



Ag percent effect on microstructure and tribological performance of Clay-Ag composite films

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ABSTRACT

Clay-Ag composite films were based on polyethylene, 0.75 degree and master batch which were produced under the temperature 195-165 degrees Celsius, at 50rpm speed. The morphology and microstructure of the composite films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and transmission electron microscopy (TEM). The tribological behavior was investigated by using a ball-on-disk tribometer in vacuum and in humid air. The crystalline Ag phase dispersed in amorphous Clay and the size of the crystalline Ag increased with the Ag content in the films. The mechanical and tribological properties of Clay-Ag composite films varied with the Ag content. At the content of 42 at %Ag, the composite film had the highest microhardness and elastic modulus. The amorphous Clay in the Clay-Ag 42% composite film made the main function during wear, so the film showed the lowest friction coefficient. The friction coefficients of the Clay-Ag composite films in vacuum were lower and more stable than those in humid air, but the environmental sensitivity of tribological behavior decreased obviously due to the addition of Ag in the films.

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1. Introduction

Composite metal are widely used for solid lubricants due to their extreme degree of anisotropy of the layered crystal structures. The basic structure and performance of Ag are similar to the well researched Ag disulfide [1-5]. A great many researchers have been carried out to deposit Ag film for tribological applications using different techniques [6-10]. Clay has poor tribological behavior in humid air. Previous studies have shown that Composite metal with metals such as clay, Ag, Pb, Ni, Fe and Ti densify the thin films, thereby increasing hardness, lowering friction, reducing crystallite breakage and improving the lubricating behavior in humid environments [11-15]. Metal Ag is face-centered cubic structure, and has low shear strength. The soft metallic Ag film onto a hard metallic surface modified the contact interface and decreased the friction coefficient due to the plastic flow in the process of relative slip [13]. Therefore, it is expected to improve the microstructure and tribological performance by adding Ag to Clay film. In this present work, the influence of Ag content on the microstructure and mechanical properties of the composite films was investigated. And the tribological performance was evaluated in vacuum and in humid air.

2. Experimental

2.1. Preparation of Clay-Ag composite films

Clay-Ag composite films were based on polyethylene, 0.75 degree and master batch which were produced under the temperature 195-165 degrees Celsius, 50rpm speed.

Clay-Ag composite films were deposited by magnetron co-sputtering on medium carbon steel substrate, and Si (100) wafer substrate for analytical purposes, using a pure clay target ($\geq 99.1\text{wt. } \%$) and a pure Ag target ($\geq 99.5\text{wt. } \%$). The medium carbon steel substrates (30mm in diameter and 3mm in

thickness) with hardness of HRC 42 were polished and degreased ultrasonically in acetone for 30min. The distance between substrate and target was about 12cm. Before deposition, a titanium target was sputtered under argon ion cleaning the substrates, and then used to deposit an interlayer, which led to an improvement in adhesion. Prior to deposition, the system base pressure was approximately 2.8×10^{-3} Pa.

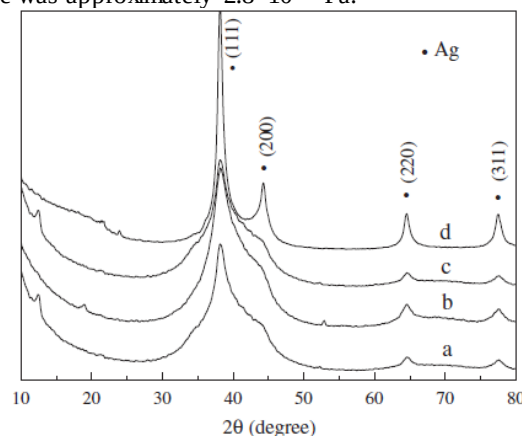


Fig. 1. XRD patterns of Clay-Ag composite films: (a) Clay - Ag32%, (b) Clay - Ag42%, (c) Clay-Ag65%, (d) Clay - Ag80%

The substrate was not heated before deposition. The substrate bias voltage was -100V and the deposition time was 120min, with a background argon pressure of 0.4Pa. The content of Ag in Clay-Ag composite films was controlled by the power on the pure Ag target, 0, 5, 10, 20, 40W, respectively. And the power on the pure Clay target was 150W constantly. The thickness of the as-deposited films was approximately 1μm,

which were measured with Alpha-step 200 profilometry (TENCOR).

2.2. Films analysis and tribological measurement

The microstructure and morphology of Clay–Ag composite films were characterized by X-ray diffraction (XRD, Thermo X’ TRA X-ray diffractometer, Cu K α 1), scanning electron microscopy (SEM, SIRION JY/T010-1996), energy dispersive X-ray spectroscopy (EDS) and transmission electron microscopy (TEM, JEM-2010). The microhardness and elastic modulus measurements were determined with MTS Nano indenter XP using a load of 460mN. The tribological properties were investigated using a ballon- disk tribometer (WTM⁻¹E) in vacuum (10⁻¹ Pa) and in humid air (relative humidity of 60%). The ball fabricated by quench-and-tempered GCr15 steel with hardness of HRC 65 was 3mm in diameter, and the deposited film specimens served as the disk. The tests were performed at a load of 0.5N and a sliding speed of 0.15ms⁻¹ for duration of 15000 cycles. The diameter of the wear track is 11mm. Friction coefficient was calculated by dividing the friction force, which was recorded on line via torque as measured by the strain gauge. The worn surfaces of the composite film specimens were examined using SEM.

3. Results and discussion

3.1. Microstructure and morphology of Clay–Ag composite films

Fig. 1 shows the XRD patterns of the as-deposited Clay–Ag composite films. No detectable typical Clay peaks can be seen, and this indicates that it is amorphous. Combined with the result of EDS (Table 1), there are Clay and Silver in the composite films, and Ag content is 32, 42, 65 and 80 at.%, which is deposited by the power of 5, 10, 20, 40W on the Ag target, respectively. From these patterns, it can be also seen that Ag is crystalline and the size of the crystalline Ag increases with the Ag content.

Fig. 2 shows the SEM images of Clay–Ag composite films with different Ag content. The surface morphology of the films varies with increasing the Ag content. The Clay–Ag32% and Clay–Ag 42% composite films have compact microstructure (Fig. 2a and b). But when the Ag content is 65% and 80%, the surface morphologies of Clay–Ag composite films are coarse, and the particle sizes become large (Fig. 2c and d). TEM and HRTEM micrographs of Clay–Ag composite films with Ag contents of 42% and 80% are illustrated in Fig. 3. The crystalline Ag phase disperses uniformly in the amorphous Clay matrix for the Clay–Ag42% composite film, and the size of crystalline Ag is about 10nm (Fig. 3a and b). But in the Clay – Ag80% composite film, the size of crystalline Ag is uneven, about 10–42nm (Fig. 3c). These results are in agreement with the XRD analysis. Fig. 3d shows the crystal lattice lines with different width and direction, indicating that a great deal of crystalline Ag gets together and disperses asymmetrical in the Clay –Ag80% composite film.

3.2. Tribological performance

Fig. 4 shows the effect of Ag content on the microhardness and elastic modulus of Clay–Ag composite films. The microhardness and elastic modulus of the composite films vary with the Ag content, and the trend of both curves is quite similar. With addition of Ag in the film, the microhardness and elastic modulus were prominently increased compared to the pure Clay film. At the content of 42 at % Ag, the composite film has the highest microhardness and elastic modulus, which are 6.8GPa and 135GPa, respectively. With further increasing the

Ag content, the crystalline Ag is in the majority and Ag particles connect with each other in the film. Actually, they form the Ag based composite film, so the microhardness and elastic modulus of the composite film decrease.

Table 1
Quantitative analysis of the Clay–Ag composite films and the wear debris by EDS

Power of Ag target (W)	Composite films		Wear debris	
	Clay (at.%)	Ag (at.%)	Clay (at.%)	Ag (at.%)
5	45	32		
10	42	42	45	42
20	30	65		
40	15	80	10	80

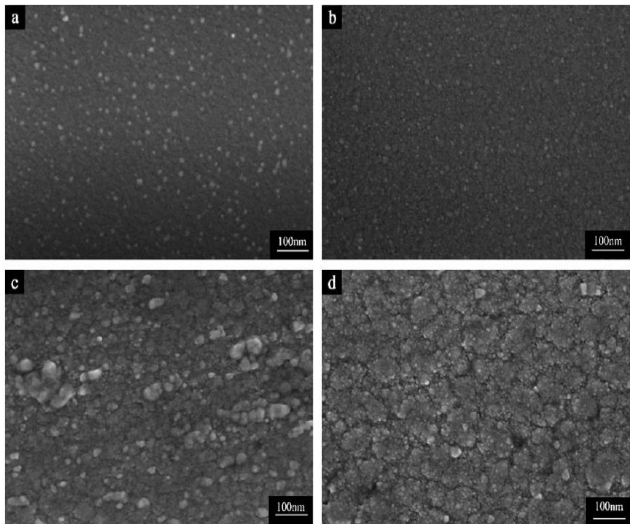


Fig. 2. SEM images of Clay–Ag composite films: (a) Clay–Ag32% , (b) Clay–Ag42% , (c) Clay –Ag65% , (d) Clay–Ag80% .

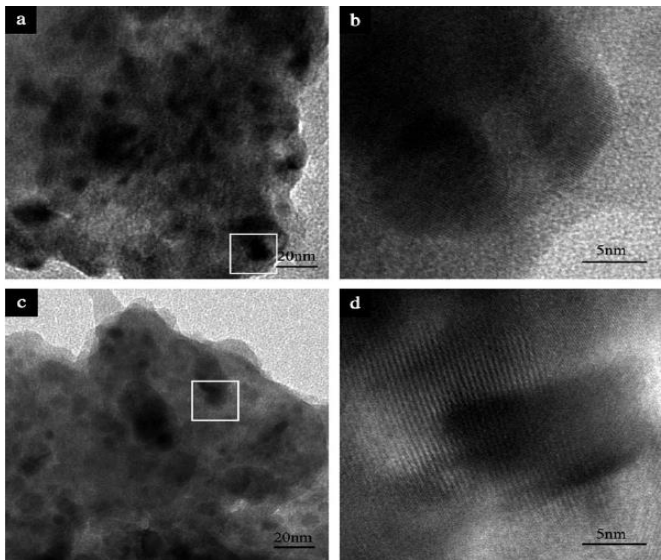


Fig. 3. (a) TEM and (b) HRTEM micrographs of Clay–Ag42% composite film, (c) TEM and (d) HRTEM micrographs of Clay–Ag80% composite film.

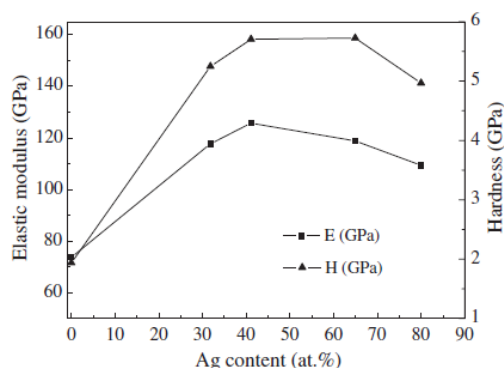


Fig. 4. Effect of Ag content on microhardness and elastic modulus of Clay–Ag composite films

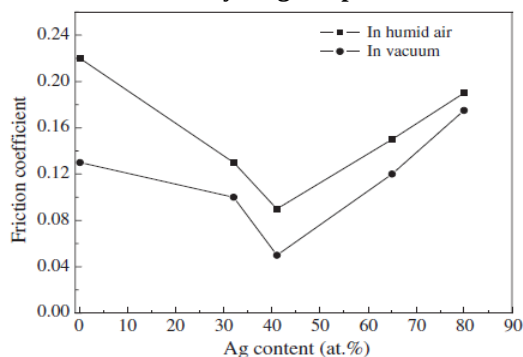


Fig. 5. Effect of Ag content on friction coefficient of Clay–Ag composite films in vacuum and in humid air

The effect of Ag content on the friction coefficient of Clay–Ag composite films is shown in Fig. 5. The tests were performed at a load of 0.5N and a speed of 0.15ms^{-1} in vacuum (10^{-1} Pa) and in humid air (relative humidity of 60%). As the Ag content increases, the friction coefficient of the composite films decreases sharply to the lowest level, approximately 0.09 in humid air and 0.05 in vacuum. The friction coefficient of the composite film increases again with further increasing the Ag content. As shown in Table 1, for the Clay–Ag 42% composite film, the Ag content of the wear debris reduces compared to the film, but the clay content of the wear debris increases. It is supposed that amorphous Clay make the main function during wear. For the Clay–Ag80% composite film, however, the content of Ag, and clay of the wear debris is hardly any change compared to the film before wearing. Ag makes the main function during wear and the friction occurs between Ag and steel to a great extent, so the friction coefficient of the Clay–Ag80% composite film is relatively high.

Fig. 6 shows the variation of friction coefficient of Clay–Ag42% composite film versus cycles in vacuum and in humid air. It is the cross-sectional difference of tribological performance of the composite films between vacuum and humid air. It can be seen that the friction coefficients of the composite films in vacuum are lower than those in humid air, and the variation of friction coefficient with cycles in vacuum is more stable compared to that in humid air (Fig. 6). It is mainly that there is hardly any water vapor and oxygen in vacuum. In nano composite film, the addition of metal could prevent the ingress of the water vapor, getter oxygen through preferred oxidation of the metal during sliding and protect structure from oxygen contamination, leaving unoxidized free to act as a lubricant [16]. In this work, the friction coefficient of pure Clay film was 0.13 and 0.22 in vacuum and in humid air, respectively, indicating that the water vapor and oxygen in testing environment had a distinct influence on the tribological behavior. As shown in Fig.

5, the addition of Ag in the films decreases obviously the environmental sensitivity of tribological behavior. In the Clay–Ag 42% composite film, the fine Ag phase dispersed uniformly in amorphous Clay and the film formed a compact microstructure. The difference of friction coefficients for the composite film in vacuum and in humid air was small. Although the microstructure was coarse for Clay–Ag 80% composite film, a great deal of crystalline Ag existed in the Clay–Ag 80% composite film and the contact was between Ag and steel to a great extent during the friction. Therefore, the difference of friction coefficients for the composite film with high content of Ag in vacuum and in humid air was also smaller compared to Clay film.

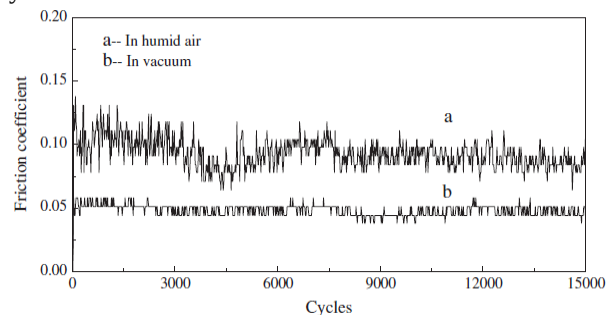


Fig. 6. Variation of friction coefficient of Clay–Ag 42% composite film versus cycles in vacuum and in humid air

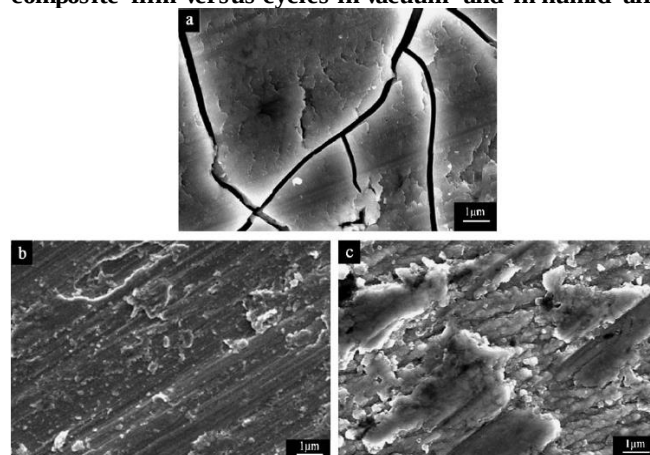


Fig. 7. Worn surface morphologies of films after testing in humid air: (a) pure Clay film, (b) Clay–Ag 42% composite film, (c) Clay–Ag 80% composite film

Fig. 7 shows the worn surfaces of Clay and Clay–Ag composite films after testing in humid air. Cracking is observed for the pure Clay film (Fig. 7a). A great deal of fine wear debris can be seen on the Clay–Ag 42% composite film, as shown in Fig. 7b. The thin and small wear debris dispersed uniformly on the surface of the frictional bodies and modified the contact of rugged face. Therefore, the composite film revealed a low friction coefficient. For the Clay–Ag 80% composite film (Fig. 7c), however, the thick and big wear debris includes a great deal of Ag. The frictional contact is between Ag and steel to a great extent, resulting in an increase in the friction coefficient.

4. Conclusions

Clay–Ag composite films were deposited on medium carbon steel substrate by magnetron co-sputtering method. The crystalline Ag phase dispersed in amorphous Clay, and for Clay–Ag 42% composite film Ag distributed uniformly and the film formed a compact microstructure. The mechanical and tribological properties of the Clay–Ag composite films varied with Ag content, and were better than those of pure Clay film. The Clay–Ag 42% composite film had the highest hardness and

elastic modulus, which were 6.8 GPa and 135 GPa, respectively. The main composition of wear debris in the Clay–Ag 42% composite film was clay, indicating Clay made the main function during wear. The film showed the lowest friction coefficient, approximately 0.09 in humid air and 0.05 in vacuum. The friction coefficients of the composite films in vacuum were lower and more stable than those in humid air, but the addition of Ag in the films decreased obviously the environmental sensitivity of tribological behavior compared to Clay film.

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