

Short Communication

Study on Performance of Co-W/SiC Composite Coatings Electrodeposited on Copper

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In this paper, CoW/SiC composite coatings were electrodeposited from plating bath with various nano SiC concentrations. The effect of SiC concentrations on deposition rate, hardness, corrosion resistance and surface morphology of CoW/SiC coatings were studied. It was found that the appropriate concentration of SiC was beneficial to increase the deposition rate, refine the surface particles and improve hardness of the composite coatings. However, when the SiC concentration was greater than 12 gL^{-1} , the agglomeration effect of the suspended SiC particles greatly reduced the deposition rate and mechanical properties of the CoW/SiC composite coatings. The coating prepared at the concentration of 8 gL^{-1} SiC possessed the best hardness and corrosion resistance.

Keywords: CoW/SiC composite coatings; plating technology; nano SiC; Corrosion resistance;

1. INTRODUCTION

With the rapid increase of electronic science, electronic components start to develop towards miniaturization, intelligence and integration. Thin coating materials are increasingly favored by electronic components, industrial manufacturing, microcomputer control and other fields due to their advantages. Cobalt based coatings possess high hardness, excellent magnetic properties and optimal corrosion resistance which are widely used in military industry, electronic equipment, computer chip and other high-tech fields[1-5]. In recent years, many works have been reported that the addition of metal and nonmetal particles could significantly improve the mechanical and anticorrosion properties of cobalt coating materials fabricated by electrodeposition. For example, Kosta investigated the structure and performance of CoP coatings obtained by direct current and pulse plating[6]. CoNi and CoNiP alloy coatings with optimal performance were reported by Cojocar[7]. Moreover, Dulal reported a kind of CoWP coatings with excellent property prepared by electrodeposition[8]. In addition

to the elements such as phosphorus and tungsten that can effectively improve performance of cobalt based coatings, nano silicon carbide is also considered as a kind of potential materials. The nano silicon carbide has large specific surface area, high surface activity, excellent mechanical and chemical properties which could extremely improve coatings performance as composite materials[9-12]. A kind of CoW/SiC composite coatings with excellent hardness and anticorrosion performance was electrodeposited in the paper. Effects of SiC concentrations on deposition rate, thickness, mechanical performance, surface morphology and corrosion resistance of CoW/SiC coatings were studied.

2. EXPERIMENTAL METHOD

Electrodeposition is used to prepare CoW/SiC composite coatings on copper substrate to investigate the influence of SiC concentration on physical and chemical properties of CoW/SiC samples. The detail information about bath composition is shown in table 1.

Table 1. Bath compositions of CoW/SiC composite coatings

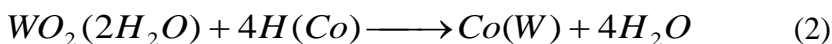
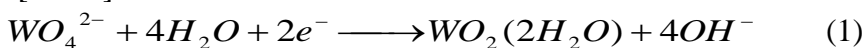
Chemical Agent	Concentration (gL ⁻¹)
CoSO ₄ ·7H ₂ O	30
Na ₂ WO ₄ ·2H ₂ O	15
C ₆ H ₈ O ₇	50
Na ₂ SO ₄	30
H ₃ BO ₃	30
SiC	0~12

The pure copper plate with 2 cm×2 cm size is chosen as cathode while the pure platinum plate with 3 cm×3 cm is selected as anode. The copper plate is polished firstly, after that alkali and acid solution are used to wipe off the copper surface respectively. Because SiC is prone to agglomeration, ultrasonic cleaning is required to vibrate the SiC solution before adding to the plating bath. The pH value of plating bath is adjusted to 3 before the experiment. When the pretreatment process is finished, the copper substrate is immersed into 100 ml plating bath to prepare CoW/SiC for 1 hour in the condition of 1.5 A/dm² current density at 60 °C. The electrochemistry station (Parstat 2273) is used to study the cyclic voltammetry and polarization process of samples. Meanwhile, CoW/SiC with 1×1 cm² size is chosen as cathode while pure platinum sheet with 2 ×2 cm² size is selected as anode. The saturated calomel electrode is reference electrode. Surface profiler (Tencor P6) is used to measure the thickness of CoW/SiC coatings. The hardness of samples is tested by Vickers (HVS-1000B) with 4.9 N for 15 s. Surface morphology is examined using SEM (Hitachi S-4700).

3. RESULTS AND DISCUSSION

3.1 Inductive codeposition of CoW alloy coatings

The deposition process of CoW is considered as a kind of inductive codeposition. Although tungsten cannot be deposited directly from aqueous solution, it is found out that tungsten could be electrodeposited from the solution with cobalt ions. In a word, tungsten and cobalt can be codeposited together [13-14]:



According to the equations above, tungstate oxide is firstly obtained due to the reduction reaction of tungstate ion. And then, tungstate oxide combined with H(Co) changes to CoW alloys. It is reported that the CoW alloy is formed by the tungsten oxide catalyzed by the primary ecological hydrogen on the cobalt surface.

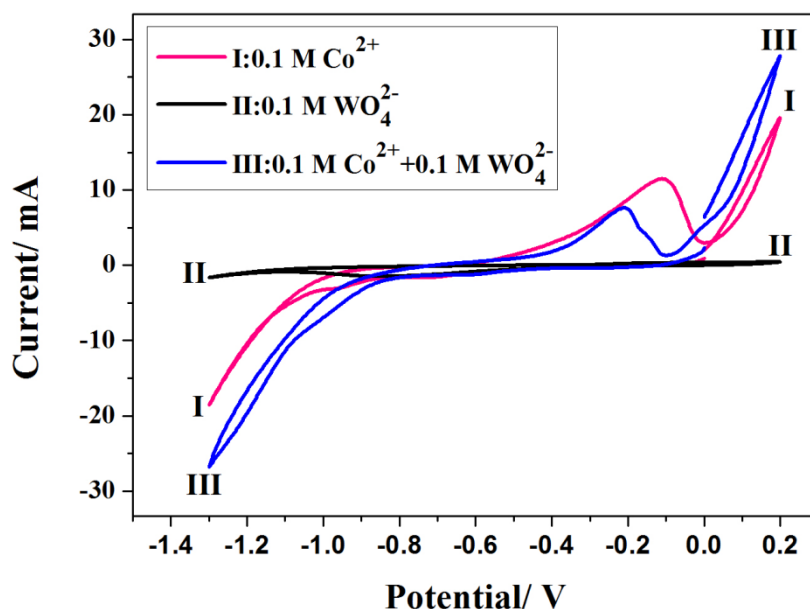
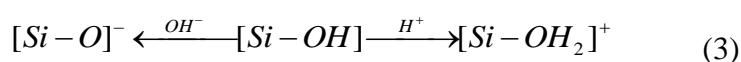


Figure 1. Cyclic voltammety curves of plating solution with 3 mV/s scanning rate based on three electrodes system (cathode: copper, anode: Platinum and reference: Saturated Calomel Electrode) in 100 ml bath; I: 0.1 M Co^{2+} ; II: 0.1 M WO_4^{2-} ; III: 0.1 M Co^{2+} +0.1 M WO_4^{2-}

Figure 1 gives the cyclic voltammety curves of different plating solutions. According to curve I, the deposition current starts to sharply increase at the potential of -0.7 V which means the reduction process of cobalt. There is almost no reaction current found at cure II, because tungsten could not be deposited directly from aqueous solution. Regarding to curve III, the reaction current begins to increase at the potential of -0.6 V which is more positive than current II. The adding of sodium tungstate promotes the deposition process of cobalt because of inductive codeposition mechanism. This phenomenon is also reported by some researchers.[15-16]

3.2 Surface charge of SiC

Nano SiC is easy to agglomerate due to its special structure and high surface energy. Therefore, it is necessary to make ultrasonic vibration cleaning and filtration treatment to eliminate the agglomeration status. The surface charge distribution of ions is important in plating system. However, the charge distribution on the surface of SiC in aqueous solution is totally different. According to the research, the charge on SiC surface in aqueous solution is generated due to the decomposition of silanol. The silanol formed on the surface of SiC nano powder is amphoteric materials. When the pH value is less than 4, the generation of $[\text{Si-OH}]^{2+}$ makes the surface of SiC positively charged. However, if the pH value is greater than 4, the reaction between silanol and hydroxide ions makes the surface of SiC negatively charged [17-18]. Therefore, the electrodeposition bath of CoW/SiC should be acid.



3.3 Effect of SiC concentration on deposition rate and thickness

The influence of SiC concentration on deposition rate and thickness of CoW/SiC is investigated in Figure 2. It can be seen from Figure 2, with the increase of SiC concentration in the plating solution, the deposition rate and thickness of composite coating increase firstly and then decrease gradually. When the concentration of SiC is 8 gL^{-1} , the maximum deposition rate and thickness of CoW/SiC could be obtained. SiC in the plating bath is conducive to improving the deposition rate of composite coating, mainly because positively charged silicon carbide particles enter into the CoW alloy grain boundary and crystal lattice under the action of electric field resulting in the increase of deposition rate. However, much higher concentration of SiC significantly decreases the deposition rate. The large amount of SiC particles suspended in the plating bath cover the reactive point of cathode surface that contribute directly to the decrease of deposition rate and thickness. The effects of SiC on deposition rate during plating process were also reported and analyzed [19-20].

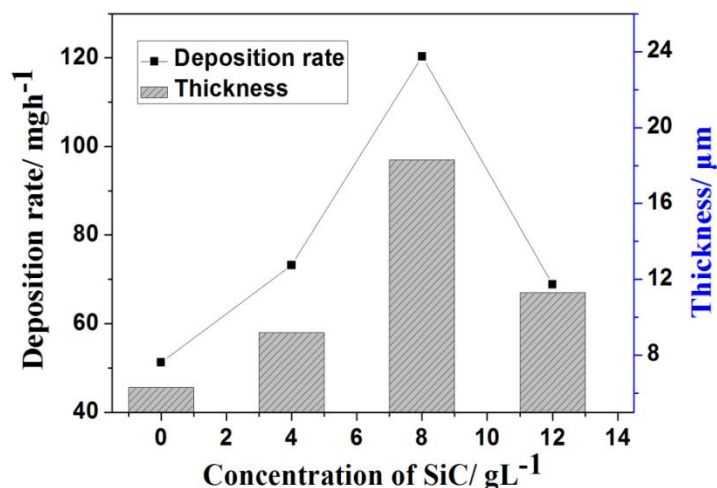


Figure 2. Effect of SiC concentrations on deposition rate and thickness of CoW/SiC

3.4 Effect of SiC concentration on hardness of CoW/SiC coating

In this section, Figure 3 studies the hardness of CoW/SiC composite coatings electrodeposited from solutions with different concentrations of SiC. It can be found that the silicon carbide concentration has a significant influence on the hardness of the composite coating. The composite coating prepared at 8 gL^{-1} SiC concentration possesses the best surface hardness with about 480 HV. This is mainly due to entry of silicon carbide nano particles into the CoW alloy lattice, which induces heterogeneous nucleation and refines the grain size resulting in the enhancement of mechanical property. However, large amount of SiC in the plating solution would decrease the deposition rate and worsen the coatings surface resulting in the decrease of hardness.

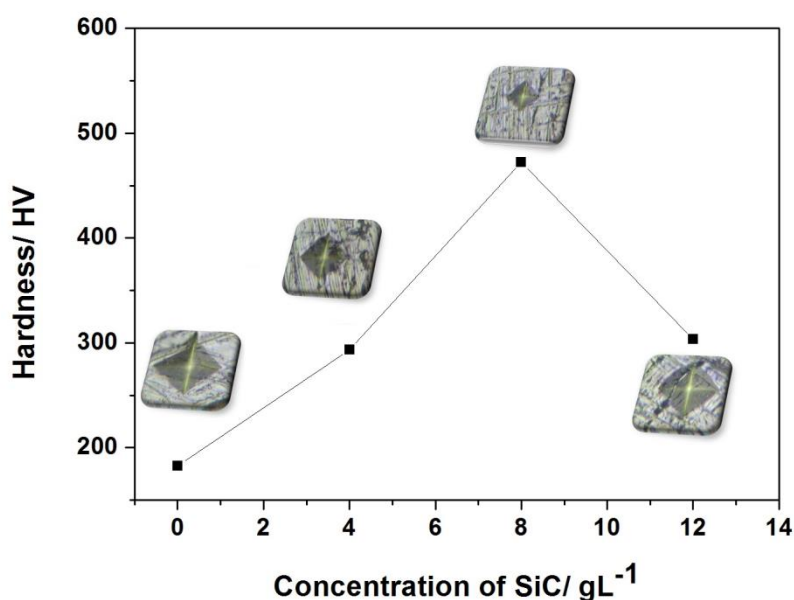


Figure 3. Effect of SiC concentration on hardness of CoW/SiC in the condition of 4.9 N for 15 s

3.5 Effect of SiC concentration on morphology and anticorrosion of CoW/SiC

The surface morphology of CoW/SiC deposited from plating bath with different concentrations of SiC is shown in figure 4. It is conspicuous that the CoW/SiC shows various surface morphologies. The CoW/SiC composite coating is a kind of typical nodular structures. The adding of SiC with appropriate concentration is conducive to the decrease the particle size of surface nodular resulting in dense and uniform surface morphology. Whereas, higher concentration of SiC in the plating bath covers the reactive area of cathode surface resulting in rough and agglomerate surface shown in figure 4(d).

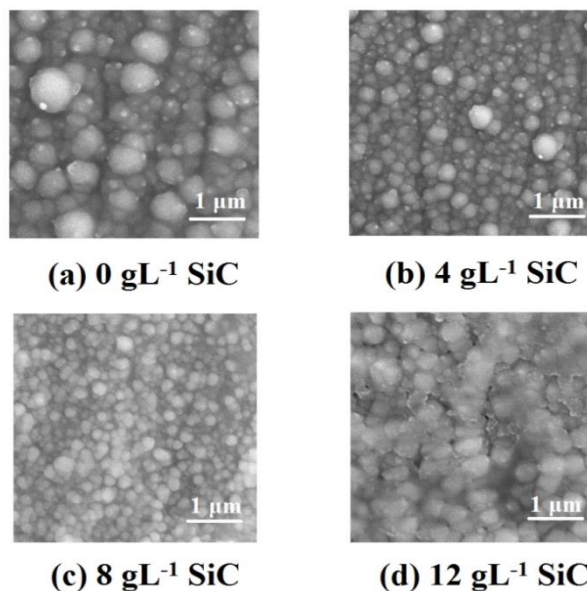


Figure 4. Surface morphology of CoW/SiC composite coatings prepared from baths with different concentrations of SiC

Polarization curves are used to test the CoW/SiC composite coatings prepared from the bath with different concentrations of SiC. According to the results of figure 5 and table 2, it is found out that with the increase of SiC concentrations in the bath, the corrosion potential of obtained CoW/SiC composite coatings moves more positive while the corrosion current density decreases gradually. The CoW/SiC composite coating fabricated from the bath with 8 gL⁻¹ SiC possesses the optimal anticorrosion performance with about -10.23 μAcm⁻² current density. The nano SiC particles enter into CoW alloy lattice help to decrease the grain size and form dense surface that contribute to the decrease of corrosion current density resulting in better anticorrosion performance. Same results about the relationship between SiC and anticorrosion performance were also presented in the literature [21-22]. However, the CoW/SiC prepared from the bath with 12 gL⁻¹ SiC possesses rough and worsen surface morphology, resulting in the increase of corrosion current density.

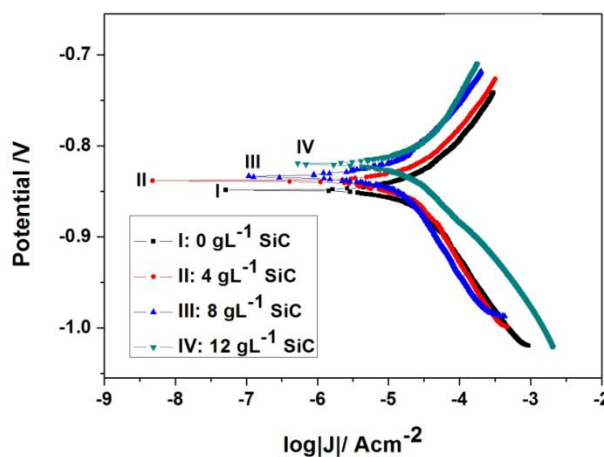


Figure 5 Polarization curves of CoW/SiC composite coatings in 3.5% NaCl solution with 1 mV/s scanning rate from -1.0 V to 0.7 V

Table 2. corrosion potential and current of CoW/SiC composite coatings

SiC Concentration / gL ⁻¹	Corrosion Current/ μAcm^{-2}	Corrosion Potential/ V
I: 0	-33.88	-0.849
II: 4	-19.95	-0.838
III: 8	-10.23	-0.833
IV: 12	-23.61	-0.818

4. CONCLUSIONS

CoW/SiC composite coatings were prepared by plating technology from solution with different nano SiC concentrations. The influences of SiC concentrations on deposition rate, hardness, anticorrosion and surface morphology of CoW/SiC composite coating were investigated. The results showed that increasing the SiC concentration in the plating bath can increase the deposition rate, improve the surface hardness and enhance corrosion resistance due to entry of SiC nano particles into the CoW alloy lattice, which induced heterogeneous nucleation and refined the grain size. When the SiC concentration was 12 gL⁻¹, the excess nano silicon carbide was prone to agglomerate and cover the reaction area of cathode, resulting in the decrease of deposition rate and hardness. The composite coating prepared under the condition of 8 gL⁻¹ SiC possessed uniform and dense surface morphology with the best mechanical properties and corrosion resistance.

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