Powder Technology 281 (2015) 83–90

Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Hydrophilicity characterization of Al_2O_3-coated MoS_2 particles by using thin layer wicking and sessile drop method

Ping Liu [a,b], Yongwei Zhu [a,*], Shangwen Zhang [a]

[a] College of Mechanical and Electrical Engineering, Nanjing University of Aeronautics & Astronautics, Nanjing, 210016, PR China
[b] College of Engineering, Nanjing Agricultural University, Nanjing, 210031, PR China

ARTICLE INFO

Article history:
Received 12 August 2014
Received in revised form 4 March 2015
Accepted 9 May 2015
Available online 15 May 2015

Keywords:
Contact angle
Surface free energy
Thin layer wicking
Sessile drop method
Molybdenum disulfide
Particle

ABSTRACT

When hydrophobic particles are employed to prepare self-lubricating electroless composite coatings, they usually require surface modification to improve their wettability. The study focuses on the resultant change in wettability of the MoS_2 particles with an inorganic coating. Al_2O_3-coated MoS_2 particles were prepared by using a heterogeneous nucleation process. Then, particle surface morphology and structure were examined by using SEM, EDS and XRD. Contact angle measurements were conducted by using a thin layer wicking technique and a sessile drop method in order to determine the surface free energy components of the bare and the coated MoS_2 particles. Our results showed the MoS_2 particles were successfully coated with an Al_2O_3 layer, which is an amorphous structure. The decreased water contact angle indicates an enhanced hydrophilicity for the coated particles. This decrease depends more strongly on a significant decrease of a new parameter ratio, γ^+/γ^-, than on a slight increase in total surface free energy. The surface energy component of the bare MoS_2 is very consistent with that of Talc, and that of the Al_2O_3-coated one is very similar to that of alumina, apart from the base component.

1. Introduction

The co-deposition of inert solid particles with electroless nickel based coating can produce a new generation of composite coatings [1]. Depending on the particles embedded, the coatings fall into two categories: One is wear-resistant coatings containing hard particles (such as SiO_2, Al_2O_3, SiC and diamond) [2–5], and the other is self-lubricating coatings containing soft particles(such as MoS_2, PTFE and graphite) [6–8]. The latter would be applied to spacecraft, guides for computers, silicone rubber molds, and vacuum and nuclear systems [9].

The excellent properties of composite coatings are highly dependent on a stable dispersion of fine particles in plating bath first, and then a good dispersion of them throughout coating matrix [10–12]. Currently, this purpose is realized by using surfactants [13]. Surfactants play a significant role in the incorporation of second phase particles [14–16], and it is even more so for water repellent materials, i.e., MoS_2 or PTFE particle, because they are hardly to be dispersed in plating bath without them. [17,18]. However, surfactants can influence both the stability of plating bath and the composition of coating. Firstly, the choice of appropriate surfactants is still not an easy task because unsuitable one would accelerate the decomposition of plating bath [19,20]. Secondly, the surface coverage of surfactant on substrate would result in a delay of coating formation due to the indirect contact of electrolyte with substrate [20]. In addition, the presence of surfactant in bath will decrease the amounts of nickel and phosphorus in coating matrix by hampering the reduction process of nickel ion [21,22].

Our previous work presents an inorganic coating on particles are more effective than surfactants in improving their dispersion in electroless nickel solution, and the resultant properties of composite coating are enhanced [23,24]. For example, compared to the Ni-P-MoS_2 composite coating fabricated in the present of surfactant, the Ni-P-MoS_2/Al_2O_3 one prepared without surfactant show a decrease by 49% in friction coefficient and increase by 15% in wear resistance [25]. Therefore, surface coating on particles, which has been successfully applied in many fields [26–28], is expected to displace surfactants. However, the surface properties of particles before and after coating are still not well documented. This requires the measurement of their surface free energy.

Surface free energy of a solid material can be calculated from contact angle rather than measured directly. On a flat and very smooth surface, contact angle is readily measured by sessile drop method [29]. However, this method is unsuitable for most powdered materials due to the existence of numerous pores [30], apart from some compressible materials, i.e., MoS_2, which can be compressed into disc sample to meet the

---

* Corresponding author.
E-mail address: meeywzhu@nuaa.edu.cn (Y. Zhu).

http://dx.doi.org/10.1016/j.powtec.2015.05.011
0032-5910/

requirements. Unfortunately, the same process tends to be irreproducible for the coated particles, because the coating layer might be destroyed under a very high pressure. This case will induce an inaccurate and unreliable result accordingly.

Among the methods of contact angle measurement for powdered materials, thin layer wicking method is a very promising technique, which has been successfully applied to all mineral materials [31–34]. This method is based on the phenomenon of a liquid penetration (wicking) into a solid porous layer deposited on a glass plate (microscope slide) and contact angle is then calculated from the Washburn's equation.

$$x^2 = \frac{Rt}{2\eta}\gamma_L \cos\theta \tag{1}$$

where x is the penetrated distance, R the effective radius instead of capillary radius for porous layer, t the penetration time of the distance x, η the liquid viscosity and γ_L the surface free energy of liquid. In Eq. (1), there are two unknowns, R and $\cos\theta$. Generally, R is determined by using a series of low-energy nonpolar liquids such as heptane, octane, decane and dodecane. They spread on the surface of s solid so that $\cos\theta = 1$, and a plot of $2\eta x^2/t$ versus γ_L yields a straight line with the slope yielding the value of R. Once R is determined, $\cos\theta$ can be obtained by using nonspreading liquids to wick through the thin layer.

Van Oss [35,36] proposed a new formulation of surface free energy, as well as a determination of energy components from contact angle. They consider the surface free energy as a sum of nonpolar Lifshitz-van der Waals and polar interactions for the first time.

$$\gamma_i^T = \gamma_i^{LW} + \gamma_i^{AB} = \gamma_i^{LW} + 2\left(\gamma_i^+\gamma_i^-\right)^{1/2} \tag{2}$$

where γ_i^{LW} is the nonpolar Lifshitz-van der Waals. Nonpolar interactions consist mainly of London dispersion interactions, but induction and orientation interactions may also participate. γ_i^{AB} is the polar interactions, which are entirely due to the hydrogen bonding in most systems and in the most general sense they are electron acceptor, γ_i^+, and electron donor, γ_i^-, interactions.

Total interfacial free energy interactions between solid(s) and liquid (l) can be written as

$$\gamma_{sl}^T = \gamma_s^T + \gamma_l^T - 2\left[\left(\gamma_s^{LW}\gamma_l^{LW}\right)^{1/2} + \left(\gamma_s^+\gamma_l^-\right)^{1/2} + \left(\gamma_s^-\gamma_l^+\right)^{1/2}\right] \tag{3}$$

Then, applying the Young equation, from Eqs. (2) and (3) one can obtain

$$\gamma_l^T(1 + cos\theta) = 2\left[\left(\gamma_s^{LW}\gamma_l^{LW}\right)^{1/2} + \left(\gamma_s^+\gamma_l^-\right)^{1/2} + \left(\gamma_s^-\gamma_l^+\right)^{1/2}\right] \tag{4}$$

To determine the surface free energy and its component parameters of a solid, contact angles of three different liquids for which nonpolar and polar components being known need to be measured. Then, these three Eqs. (4) can be solved simultaneously by using the measured contact angles.

This paper aims at determining the surface free energy and contact angle of pristine MoS_2 particles and the coated MoS_2 ones by using a thin layer wicking method. We choose the material of MoS_2 because it shows a good compressibility so that a sessile drop method can be feasible for comparison. We first prepared the Al_2O_3-coated MoS_2 particles by using a heterogeneous nucleation process. And then we measured the contact angle for two types of MoS_2 particles by using two methods, respectively. Lastly, we calculated and analyzed the surface free energy for both two types of particles under consideration.

2. Experimental

2.1. Preparation of coated MoS_2 particles

Samples of Al_2O_3-coated MoS_2 particles with a mass fraction of 25% Al_2O_3 were prepared by using a heterogeneous nucleation process, which is based on the precipitation of supersaturated metal hydroxide from aqueous solution in the presence of particles [37]. MoS_2 particles with a diameter of 3–5 μm (Shanghai Shenyu Company, China) and $Al(NO_3)_3 \cdot 6H_2O$ (AR) were used as starting materials. According to our previous work [23], MoS_2 powder were etched 30 min with 20%wt H_2SO_4 solution at 80 °C to eliminate the oxide on surface. Then, it was cleaned with deionized (DI) water by centrifuging several times until the solution reached the neutral pH. 3 g of MoS_2 powder was then thoroughly dispersed in 300 mL of the buffered solution composed of NaOAc and HOAc with pH = 4.5, and sonicated for 20 min. An aqueous solution of 0.2 M $Al(NO_3)_3$ was added dropwise to the MoS_2 suspension with vigorous stirring. During the process of precipitation, pH value was maintained at 4.5 ± 0.2. Later on, the precipitates were washed with DI water by centrifuging several times. Dried at 120 °C for 12 hours, calcined in air at 350 °C for 2 hours, Al_2O_3-coated MoS_2 samples were obtained.

2.2. Characterization of MoS_2 samples

Surface morphology of MoS_2 particles was observed with a SEM (Hitachi S-4800). Surface chemical composition was analyzed with an EDS (Bruker EDS QUANTAX). Coating structure was determined by using a XRD (X'Pert PRO) with Cu Ka radiation.

2.3. Contact angle by thin layer wicking

Thin layer wicking tests were performed on glass plates (25 × 75 mm), on which a suspension of MoS_2 powder was deposited. The suspension was prepared with 5.3 g of MoS_2 in 100 ml of DI water and 4 ml portions were pipetted onto the plate placed horizontally to obtain a uniform layer. After water evaporation the plate was dried at 120 °C for 2 h to remove any residual water. Thus, the plate adhered with a uniformed film of MoS_2 was obtained and then kept in a desiccator.

Wicking test apparatus is the same as that described in literature [38]. The plate was placed in a glass chamber in a horizontal position. The chamber's size is 120 × 60 × 15 mm and 1 cm sections were marked on the edges of top wall, so that penetration time for particular distance

Table 1
Origin, purity and properties (at 20 °C) of probe liquids used in this study [29,34].

Lquids	Origin and purity	γ^T (mJ/m^2)	γ^{LW} (mJ/m^2)	γ^{AB} (mJ/m^2)	γ^+ (mJ/m^2)	γ^- (mJ/m^2)	$\eta \times 10^{-3}$(Pa·s)
n-heptane	Kermel, AR, min. 99.5%	20.3	20.3	0	0	0	0.409
n-octane	Kermel, AR, min. 98.5%	21.6	21.6	0	0	0	0.542
n-decane	Aladdin, GC, min. 99.0%	23.8	23.8	0	0	0	0.907
Diiodomethane	Aladdin, GC, min. 98.0%	50.8	50.8	0	0	0	2.682
1-bromonaphthalene	Sinopharm,GR,min. 99.0%	44.4	44.4	0	0	0	4.890
Water	DI, 18.2Ω	72.8	21.8	51.0	25.5	25.5	1.000
Formamide	Sinopharm,AR,min. 99.5%	58.0	39.0	19.0	2.28	39.0	3.116
Ethylene glycol	Kermel, AR, min. 99.0%	48.0	29.0	19.0	1.92	47.0	19.900