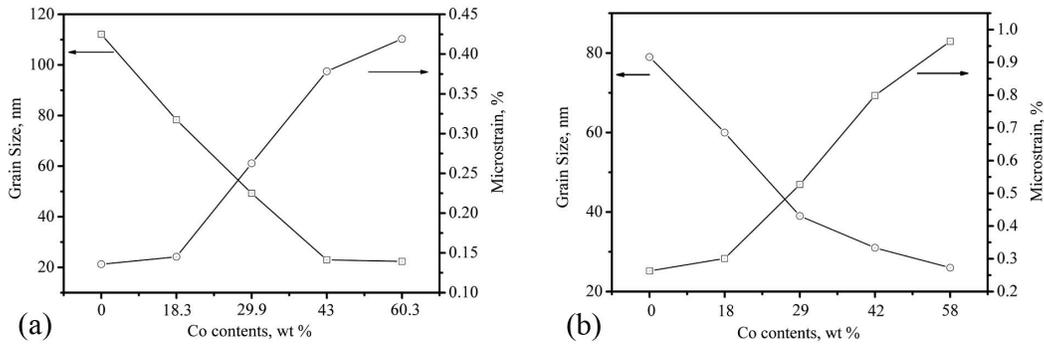


Fig.4 Grain size and microstrain of (a) NiCo-Al coatings and (b) NiCo-Zr coatings with various Co contents by using single peak method

Fig.5 shows the FWHM of (331) diffraction peak as a function of NiCo-Al and NiCo-Zr coatings with various Co contents and it could be found that the FWHM increased with increasing Co content for the NiCo-Al and NiCo-Zr coatings. Fig. 6 present the residual stresses of composite coatings with different Co contents. It could be found that all the coatings exhibited the tensile residual stress. From Fig. 6, it could be found that the residual stresses of the composite coatings increased from with increasing Co contents.

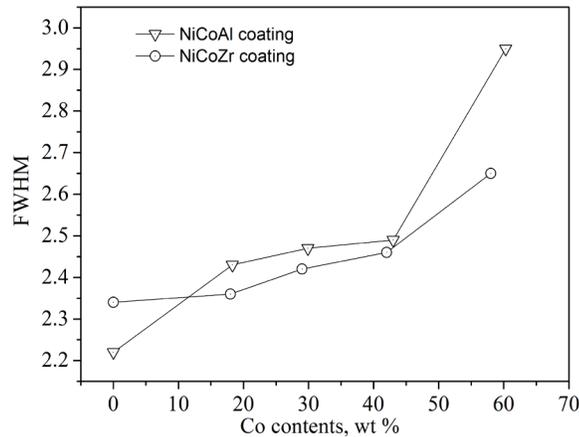


Fig.5 FWHM as a function of NiCo-Al and NiCo-Zr coatings with various Co contents

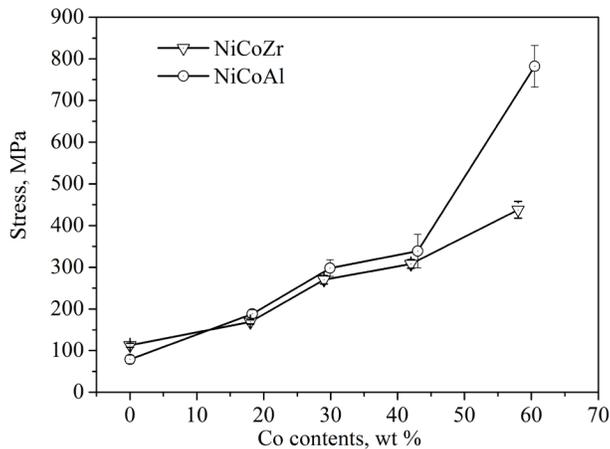


Fig.6 Stresses of composite coatings with various Co contents

The increase in residual stresses was closely related to the formation of solid solution NiCo and the texture evolution from the (200) preferred orientation to a random orientation or slight (111) orientation. As mention above, the substitution of Ni atoms by Co atoms resulted in the distortion of the composite coatings, which could increase the residual stress of the coatings. Therefore, the residual stresses increased with increasing microstrain by increasing the Co contents in the composite coatings. Moreover, the Young's moduli in different directions are different and the average Young's moduli are 303 GPa and 137 GPa for (111) and (200), respectively [14]. The higher strain energy density in (111) texture film likely led to the higher tensile internal stress in the (111) texture coatings compared with that in (200) texture coating, as reported in references [15]. However, the higher stresses in NiCo-Al and NiCoZr composite coatings might be due to a contribution from magnetostriction since NiCo is definitely ferromagnetic.

Conclusions

NiCo-Al and NiCo-Zr composite coatings with different Co contents were prepared by the conventional direct current electrodeposition from modified Watt baths containing different Co^{2+} concentrations. The Co content in the deposits increased with increasing the Co^{2+} concentration. The crystal structures of the composite coatings were mainly dependant on the Co contents. At low Co contents, the composite coatings exhibited solid solution NiCo crystal structure. However, hcp Co was detected with further increasing the Co content. Increasing Co contents in the NiCo-Al composite coatings resulted in the texture evolution from the (200) preferred orientation to the random orientations or the slight (111) preferred orientation. The grain size decreased and microstrain increased with increasing Co content. The residual stress also increased with increasing Co content.

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