Effects of the Electroplating Duration on the Mechanical Property of the Ni-Co-SiC Composite Coatings

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Abstract

In this work, Ni-Co composites incorporated with nano-sized SiC particles in the range of 45-55 nm are prepared by electroplating. The effects of plating duration on the chemical composition, surface morphology, crystalline structures and hardness have been studied. The maximum hardness of Ni-Co-SiC composite coating is approximately 633 Hv at plating duration of 1 h. The hardness is gradually decreased with increasing plating duration, which can be attributed to the growth of crystalline size and the agglomerates of SiC nano-particles. It is therefore explained that the grain refinement of Ni-Co matrix and stable dispersion of SiC particles play an important role for strengthening, which indicate Hall-Petch relation and Orowan model were dominant for hardening of Ni-Co-SiC composite coatings.

Keywords: Composite coating, Ni-Co-Sic

1. Introduction

Composite electroplating is a method of codepositing of second phase particles of metallic, nonmetallic compounds or polymers with a metal or alloy matrix. The simultaneous deposition of the non-metal inclusions and metal phases to form composite layers leads to a significant improvement on physical and mechanical properties of the coatings[1]. The second phase particles can be hard ceramic particles such as Al_2O_3, TiO_2, SiO_2, SiC, WC or liquid containing polymeric microcapsules or a solid lubricant such as PTPE that improve mechanical properties and wear resistance[2-5]. With increasing availability of micro- and nano-sized particles, there is growing interest in the electrolytic co-deposition of these particles due to easy maintainability, low processing temperatures and low cost.

Especially, Ni-Co-SiC composite coatings have shown high strength and hardness, specific magnetic properties and good wear resistance[6,7]. There have been many attempts on improving hardness with various experimental conditions such as changing current density, chemical composition in electrolyte, stirring rate, SiC content, and the size of SiC particle between micro and nano size[6-8]. However, many detailed investigations have not been performed on the characteristics of Ni-Co-SiC composite coatings, particularly the plating duration effect. It is therefore interesting to study the influence of the plating duration on the characteristics of deposits, which thereby can affect the mechanical property of the coating. In order to understand the effects of duration time on the crystalline structures and mechanical properties of the Ni-Co-SiC composite coatings, Ni-Co composite coatings incorporated with nano-sized SiC particles in the range of 45-55 nm were electrodeposited at a current density of 2.0 Adm^{-2} with increasing plating duration and the focus will be drawn to the effect of plating duration.

2. Experimental

The basic compositions of electroplating bath used

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Table 1. Operating parameters for Ni-Co-SiC composite coatings

Plating conditions	Experimental Range	Unit
Current density	2	Adm^{-2}
Temperature of bath	50	^{o}C
pH	4.5	pH
Stirring rate	200	Rpm
Plating time	1-8	hour

Table 2. Chemical compositions of Ni-Co-SiC composite coatings

Plating time (h)	Chemical composition (wt. %)	Crystalline size (nm)
1	$Ni_{64.3}Co_{34.3}SiC_{1.4}$	10.6
2	$Ni_{64.3}Co_{34.0}SiC_{1.7}$	12.8
3	$Ni_{66.1}Co_{32.1}SiC_{1.8}$	13.5
5	$Ni_{68.0}Co_{30.6}SiC_{1.4}$	17.2
8	$Ni_{71.6}Co_{26.5}SiC_{1.9}$	17.8

for the Ni-Co-SiC composite coatings are as follows: 250 g/l Ni(NH$_2$SO$_3$)$_2$, 30 g/l Co(NH$_2$SO$_3$)$_2$, 40 g/l H$_3$BO$_3$, 3 g/l NiBr$_2$ as a stress relaxant, 1.1 g/l additives (saccharin as a stress reducer and sodium lauryl sulfate as a surfactant), and 10 g/l SiC. The crystal structure of SiC powder shows cubic β-phase and an average particle size is approximately 55 nm. A Cu plate as a cathode with dimension of 50 mm× 25 mm×1.0 mm is used and the anode uses a Pt deposited on Ti basket. Before plating, a sequence of cleaning and acidic etching of the Cu plate by diluted sulfuric acid is applied to remove contamination on the surface. The each plating solution is thoroughly mixed by a magnetic stirring for 12 h, and heated/ maintained at 50 ^{o}C. The current density of 2 Adm^{-2} (ASD) was applied and the pH is kept at 4.5, adjusted by NaOH. Detailed operating parameters for Ni-Co-SiC composite coatings were shown in Table 1.

The surface morphology of the coatings is observed using Scanning Electron Microscope (SEM, FEI Sirion). The Ni, Co and SiC contents of composite coatings were determined using energy dispersive X-ray analysis (EDX, Noran Vantage) which is equipped with the SEM at 10 KeV. The concentration of Co in electrolyte was analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES, GBC Integra XL 100 model). The phase structure was identified by an X-ray diffractometer (XRD, X'Pert PRO MPD, PANalytic) with Cu Kα radiation (λ=0.15406 nm) at a scanning rate of 0.05^{o}/s. The microhardness was measured with SHIMADZU Vickers hardness tester under a load of 5 N for 10 s. The final value quoted for the microhardness of a deposit was the average of 5 measurements.

3. Results and Discussion

The Table 2 indicates that the chemical composition of all composite coatings with various plating duration was determined by EDS. The Co composition relatively decreased with increasing plating time
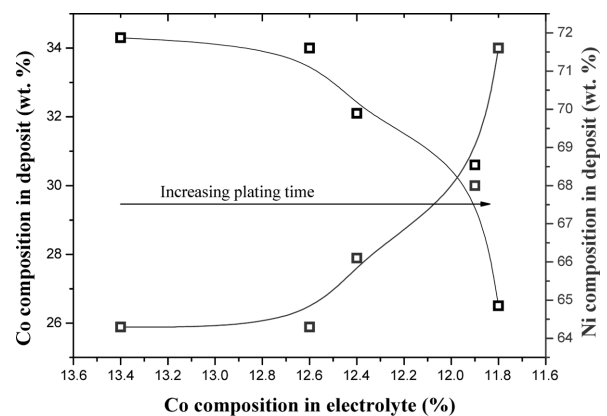

Fig. 1. Anomalous behaviors dependent on the Co composition in electrolyte.

compared to an increase in Ni composition, as shown in Fig. 1. This could be explained by the characteristics of anomalous co-deposition. Qiao *et al.*[9] have reported anomalous behavior of Ni-Co alloys associated to the fact that the cathode diffusion layer becomes relatively more depleted with respect to Co^{2+} ions. Therefore, the Co content in the bath tends to affect the Co^{2+} ion in the cathode layer and accordingly lessen the Co content in the electrodeposited alloy. In addition, the effect of SiC particle on the variation of chemical composition should be taken into consideration in this experiment. Srivastava *et al.*[8] have indicated the Co content was influenced by the content and dispersion of SiC particles in the electrolyte. Co^{2+} would be adsorbed easily compared to Ni^{2+} on the SiC, giving particle surface a more positive charge, and increasing the electrostatic attraction between the SiC particles and the negatively charged cathode leading to the higher particle codeposition. However, this behavior is impossible to explain that Co content was decreased with increasing plating duration although SiC composition was almost constant (1.4-1.9 wt.%). Therefore, it is thought that dispersion of SiC nanoparticles played a role for variation of Co contents. The adsorption can be higher on the surface of SiC nanoparticles compared
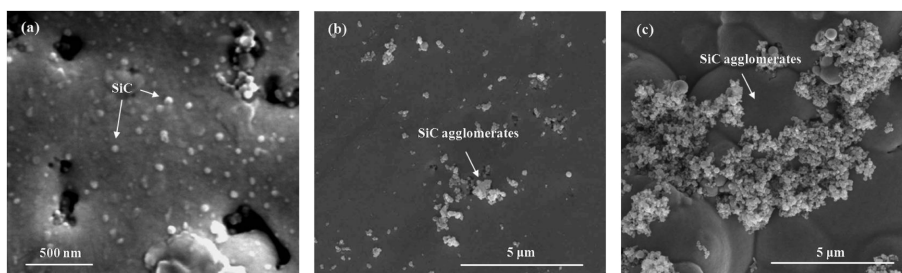
Fig. 2. Surface morphologies of Ni-Co-SiC composite coatings (a) 1 h, (b) 3 h, (c) 8 h.
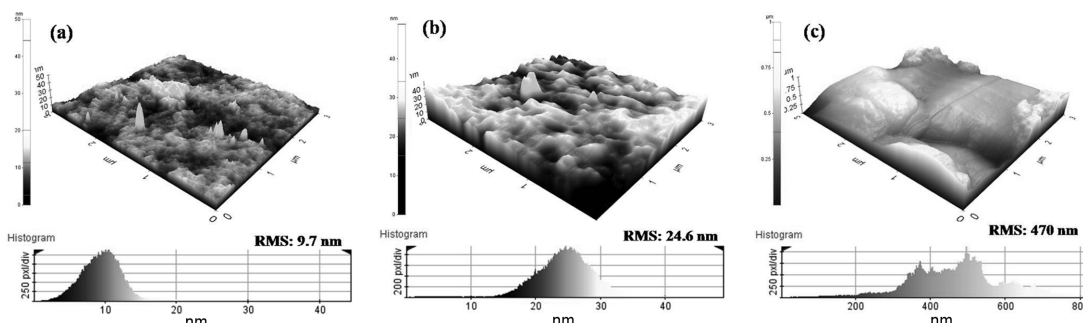

Fig. 3. Surface roughness of Ni-Co-SiC with, (a) 1, (b) 3, (c) 8 h.

to agglomerated SiC particles due to the larger active surface area resulting in higher SiC incorporation in the coatings.

A typical surface morphology, consisting of spherical shaped nanoparticles of SiC embedded in a Ni-Co matrix, is revealed by the FE-SEM micrograph of Ni-Co-SiC composite coatings. Fig. 2(a) shows SiC nanoparticles are uniformly distributed throughout the Ni-Co matrix. However, agglomerates of SiC particles with cluster sizes larger than 1 μm are observed in Fig. 2(b) and (c), which suggesting the agglomerates of SiC nanoparticles were extensively accelerated with increasing plating duration due to decomposition of additives. The morphology of Ni-Co matrix in the Ni-Co-SiC composite coatings was also changed with increasing plating time. With plating time up to 3 h, there is no pyramidal or colony-like morphology. However, the morphology of Ni-Co matrix with plating time of 8 h was found to be the cluster of colony which defined as a cluster of grains surrounded by a deep crevice as shown in Fig. 2(c).

The result from surface roughness analyzed AFM also showed similar tendency to FE-SEM result. The average root mean square (rms) value of Ni-Co-SiC composite coatings with 1, 3 and 8 h was measured to be approximately 9.7, 24.6 and 470 nm respectively, as shown in Fig. 3. An rms value at 8 h significantly increased due to agglomerates of SiC nanoparticles
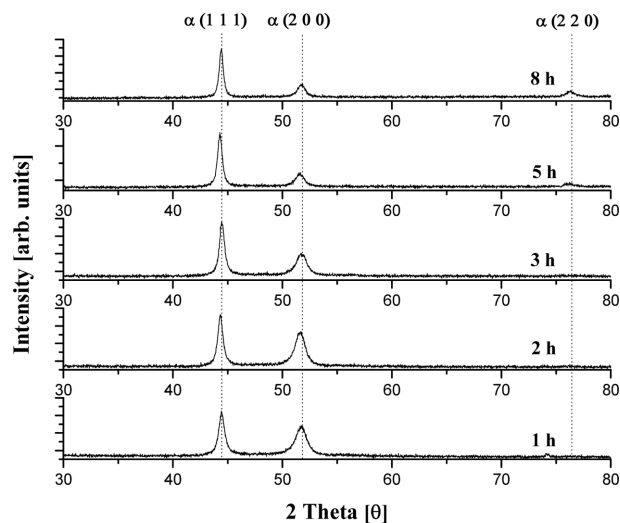

Fig. 4. XRD patterns of Ni-Co-SiC composite coating.

and colony-like morphology. It is considered that the decomposition of additives (sodium lauryl sulfate and saccharin) led to poor dispersion by increasing surface tension[10] and the surface charge of suspended particles resulting in agglomerates of SiC particle.

The XRD diffractograms of the Ni-Co-SiC composite coatings are indicated in Fig. 4. The phase structure of Ni-Co-SiC composite coating was found to be α-phase (FCC structure), and the deposit exhibited similar reflections with the orientation of (111) and (200) reflections. As plating duration increased, no strong modifications of textures were observed but a

decrease in intensity of (200) lattice orientation was observed. However, no peaks of crystalline β-SiC phase were detected in all composite coatings, indicating SiC particles in Ni-Co matrix are small amount in the range of 1.4-1.9 wt.% as mentioned in Table 2. Plating time dependence of the crystalline size calculated from the width of the reflection peak is shown in Table 2. The average crystalline size of Ni-Co-SiC was calculated from the full width at half maximum value (FWHM) of the XRD peaks using the Scherrer equation[11],

$$D_{hkl} = \frac{K\lambda}{\beta_{hkl}\cos\theta_{hkl}}$$

where D is the grain size (nm), K is Scherrer constant (0.89), λ is the X-ray wavelength, β is FWHM after instrumental broadening correction, and θ is the diffraction angle. All deposits showed a very fine grain size in the range of 10.6-17.8 nm. As increasing plating time, the grain size of composite coating gradually increased. The behavior of the grain refinement can be explained by the fact that the mean free path for a grain growth was decreased due to the additives adsorbed at a deposit during an electroplating[12].

Microhardness values as a function of plating duration are shown in Fig. 5. The hardness values ranged from a minimum of 453 Hv to a maximum value of 632 Hv for plating time 8 and 1 h, respectively. It is of interest to note that the hardness values of the Ni-Co-SiC composite coatings decreased with increasing plating duration.

Many report[7-9] that the hardness increase of the composite coatings is mainly related to the combination of solid solution, Hall-Petch relation[13,14] and by Orowan model for strengthening. The mechanism of
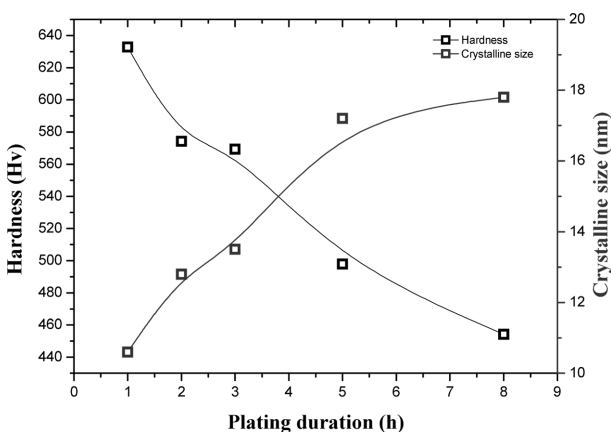

Fig. 5. Hardness and crystalline size as function of plating time.

solid solution strengthening is not suitable for the hardness variation of Ni-Co-SiC composite coating experimented here. The lattice parameter (approximately 3.534 Å) of all deposits from XRD analysis was identical, which means there is no peak shift with variation of compositional ratio between Ni and Co. Therefore, there is no need to think of the influence on crystal orientation during discussion of hardness enhancement.

A Hall-Petch relation strengthening appears to be operative in the nanocomposite Ni-Co-SiC composite coating. The maximum and minimum hardness was observed at plating duration with 1 h and 8 h, respectively. According to the crystalline size measured by XRD, the hardness increment has an obvious direct correlation to the grain size reduction. It is well know that the Hall-Petch relation is based on the concept that grain boundaries act as barriers to the motion of dislocations by forming dislocation pile-ups at grain boundaries, resulting in hardness enhancement. The additives seemed to be responsible for the refinement in grain size. The additives anions can be adsorbed on active growth sites on the cathode and produce transient chemical or physical barrier layers to transport adions and adatoms on the cathode surface and thereby promoting fine grain structure[15].

Conventional Orowan strengthening from fine particles is dependent on volume fraction, average particle size, and mean interparticle spacing. The relation between dispersion state of particles and microhardness can be expressed by

$$Hv = \frac{2Gb}{\lambda}$$

where G, b and λ refer to the shear modulus of the matrix, Burger's vector of the dislocation, and the distance of dispersed particles, respectively. In the present experiment, SiC content in the deposits which is almost constant in the range of 1.4-1.9 wt.%, which suggesting a negligible effect on the variation of hardness. However, taking the dispersion state of SiC particle into consideration, stably distributed particle compared to the agglomerated particles could decrease the average distance between particles for constant SiC content in Ni-Co matrix and thereby enhance the hardness. The particle aggregation could be attributed to the depletion of additives which not only reduces the surface tension but also enhance the electrostatic adsorption of suspended particles on a cathode surface by increasing their positive charge.

4. Conclusion

Ni-Co-SiC composite coatings were successfully electrodeposited with variation of plating duration.

(1) With increasing plating duration, the Co content in the coating was decreased because of the characteristics of anomalous co-deposition and the agglomerates of SiC nanoparticles.

(2) The colony-like surface morphology in the Ni-Co matrix and the agglomerates of SiC nanoparticles were more observed at plating duration of 8 h.

(3) Lattice parameter of all Ni-Co-SiC composite coatings was constant but the crystalline size was increased as plating duration increased.

(4) With increasing plating duration, the hardness of the Ni-Co-SiC composite coatings was decreased, which was attributed to an increase in grain size and agglomerates of SiC particles due to the depletion of the additives. Hall-Petch relation and Orowan model were dominant for hardening of Ni-Co-SiC composite coatings.

Acknowledgement

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