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Influence of Size of Dispersed Silica Particles on Preparation of Thick Silica Films by Using Electrophoretic Sol–Gel Deposition

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Monodispersed silica particles, which ranged from 0.14 to 0.42 μm in diameter, were prepared by the sol–gel method. These particles were first separated from original sols, and dried, heat-treated, and then re-dispersed in a mixture of ethanol, water, and triethoxy(methyl)silane. Thick silica films without micro-cracks were formed by electrophoretic deposition of the particles on a stainless steel sheet in the re-dispersed sols. The weight of the silica films deposited was increased with increasing particle size at a given applied voltage. On the other hand, density of the films was increased with decreasing particle size. When the particle size was 0.32 μm in diameter, crack-free films of ca. 20 μm in thickness were prepared after heat treatment at 800 °C for 1 h.

The sol–gel method is an excellent procedure for thin oxide film coating.[1—3] However, the thickness of the films prepared by the conventional sol–gel coating is limited to less than 1 μm, although there are strong demands in practical applications to prepare sol–gel coating films thicker than a few μm. The electrophoretic deposition is well known as one of the useful procedures for thick film coating. This process has been applied to various fields: for example, ferroelectric materials,[4,5] superconductors,[6] micro-laminate ceramic composites,[7] and biomaterials.[8,9] We have developed "the electrophoretic sol–gel deposition," a procedure combining the electrophoretic deposition method with the sol–gel method to prepare thick silica films on metal sheets like anodized aluminum[10] and stainless steel.[11] However, our previous study found that some micro-cracks on the surface of the silica films deposited on a stainless steel sheet occurred when the electrophoretic sol–gel deposition was carried out directly using the sols originally prepared by hydrolysis of silicon alkoxides.[11] Such micro-cracks of the films might originate from the shrinkage of the particles as well as from a capillary force in the drying process.

Recently, we have prepared thick silica films by the electrophoresis of the particles separated from the original sols, heat-treated, and then re-dispersed in mixtures of ethanol, water, and triethoxy(methyl)silane (TEMS). It was found that the heat-treatment of such particles at around 600 °C for more than 12 h prevented the films obtained from cracking at the drying process.[12] The size of silica particles, which can be controlled by changing the concentration of sodium dodecyl sulfate (SDS),[13] is also expected to influence the prevention of cracks, thickness, and density of the films.

In the present study, monodispersed silica particles with various particle sizes were prepared by changing the amount of SDS. After the heat-treatment, the particles were re-dispersed in a mixture of ethanol and water with small amounts of TEMS. The electrophoretic sol–gel deposition of the particles was carried out on a stainless steel sheet to prepare thick silica films in the sol re-dispersed. This paper reports the influence of size of re-dispersed silica particles on the formation of thick silica films by electrophoretic sol–gel deposition.

Experimental

Preparation and Heat Treatment of Silica Particles. Silica particles were prepared by hydrolysis of tetraethoxysilane (TEOS) in the presence of sodium dodecyl sulfate (SDS). The starting materials except SDS are similar to those used for the preparation of monodispersed silica particles developed by Stöber, Fink, and Bohn;[14] the addition of SDS easily controlled the size of the monodispersed particles, as previously reported.[13]

Deionized and distilled water, unhydrous ethanol (EtOH), and reagent grade chemicals of TEOS, aqueous ammonia, and SDS (Wako Pure Chemical Industries, Ltd.) were used as starting materials. SDS dissolved in 0.5 mol dm^{-3} aqueous ammonia and TEOS were diluted separately with the same amount of EtOH. The two solutions were mixed and then stirred at 25 °C for 10 h. The mole ratio of TEOS/H_2O/EtOH was fixed to be 0.2/10/10. The concentration of SDS added was 0.01—0.075 mass% against the total weight of the sols (1 kg). The particles collected by centrifugation were washed by EtOH in the re-dispersion-centrifugation procedure three times, and then dried in vacuo at room temperature for 3 h. Heat treatment of the particles prepared were carried out in air at 600 °C for 12 h.

Preparation of Thick Films. The pH of water was adjusted to be 11.7 by adding aqueous ammonia. The particles after heat treatment were re-dispersed in the mixture of H_2O (pH = 11.7) and EtOH by ultrasonication. Triethoxy(methyl)silane (TEMS) (Shin-Etsu Chemical Co., Ltd.) diluted with EtOH was mixed with the re-dispersed sol and then the mixture was stirred for 1 h at 25 °C. The mole ratio of TEMS/H_2O/EtOH was fixed to be 0.2/10/10. The amount of silica particles was 0.7 g against the total weight of the sols (70 g). Electrophoretic deposition of silica films on the stainless steel sheet (SUS430) was carried out in the manner reported previously.[12] The films after drying were heat-treated at

800 °C for 1 h after drying at room temperature and pre-heated at 400 °C for 1 h in air.

Characterization of the Particles and the Films. Densities of the particles were determined by using a picnometer. Zeta potentials of the particles in water were measured by a laser Doppler system (Malvern Zetamaster). The pH of dispersed phase for the measurement of zeta potentials was adjusted by adding HNO_3 and KOH.

The weight of coating films on a stainless steel sheet was measured with a microbalance (Mettler M5SA). A scanning electron microscope (SEM) (JEOL JSM-5300) was used for the observation of particles and films deposited. It was also used for the estimation of the film thickness. The density of the films was estimated from the film thickness and the weight deposited.

Results and Discussion

Table 1 lists the contents of SDS added and the average sizes in diameter and geometrical standard deviations (σ_g) of silica particles heat-treated at 600 °C for 12 h. The particle size is increased with an increase in the amount of SDS added. All the particles have narrow size distributions (σ_g ranging from 1.04 to 1.09) at any concentration of SDS. The increase of particle size with an increase of the content of SDS must be caused by the coalescence of the particles, which was already reported in our previous paper to be induced by the addition of SDS in earlier reaction period of the particles.[13]

Figure 1 shows the weights of silica films prepared by the electrophoretic sol–gel deposition as a function of applied voltage. The period during which voltage was applied was fixed to be 5 min. The weights of the films are increased with an increase in the applied voltage for any particle size. When 10 to 50 V is applied, the weight deposited is increased with an increase in the particle size and finally saturated at the particle size of 0.3 μm in diameter.

Figure 2 shows the zeta potentials of the silica particles with various sizes. The isoelectric points (IEP) of the particles are around 3 in any case. When pH is larger than IEP, the negative values of zeta potential of the particles are increased from 0 to −70 mV with an increase in the pH value. Ogino et al. have reported that the mobility of silica particles modified with alumina was increased with an increase of the particle size.[15] In the present study, at a given pH value in a basic region, the negative value of zeta potential is increased with an increase in the particle size, which is caused by the fact that each larger particle with larger surface area has a greater number of deprotonated silanol groups (Si–O^-) on the surface than that of smaller particles. Ogino et al. have also pointed out that the increase of mobility of the particles with increasing particle size was in accordance with Henry's theory.[15] The large deposited weight observed in case of large particle size shown in Fig. 1 is thus caused by the larger charge of the particles, because the negative zeta potential of the particles was increased with an increase in the particle

Table 1. Size and Geometrical Standard Deviation (σ_g) of Silica Particles after Heat-Treated at 600 °C for 12 h

SDS/mass%	Particle size/μm	σ_g
0.01	0.14	1.09
0.02	0.17	1.07
0.05	0.32	1.05
0.075	0.42	1.04

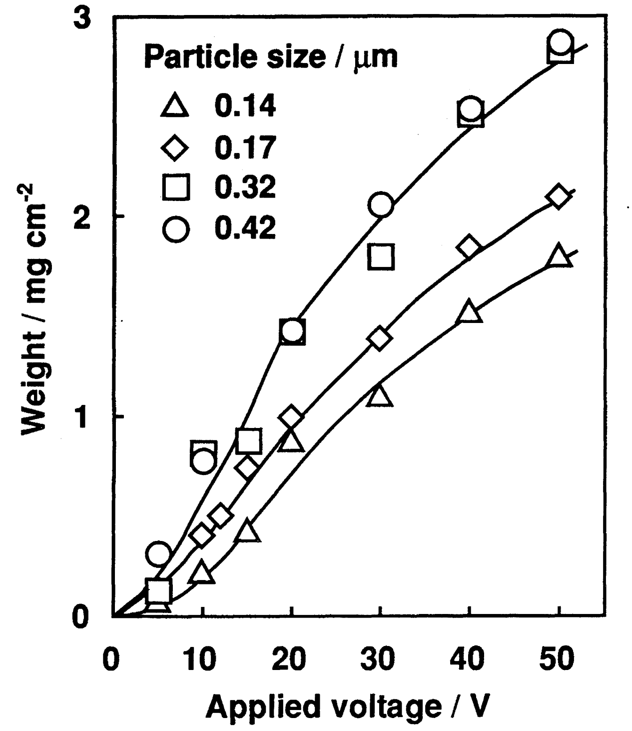

Fig. 1. Weights of silica films deposited as a function of applied voltage.

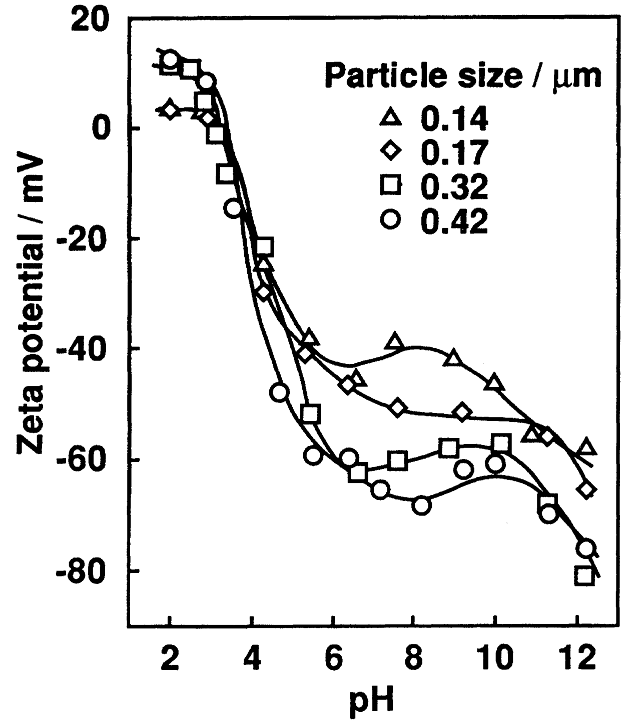

Fig. 2. Zeta potential of silica particles with various particle diameters.

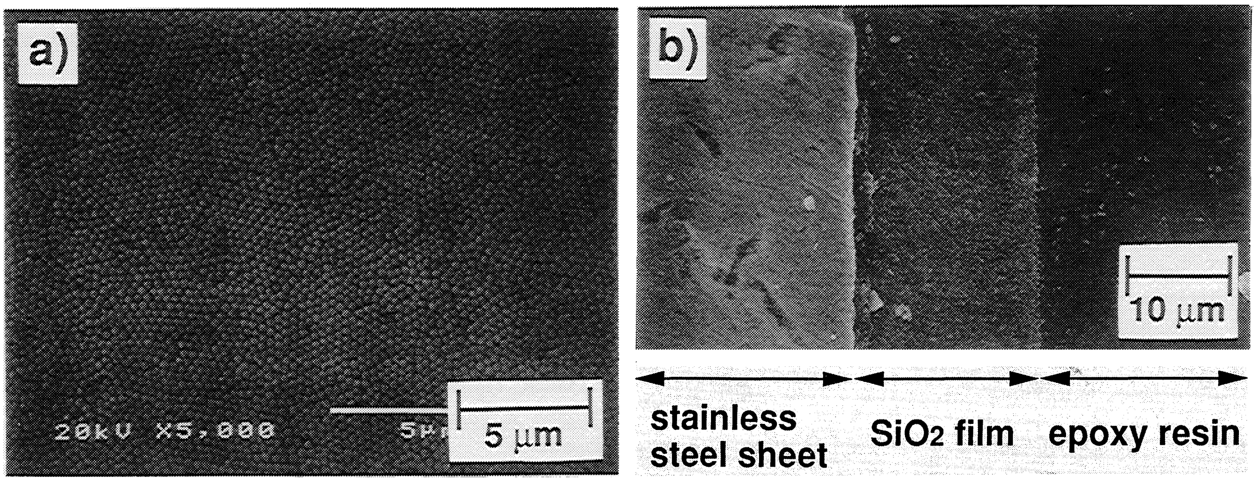

Fig. 3. SEM photographs of the surface (a) and the cross section (b) of the heat-treated thick silica film. The size of the particles used for the electrophoresis is 0.32 μm in diameter. The film was prepared by an applied voltage of 60 V for 5 min and heat-treated at 800 °C for 1 h in air after pre-heating at 400 °C for 1 h.

size.

Table 2 lists the densities of the silica particles (0.17, 0.32, and 0.42 μm in diameter) heat-treated at 600 °C for 12 h and those of as-deposited films prepared by the electrophoretic deposition of the heat-treated particles. To compare the densities of the films prepared using silica particles with different sizes, the thickness of the films was controlled to be ca. 10 μm by changing the applied period at a fixed applied voltage of 30 V. The films (with 10 μm in thickness) prepared by the particles larger than 0.17 μm in diameter were free from cracks. However, some micro-cracks were observed in the films constructed by the smaller particles (0.14 μm in diameter).

The density of all the particles heat-treated is as high as 2.2 $\mathrm{g\,cm^{-3}}$ independent of the particle size. This value of density of the particles is really the same as that of fused silica.[16] The density of the corresponding films becomes larger with a decrease in the particle size, and it is noteworthy that the value agrees with that of the particles, 2.2 $\mathrm{g\,cm^{-3}}$ within the accuracy of the measurement, when the diameter of the particles is 0.17 μm. If the silica spheres with density of 2.2 $\mathrm{g\,cm^{-3}}$ in the film are packed with the packing fraction of 74%; i.e. the fraction of the closest packing, the film density becomes 1.6 $\mathrm{g\,cm^{-3}}$. The densities of the prepared films using the particles with 0.17 and 0.32 μm in diameter are larger than this value of the closest packing. In fact, the particles would be swelled by re-dispersion in basic disperse medium. The swelled particles deposited on the sheet by the electrophoresis are distorted and void space among interparticles in the films decreases. The swelled particles in the films will contract in the drying process and then thick silica films with high density were obtained. The void space much decreases with a decrease in particle size, because the extent of swelling of smaller particles must be greater than that of larger particles. Therefore, the density of the film was increased with a decrease of particle size, although all the particles have the same density before re-dispersion.

Table 2. Density of the Silica Particles and Films

Particle size/μm	Density/$\mathrm{g\,cm^{-3}}$	
	Particle	Film
0.17	2.2	2.2
0.32	2.2	1.8
0.42	2.2	1.6

Figure 3(a) shows a SEM photograph of the surface of the heat-treated film. The film was prepared using the particles with 0.32 μm in diameter under an applied voltage of 60 V for 5 min. Heat treatment of the film was carried out at 800 °C for 1 h after being pre-heated at 400 °C for 1 h. The particles as constituents of the film are closely packed and no cracks are observed on the surface of the film. Figure 3(b) shows a SEM photograph of the cross section of the same film. The photograph is composed of three parts: stainless steel sheet, silica film, and epoxy resin for embedding the film. Thickness of the film is ca. 20 μm. The density of the film estimated by the film thickness and the weight of the deposited film was 1.8 $\mathrm{g\,cm^{-3}}$. When the particle size was smaller than 0.2 μm, the crack-free films thicker than 10 μm after heat treatment were difficult to obtain. On the other hand, thick films of ca. 20 μm in thickness with no cracks were prepared by use of the particles with 0.32 μm in diameter, as shown in Fig. 3. These films exhibited fairly high density and high adhesion to the stainless steel sheet.

Conclusions

Thick silica films of ca. 20 μm in thickness with no cracks and high density were prepared on a stainless steel sheet by electrophoretic sol–gel deposition of silica particles separated from the sol prepared and heat-treated before the re-dispersion. The negative zeta potential of silica particles was increased with an increase in the particle size at a given pH value in basic condition. The weight of the films deposited was increased with increasing particle size when a given voltage from 10 to 50 V is applied for 5 min, and finally saturated at the particle size of 0.3 μm in diameter.

References

1) S. Sakka, *J. Sol–Gel Sci. Technol.*, **2**, 451 (1994).

2) C. J. Brinker, A. J. Hurd, G. C. Frye, P. R. Schunk, and C. S. Ashley, *Seramikkusu Ronbunshi*, **99**, 862 (1991).

3) C. J. Brinker, A. J. Hurd, P. R. Schunk, G. C. Frye, and C. S. Ashley, *J. Non-Cryst. Solids*, **147&148**, 424 (1992).

4) S. Sugiyama, A. Takagi, and K. Tsuzuki, *Jpn. J. Appl. Phys.*, **30**, 2170 (1991).

5) M. Nagai, K. Yamashita, T. Umegaki, and Y. Takuma, *J. Am. Ceram. Soc.*, **76**, 253 (1993).

6) H. Nojima, H. Shintaku, M. Nagata, and M. Koba, *Jpn. J. Appl. Phys.*, **30**, L1166 (1991).

7) P. S. Nicholson, P. Sarkar, and X. Haung, *J. Mater. Sci.*, **28**, 6274 (1993).

8) M. Shirkhanzadeh, *J. Mater. Sci. Lett.*, **10**, 1415 (1991).

9) X. Ding, K. Yamashita, and T. Umegaki, *J. Ceram. Soc. Jpn.*, **103**, 867 (1995) (in Japanese).

10) K. Kishida, M. Tatsumisago, and T. Minami, *J. Ceram. Soc. Jpn.*, **102**, 336 (1994).

11) H. Nishimori, M. Tatsumisago, and T. Minami, *J. Ceram. Soc. Jpn.*, **103**, 78 (1995).

12) H. Nishimori, M. Tatsumisago, and T. Minami, *J. Mater. Sci.*, in press.

13) H. Nishimori, M. Tatsumisago, and T. Minami, *J. Ceram. Soc. Jpn.*, **103**, 743 (1995).

14) W. Stöber, A. Fink, and E. Bohn, *J. Colloid Interface Sci.*, **26**, 62 (1968).

15) K. Ogino, I. Kuronuma, Y. Nishimura, and H. Takahashi, *Nippon Kagaku Kaishi* (*J. Chem. Soc. Jpn.*), **1978**, 462 (in Japanese).

16) R. K. Iler, "The Chemistry of Silica," Wiley & Sons, New York (1979), p. 328.