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A STUDY OF SURFACE ADSORPTION ON SILVER POWDERS

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Abstract

DSC and TG-DTA techniques were used to investigate micro-sized silver powder particles and the adsorption of ethyl cellulose on these particles in a solution of ethyl acetate. The apparent specific heat of the silver particles was determined, and the kinetics of temperature-programmed desorption (TPD) of these adsorbed silver particles was investigated. Results show that the apparent specific heat and desorption kinetic parameters obtained by thermal analysis techniques could be used to characterize certain physico-chemical properties of such a particulate system.

Keywords: adsorption, apparent specific heat, desorption kinetics, silver powder

Introduction

The principal component of the silver pastes widely employed in microelectronic techniques is metallic silver powder. When other additives are kept constant, the dynamic properties and application performances of such a dispersed system are closely related to the physical characteristics of the particles in the system, e.g. particle size, size distribution, density, shape, etc. Determination of these physical properties has been described and discussed in many papers and monographs [1–5], among others adsorption-desorption techniques having been applied to investigate the whole particulate system for statistical characterization. In recent years, thermal analysis techniques have been used to achieve this goal [6, 7]. These techniques are convenient and rapid. A more important point is that such statistical characterization includes those macro properties that are not due to the addictive contributions from the characteristic of all the individual particles. Heller and Fischer [8] recently used DSC to investigate the differences in adsorption of ethyl cellulose on silver powder reduced by two technological methods. They showed that, if oxygen-bridges were formed on the silver surface by alkoxide or carboxylic links, there was strong adsorption of ethyl cellulose. Moreover, the formation of water during the reaction period facilitated the desorption process.

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In order to study the effect of the manufacturing technology on the final performance of the silver paste, DSC and simultaneous TG-DTA were used to determine the apparent specific heats of silver powders prepared under different technological conditions and to investigate their adsorption characteristics for ethyl cellulose in a solution of ethyl acetate. In this way, a testing method was established for characterization of the application performance of silver powder in the silver paste under appropriate conditions.

Experimental

Determination of apparent specific heat

Low-temperature DSC experiments were carried out with a Rigaku Thermoflex instrument. Al_2O_3 powder was used as the standard specimen to calibrate the specific heat; scanning rate, 10 deg·min^{-1}, temperature range, 40–200°C; sample mass, about 30 mg.

Superfine silver powders were produced by reduction of Ag_2CO_3 with formaldehyde. Samples were prepared from this material after thorough washing and drying near room temperature. A small amount of lubricating agent was added and the material was mechanically pressed into flakes under various technological conditions [9]. Surface shapes and average particle sizes of various silver powders of different preparations were observed and determined by using a JEM-2000EX transmission electron microscope with a magnifying power of 2000–10000 [10, 11].

TG-DTA

Adsorption treatment of the sample

In accordance with the application conditions, ethyl cellulose was chosen as the adsorbate for silver powder. The practical procedure is to dissolve chemically pure ethyl cellulose (from Nian-Sha Chemical Plant of Shanghai, lot 900430) in ethyl acetate (analytical reagent quality, First Reagent Factory of Shanghai, lot 851004), in order to make a solution with a concentration of 2.1 g/l. Various types of silver powder samples were separately added to suitable amounts of the above solution, stirred with a supersonic stirrer for 5 min, and then allowed to settle for 24 h. After adsorption, the silver powder was separated from the solution, and washed three times with analytically pure acetone to remove surplus adsorbate that was not truly chemically adsorbed. The washed silver powder was thoroughly dried in a desiccator at room temperature and was then ready for use as testing sample.

Surface pretreatment of silver powder

Superfine silver powder was used to investigate the effect of surface pretreatment on the adsorption. Procedures for pretreatment were as follows:

a) original state without any pretreatment;

b) heating to 300°C to evaporate small amounts of adhered impurities;

c) heating to 300°C and evacuation to about 1 Pa for further cleaning of the surface, followed by cooling to room temperature under vacuum;

d) washing three times with ethylene glycol at room temperature. Stirring with a supersonic stirrer for 5 min each time.

Determination of adsorption capacity and characteristic desorption temperature

Temperature-programmed desorption (TPD) experiments were carried out in the TG-DTA part of a Rigaku Thermoflex instrument. Experimental conditions: heating rate, 10 deg·min^{-1}; TG full scale, 1 mg; DTA full scale, ±25 μV; temperature full scale, 5 mV; sample mass about 30 mg; atmosphere, static air.

Kinetic analysis of desorption process

TG curves were analysed with the single curve formula of Doyle [12]. An IBM PC computer was used to calculate the activation energy E, reaction order n and pre-exponential factor A for the desorption processes of various samples, using a self-compiled software program [13].

Results and discussion

Apparent specific heat

Since micro-sized metallic powders display a much larger specific surface area than ordinary materials, these particulate systems possess a high surface energy. When the temperature of the system is increased, local sintering occurs between particles and the surface energy is partially released. When the size of the particles decreases below a certain value, this energy release can be perceived even at temperatures slightly above room temperature. On the other hand, strain energy can be present, formed during cold deformation. This energy is also released in a stepwise manner when the material is heated.

For the two reasons mentioned above, the specific heat determined by DSC in a 'dynamic' sense is certainly smaller than that measured by a static method. The specific heat thus obtained is called the 'apparent specific heat', to differentiate it from the true specific heat. The differences in apparent specific heat

Table 1 Results of determination of apparent specific heat C_p for various silver powders at different temperature θ (°C)

Curve number	Sample code	Shape, size*	$C_p=A+B\theta+C\theta^2$ ($J\cdot g^{-1}K^{-1}$)	Correlation coefficient
0	silver sheet	≠1 mm φ 3.5 mm	$A = 0.233$; $B = 6.323\times10^{-5}$; $C = -2.047\times10^{-8}$	0.9926
1	89-52-06	flake 17.1 μ	$A = 0.336$; $B = -1.804\times10^{-3}$; $C = 4.103\times10^{-6}$	0.9937
2	89-49-07	flake 3.2 μ	$A = 0.351$; $B = -2.127\times10^{-3}$; $C = 4.247\times10^{-6}$	0.9884
3	superfine	spherical 0.5 μ	$A = 0.247$; $B = -4.538\times10^{-4}$; $C = -5.375\times10^{-6}$	0.9930

* Average value determined by TEM

between different samples reflect the differences in particle size, size distribution, surface status and deformation effects. This is the reason why this parameter can be adopted to characterize such a particulate system.

Results determined for several samples are given in Table 1 and Fig. 1. It is seen from Fig. 1 that the apparent specific heats of the particulate systems are lower than that of silver sheet. In the former case, the apparent specific heat decreases with the particle size. As concerns the variation in apparent specific heat with temperature, flake-like powders (curves 1 and 2) behave differently from superfine powder (curve 3). This may be attributed to the small amounts of lubricant and other impurities in the sample.

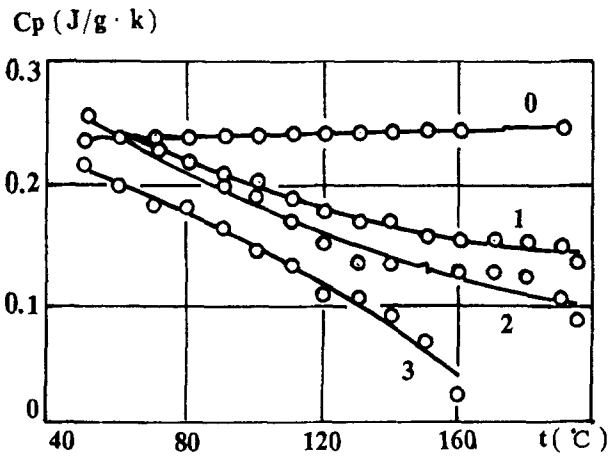

Fig. 1 Curves of apparent specific heat *vs.* temperature for various silver powders; 0 – silver sheet; 1 – 89-52-06; 2 – 89-49-07; 3 – superfine powder

Effect of surface pretreatment on adsorption characteristics

Figure 2 shows TG-DTA curves of desorption from superfine silver powder samples after different surface pretreatments. Results are given in Table 2.

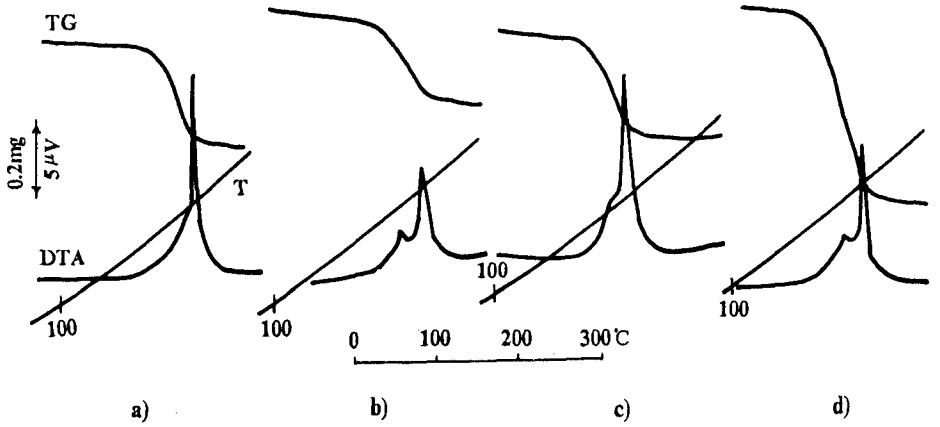

Fig. 2 TG-DTA curves of desorption from superfine silver powder after different surface pretreatments; a. original state; b. heated to 300°C; c. heated to 300 °C, evacuated and cooled; d. cleaned with ethylene glycol

It is seen from Fig. 2 that, regardless of the surface pretreatment, after the superfine silver powder has adsorbed ethyl cellulose, the desorption process is composed of two stages. Computer treatment [12, 13] of the four desorption TG curves showed that the reaction orders for the first stage are all 1 (the correlation coefficients R for the ln $F(a)$ *vs.* $1/T$ lines are more than 0.99). From the shape of the DTA desorption curve, it may be deduced that this stage corresponds to simple desorption of the adsorbate from the silver powder surface. In the second stage, however, vigorous oxidation occurs simultaneously with desorption. A similar desorption mechanism has already been discussed by Benard [3] and Heller and Fischer [8].

It is indicated in Table 2 that the activation energy of the first stage of the desorption process is higher when the silver powder surface is cleaner. This implies that the bond formed between the surface and the adsorbate should be stronger when the surface is cleaner. Examination of the variation in adsorption capacity with surface pretreatment reveals that, when the powder is heated to 300°C, the amount of adsorbent decreases significantly. This implies that some micro-sized particles are partly sintered, resulting in a decrease in specific surface area. When the several factors are taken into consideration, it may be concluded that, for the characterization of a metallic powder surface by relevant tests, the best surface pretreatment would be washing of the surface with a cleaning reagent such as ethylene glycol.

Table 2 Effects of different surface pretreatments on desorption from superfine silver powder

Method of pretreatment	Original state	Heated to 300°C	Heated, evacuated and cooled	Cleaned with ethylene glycol
Mass / mg	24.2	30.1	38.5	38.8
Ads. capacity / % wt	2.17	0.73	0.68	1.29
Desorption peak temp. / °C	243 *252	238 *264	229 *249	241 *266
Activation energy / $kJ \cdot mol^{-1}$	153 *278	184 *435	192 *300	190 *302
Reaction order	1 *2.0	1 *2.1	1 *2.2	1 *1.9
Pre-exponential factor / s^{-1}	7.0×10^{13} $*2.4\times10^{26}$	1.2×10^{17} $*3.9\times10^{32}$	4.5×10^{28} $*1.7\times10^{38}$	6.5×10^{17} $*1.5\times10^{28}$

Note: The desorption process is composed of two stages. * indicates the second stage

Kinetics of desorption

TG-DTA curves of TPD for silver powders of different types and different cold working conditions are shown in Fig. 3. Observed data and calculated kinetic parameters are listed in Table 3.

It is seen from the DTA curves in Fig. 3 that the shapes and temperatures of the desorption peaks for various types of silver powder exhibit marked differences. The desorption DTA peaks for superfine silver powders, obtained by the same method, but from different lots (the technological conditions may be different), likewise display obvious differences. This situation is more evident when they are processed into flaky powders. It is to be expected that the desorption peaks for flaky powders made from superfine silver powders, obtained by different methods, would show markedly different shapes (Fig. 4). However, the DTA desorption peaks for the processed flaky powder and the superfine silver powder from which the former was made, are more or less alike (see curves *a* and *b* in Fig. 3; 91-10-02 flaky powder is made from 91–10 superfine silver powder by mechanical processing). Therefore, it may be concluded that DTA desorption curves can be used to characterize some properties of a metallic powder. For specification, different adsorbates and different solvents may also

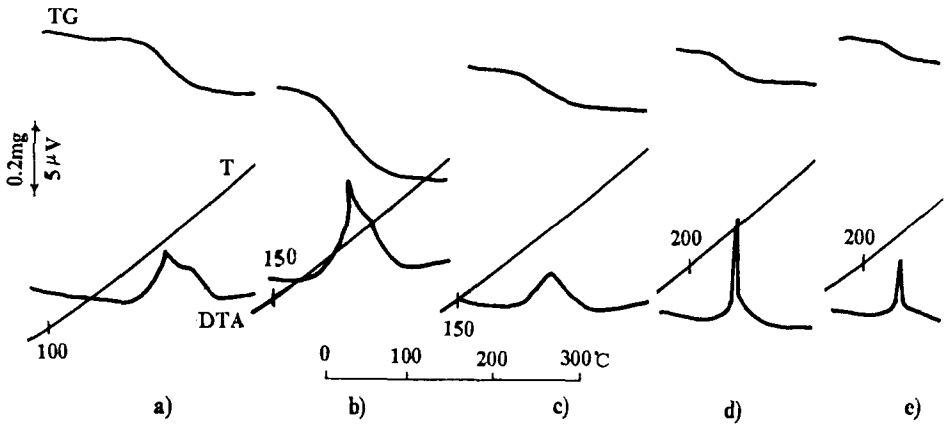

Fig. 3 TG-DTA curves of TPD for various silver powder; a. 91-10 superfine silver powder; b. 91-10-02 flake-like silver powder; c. 89-54-02 flake-like silver powder; d. 91-08-02 flake-like silver powder; e. 89-52-06 flake-like silver powder

Table 3 Adsorption capacity and kinetic parameters of the desorption process for various silver powders

	Sample code	Size / μm	Adsorption capacity/% wt	n	log A	E / kJ·mol^{-1}
Superfine	90-01	0.5	0.68	1.7	25.3	164
powder	91-10	1.0*	0.37	1.6	18.2	101
	91-10-02	3.1	0.60	1.5	18.1	99
Flaky	89-54-02	4.1	0.23	1.6	20.5	122
powder	91-08-02	4.4	0.21	1.8	24.2	158
	89-52-06	17.1	0.13	1.2	31.4	218

* Value determined by GC; measuring result by TEM: 0.3 μm

be used. In such cases, DTA curves would display entirely different shapes (cf. Fig. 5).

It is also apparent from Table 3 that the extent of adsorption and the desorption kinetic parameters (mainly the activation energy) exhibit some correlation with the silver powder particle size. For the same type of powder, whether superfine or processed flaky powder, it is seen that decrease of the particle size results in an increase in the adsorption capacity, but in a decrease in the desorption activation energy.

Conclusion

The present results reveal that some properties (e.g. particle size, surface morphology, etc.) of metallic silver powders in the silver pastes widely used in

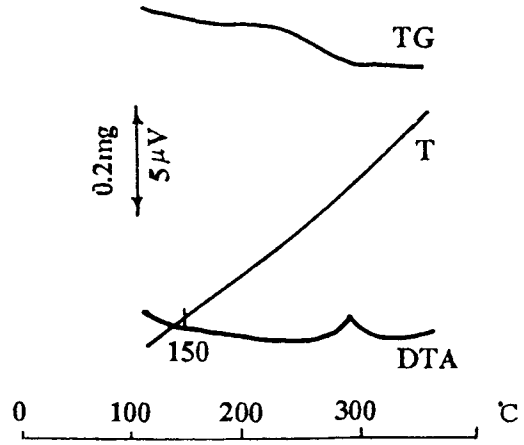

Fig. 4 Desorption TG-DTA curve for flake-like silver powder (90-02-01) obtained by mechanical processing from another type of superfine silver powder

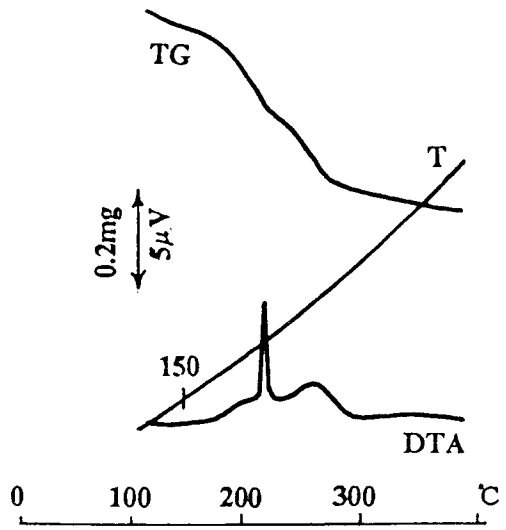

Fig. 5 Desorption TG-DTA curve for superfine silver powder (90---01) after adsorption of ethyl cellulose (terpineol)

micro-electronic techniques can be characterized by using thermal analysis methods to determine the apparent specific heat, adsorption capacity, desorption DTA peaks and kinetic parameters (mainly the activation energy). These methods are not only convenient and effective, but also avoid the tedious procedure of separate measurements on individual particles. They rather determine statistical characterization parameters for the whole particulate system.

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Zusammenfassung — Mittels DSC und TG-DTA wurden Mikro-Silberstaubpartikel und die Adsorption von Ethylcellulose an diesen Partikeln in Ethylacetatlösung untersucht. Es wurde die scheinbare spezifische Wärme der Silberpartikel ermittelt und die Kinetik der temperaturprogrammierten Desorption (TPD) dieser adsorbierten Silberpartikel untersucht. Die Resultate erweisen, daß die mittels Thermoanalyse ermittelten scheinbaren spezifischen Wärmewerte und Desorptionskinetikparameter zur Charakterisierung bestimmter physikalisch-chemischer Eigenschaften solcher Partikelsysteme geeignet sind.