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ORIGINAL PAPER

Effect of surfactant BAS on MoS_2 codeposition behaviour

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Abstract Ni–MoS_2 metal matrix composites were produced by electrodeposition in a Watts bath. The correlation of embedded particle ratio and operational parameters was studied. When surfactant BAS was adsorbed on the MoS_2 particle surface, the conductivity of the MoS_2 was significantly decreased. Thus, more Ni atoms may be deposited homogeneously over a wider area rather than on preferred conductive positions. This results in a smoother codeposition layer with lower porosity. Furthermore, strong adhesion between the codeposition layer and the substrate when using surfactant BAS may result from lower porosity of the codeposition layer.

Keywords Electrocodeposition · Nickel · Molybdenum disulfide · Surfactants

1 Introduction

The electrocodeposition of inert particles in a metal matrix was recently developed for various applications. Electrocodeposited composites can be used for wear resistance, corrosion resistance and in lubrication. Electrocodeposited Cr–Al_2O_3 and Ni–SiC composite coatings are used to increase the wear resistance of metal surfaces [1–3]. The incorporation of powders in metals such as Al_2O_3, Si_3N_4 and Cr_2O_3 decreases the metal corrosion rate [4–6].

Solid lubricants such as MoS_2, polytrafluoroethylene (PTFE) and graphite are widely used in environments with higher temperatures, lower temperatures and/or under vacuum conditions. Dispersed particles of solid lubricants such as MoS_2, graphite, PTFE and WS_2 incorporated in a metal matrix reduce surface friction [7–9]. Solid lubricants (e.g., MoS_2) are employed in situations where grease and oil lubricants cannot be applied.

Lubrication performance varies with coating composition, which is affected directly by the electroplating process parameters. The coating composition depends on factors related either to the particles such as size, density, composition, zeta potential and conductivity [10–14], or to the electrolyte such as composition, pH, temperature, current density, stirring speed and surfactants [15–20]. The effect of surfactant has been studied infrequently. Better understanding of surfactant effects are required since they may not only improve the stability of a suspension by increasing the wettability of the suspended particles, but may also confer a net positive charge to the particles which prevents them from agglomerating and attracts them electro-statically to the cathode [21].

The purpose of this study was to add understanding of the role of surfactant on MoS_2 incorporation in a Ni matrix during electrodeposition. The effects of operational parameters on the amount of MoS_2 codeposited with Ni from a Watts bath were studied.

2 Experimental procedure

The Ni–MoS_2 composite coatings were prepared on the substrate by electrodeposition from a Watts type bath. The basic bath composition was $NiSO_4 \cdot 7H_2O$, 330 g L^{-1}; $NiCl_2 \cdot 6H_2O$, 45 g L^{-1} and H_3BO_3, 40 g L^{-1}. The electrolyte was prepared using experimental grade chemicals and de-ionized water. A DC power-supply (GW, Taiwan)

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and mechanical stirring were employed. Concentrations of MoS_2 particles ranging from 5–50 g L^{-1} were added to the bath. The parameters used were a current density of 2–6 A dm^{-2}, pH 2–5, and a bath temperature of 35–75 °C. The mechanical agitation speed was 500–2,000 rpm. The mean diameter of MoS_2 particles, manufactured by Merk (Germany), was about 4.5 μm. Since MoS_2 particles are hydrophobic, surfactant is needed not only to disperse the particles but also to stabilize the particles uniformly in the plating bath. Candidate surfactants were added to 0.1 g g^{-1} MoS_2 for each experiment.

The electrolyte temperature was controlled using a constant-temperature water bath. Solution pH was adjusted with H_2SO_4 and NH_4OH before electroplating. Copper sheets with a dimension of 10 cm × 10 cm were employed as a cathode substrate. A nickel sheet was used as the anode and was placed vertically at a distance of 12 cm from the cathode. The contents in the Ni–MoS_2 codeposition layer were determined by X-ray diffraction with a copper target performed at 20 kV and 5 mA and with a scanning speed of 10 degree min^{-1}.

3 Results and discussion

3.1 Surfactant

As shown in Table 1, the strongest adhesion between the codeposited layer and the substrate was achieved by employing cationic surfactant Benzyl Ammonium Salts (BAS) in the electrolyte. The other surfactants showed poor adhesion (after wear tests) between the deposition layer and the substrate. Additional experiments were not conducted. In the earlier study [22], the zeta potential of the MoS_2 particles increased with the amount of added surfactant BAS, as shown in Fig. 1. The increase suggests that positive ions tend to be absorbed on the MoS_2 particle surface causing electrostatic attraction to the cathode. The codeposited MoS_2 increased with the amount of BAS, confirming that BAS is advantageous to MoS_2 codeposition.

During the codeposition of inert particles, the electrical conductivity of the particles plays an important role in affecting the smoothness, uniformity and homogeneity of the composite layer [14]. It is possible that if the inert particle offers significant conductivity, a rough surface and significant porosity of the codeposition layer is produced because the Ni atoms are directly deposited on this conductive inert particle surface. This effect can be enhanced when a higher current density is used during electrocodeposition. The conductivity of MoS_2 is about $2.09 \times 10^{-4}\ \Omega^{-1}\ m^{-1}$ (i.e., 2.09×10^{-6} S cm^{-1}) [23] in contrast to $3.45 \times 10^{-7}\ \Omega^{-1}\ m^{-1}$ of SiC (i.e., $2.9 \times 10^{8}\ \Omega$ cm) [24]. Therefore, in the electrodeposition process, Ni atoms can be deposited on the surface of MoS_2 resulting in porosity in the codeposition layer. The microstructure of the MoS_2 codeposition layer is shown in Figure 2a and pores (as arrowed) are observed. When BAS was added the porosity decreased (Fig. 2b). More BAS leads to less porosity in the codeposition layer as shown in Fig. 3a and b. Less porosity suggests that, when BAS is adsorbed on the particle surface, the conductivity of MoS_2 is decreased. More Ni atoms are deposited homogeneously over a wider area than deposited on preferred conductive positions. This results in a smoother layer with lower porosity similar to codeposition of non-conductive inert particles.

Strong adhesion between the codeposition layer and the substrate when employing BAS may result from the lower porosity of the codeposition layer.

3.2 MoS_2 concentration

The effect of MoS_2 concentration on the extent of MoS_2 codeposition is shown in Fig. 4. The amount of MoS_2 particles present in the layer increases with increasing MoS_2 concentration in the electrolyte.

Table 1 The result of surfactant addition on the adhesion between the codeposition layer and substrate

Surfactant	Commercial name	Codeposition adhesion to the substrate after wear test
Anionic	Stepanol (Ammonium Lauryl Sulfate)	Weak
	960SF (NH_4 P.O.E. Nonyl Phenyl Ether Sulfate)	Weak
	290MH_2 (Sodium Dialkyl Sulfosuccinate)	Weak
Cationic	960SN (Na P.O.E. Nonyl Phenyl Ether Sulfate)	Weak
	BAS (Benzyl Ammonium Salts)	Strong
Noionic	Ammonyx	Weak
	Ninol	Weak
Amphoteric	R2 (Lauryl Betain)	Weak
	L7 (Alkyl Tripolyoxyethylene Ammonium Hydroxide)	Weak

Operation condition: pH = 4, 4 A dm^{-2}, T = 45 °C, MoS_2 = 10 g L^{-1}, rpm = 1,500

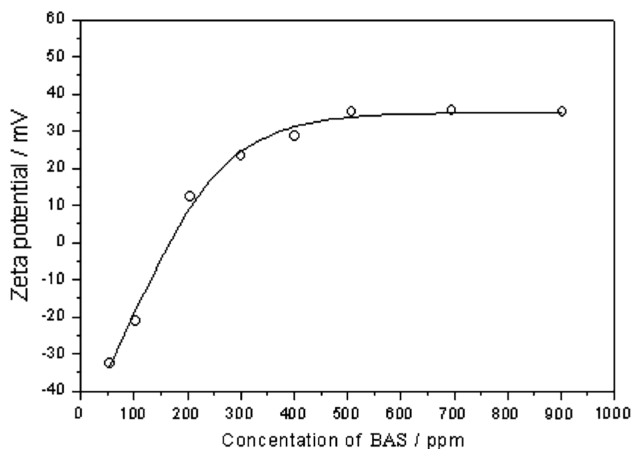

Fig. 1 Zeta potential of MoS_2 diagram after BAS surfactant addition at the condition pH = 5, T = 25 °C [22]

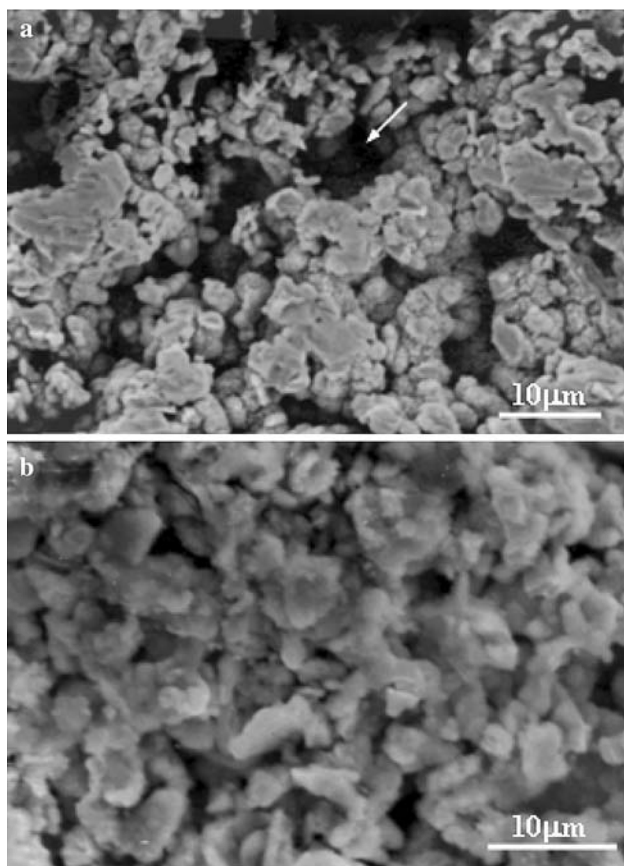

Fig. 2 (**a**) Showing the microstructure of MoS2 without surfactant addition. (**b**) Showing the microstructure of MoS_2 with surfactant addition [BAS 0.1 g g^{-1} MoS_2]

3.3 Current density

Figure 5 shows the effect of current density on the extent of MoS_2 codeposition. The maximum MoS_2 is achieved at a current density of 4 A dm^{-2}. At a higher current density, the Ni deposition rate is greater than that of the embedded MoS_2 particles. The volume fraction of MoS_2 in the layer decreases. This confirms that the particle deposition rate reaches a limiting value as reported by Hwang et al. [25].

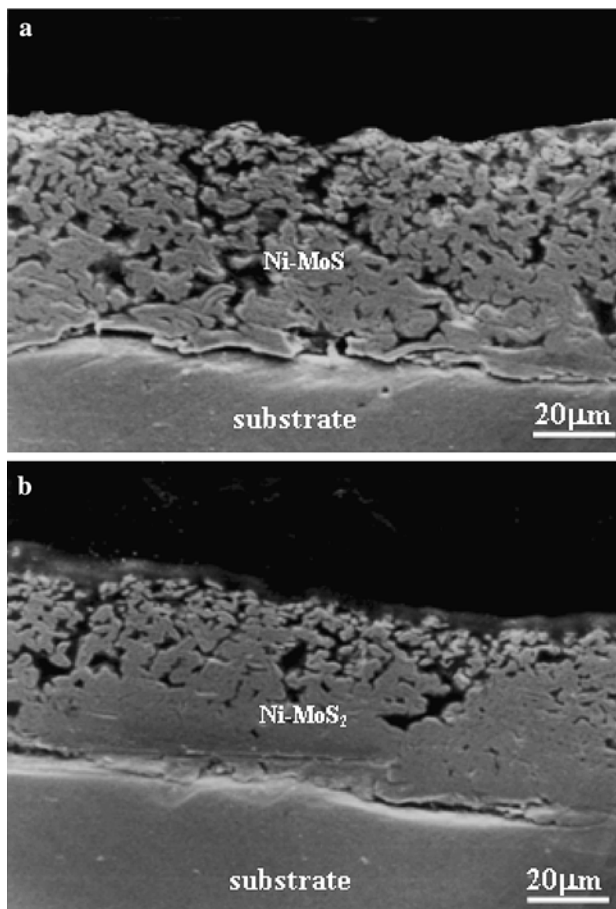

Fig. 3 (**a**) Cross-section microstructure of MoS_2 with less surfactant addition [BAS 0.05 g g^{-1} MoS_2]. (**b**) Cross-section microstructure of MoS_2 with more surfactant addition [BAS 0.1 g g^{-1} MoS_2]

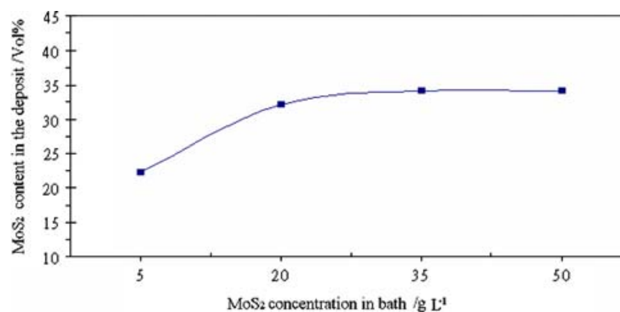

Fig. 4 Effect of MoS_2 loading on the extent of codeposition of MoS_2, pH = 5, T = 45 °C, 4 A dm^{-2}, rpm = 500, BAS 0.1 g g^{-1} MoS_2

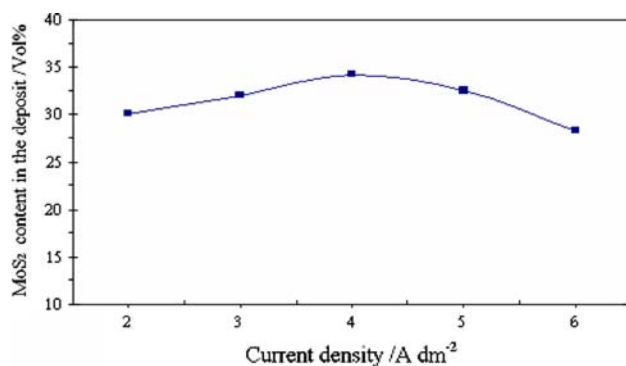

Fig. 5 Effect of current density on the extent of codeposition of MoS_2, pH = 5, T = 45 °C, 4 A dm^{-2}, rpm = 1,000, BAS 0.1 g g^{-1} MoS_2

3.4 Temperature

The bath temperature was found to have a influence on particle content (Fig. 6). The maximum deposited MoS_2 is achieved at ~45 °C which confirms that the temperature employed in Sect. 3.1 is suitable. It is possible that, at elevated temperature, the amount of absorbed surfactant decreases. Therefore, the assistance of electrical attraction (cation surfactant absorbed on the MoS_2) bringing MoS_2 to the cathode decreases. The exact reason why the amount of MoS_2 deposition is lower at ~35 °C than at elevated temperature ~45 °C is not clear. However, generally the amount of deposited MoS_2 at lower temperature is higher than that at higher temperature (Fig. 8).

The effect of temperature varies for different codeposition systems. For Ni–Al_2O_3 no effect of temperature on the percentage of embedded particles was found [26, 27], due to the fact that they are actually in a no-surfactant-added-condition. This confirms that the surfactant plays an important role in Ni–MoS_2 deposition.

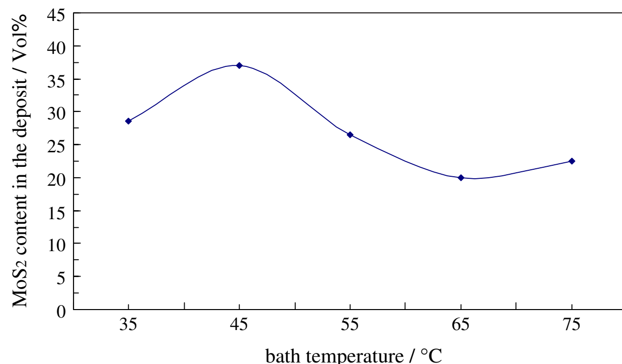

Fig. 6 Effect of temperature on the extent of codeposition of MoS_2, BAS 0.1 g g^{-1} MoS_2, pH = 4, 4 A dm^{-2}, MoS_2 = 50 g L^{-1}, rpm = 500

3.5 pH Effect

The effect of pH on the extent of MoS_2 codeposition is shown in Fig. 7. At pH = 4, a maximum amount of MoS_2 is obtained (37%) which is slightly higher than for pH = 5 (34%), confirming that the pH = 4–5 region is favourable.

At low pH, the concentration of hydrogen ions is high and H^+ and Ni^+ attraction to the cathode occurs. If H_2 is produced, a barrier to Ni deposition affects MoS_2 deposition. When the pH is higher, there are fewer H_2 bubbles and MoS_2 deposition is assisted.

3.6 Agitation rate

The effect of stirring rate on the extent of MoS_2 codeposition is shown in Fig. 8. From 500 to 1,500 rpm, the MoS_2 deposited shows limited change. It is interesting to note that if the agitation rate reaches 2,000 rpm, the MoS_2 deposition rate decreases. Too much agitation leads to a

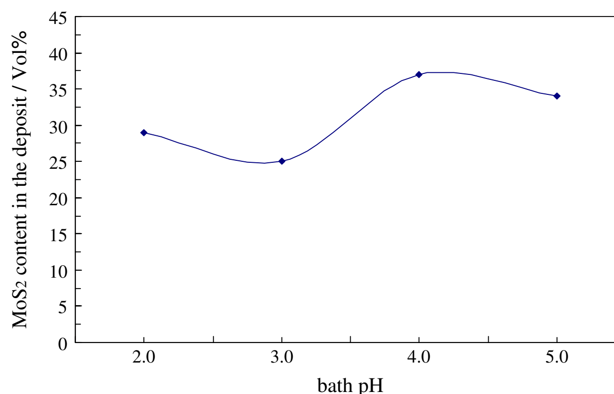

Fig. 7 Effect of pH on the extent of codeposition of MoS_2, pH = 4, 50 g L^{-1} MoS_2, 4 A dm^{-2}, rpm = 500, surfactant BAS 0.1 g g^{-1} MoS_2

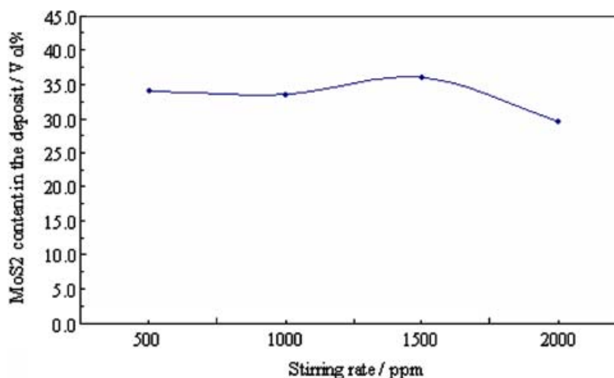

Fig. 8 Effect of stirring rate on the extent of MoS_2 codeposition, pH = 5, 4 A dm^{-2}, T = 45 °C, MoS_2 = 50 g L^{-1}, surfactant BAS 0.1 g g^{-1} MoS_2

decrease in particle codeposition because the particles are swept away from the cathode surface before they are captured. This observation confirms previous work [19, 21] suggesting that forced convection is not the dominant factor affecting MoS_2 codeposition.

4 Conclusions

Maximum codeposition of MoS_2 can be achieved by operation at a MoS_2 concentration of 50 g L^{-1} at 4 A dm^{-2} and pH = 4, T = 45 °C, by employing surfactant BAS. The stirring rate does not influence the amount of MoS_2 codeposition.

Due to adsorption on the MoS_2 surface, the surfactant itself may become part of the reduction reaction. When BAS is adsorbed on the MoS_2 particle surface, the conductivity of the MoS_2 decreases. More Ni atoms are deposited homogeneously over a wider area rather than are deposited on preferred conductive positions resulting in a smoother codeposition layer with lower porosity, similar to codeposition of non-conductive inert particles.

The stronger adhesion between the codeposition layer and the substrate when employing BAS may result from the lower porosity of the layer.

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