Deposition of silica thin film on the surface of powder by PCVD under atmospheric pressure

Tatsuya Mori, Sachiko Okazaki, Tadaaki Inomata and
Masuhiro Kogoma

Department of Chemistry, Sophia University
7-1 Kioi-cho Chiyoda-ku Tokyo 102

Abstract

Silica coating was formed on the surface of Fe_2O_3 particles by a wet method which first hydrolyzes TEOS and then which is oxidized the hydrolyzed TEOS completely by plasma treatment with O_2 and by dry method which mixes TEOS vapor into reactor and forms a silica film directly by PCVD in atmospheric pressure(1)(2). $Fe(OH)_3$ particles were coated by the dry method, but only a part of the particles was oxidized. The treated powder was characterized by XPS, SEM, z-potential, dispersibility and pH measurement. The oxidation speed of TEOS increased when N_2O was used instead of O_2 as the oxidant material.

1. Introduction

For many kinds of cosmetics, solving the skin irritation problem which arises from using inorganic powder pigment is strongly desired. To solve this problem, it is more desirable to deposit a silica thin film, which has chemical stability and doesn't spoil the tones of the pigment owing to its colorless transparency. In this work , silica film was formed uniformly on the surface of particles with an atmospheric pressure glow plasma. A silica coating was formed by a method which first hydrolyzes TEOS and then which oxidizes hydrolyzed TEOS completely by plasma treatment with O_2. Fe_2O_3 (red) powder was used as the specimen. XPS analysis showed that plasma treated powder was oxidized more than powder which was only hydrolyzed by TEOS. We tried a dry method which mixed TEOS vapor into a reactor and formed silica film directly on the surface of particles. This dry method is faster than the wet method. O_2 or N_2O was used for oxidation of plasma. Silica coating was characterized by XPS, SEM, dispersibility test, pH measurements and z-potential measurements. After the forming of silica thin film was confirmed, we tried to deposit silica film with $Fe(OH)_3$ (black) by a dry method. But the treated powder had a slight change of color, from black to red-brown, so we could imagine that $Fe(OH)_3$ was oxidized. The result of

characterization of $Fe(OH)_3$ with XPS indicated that silica film was formed, but only a small part of the particles was oxidized.

2. Experimental Materials and Methods

Helium used for discharge and fluidization of powder was 99.9999%. O_2 (99.99%) or N_2O (99.99%) was used for oxidation. $(C_2H_5O)_4Si$ (TEOS) including 5 vol.% silicon was heated at 140 ~ 150 ℃ in an oil bath and mixed with He by bubbling. Grain sizes of Fe_2O_3 and $Fe(OH)_3$ sample powder were 80 ~ 200 nm. Coating was performed by wet method and dry method. The wet method is a method which first hydrolyzes TEOS in a liquid phase and then which performs dry oxidation by plasma treatment with O_2 to the hydrolyzed TEOS. The dry method is a method which first mixes TEOS vapor into reactor and then which performs directly full dry coating on the surface of powder by PCVD.

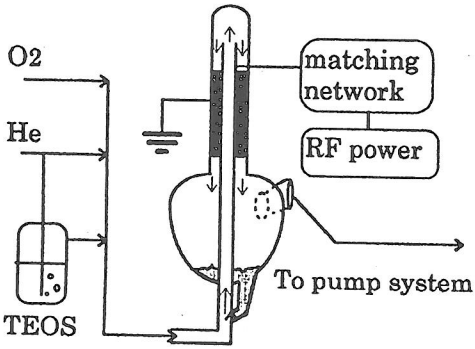

Figure 1. Diagram of the deposition equipment.

The procedure to hydrolyze TEOS is as follows. TEOS including 2 vol.% sili-

Table 1

Condition of treatment

Sample No.	Flow rate He /dm^3min^{-1}	Flow rate O_2 /cm^3min^{-1}	Flow rate N_2O /cm^3min^{-1}	TEOS /g	Power /W	Time /min
1 (Fe_2O_3,wet)			Only hydrolyzed TEOS			
2 (Fe_2O_3,wet)	1.5	4.3	-	-	50	15
3 (Fe_2O_3,dry)			Untreated			
4 (Fe_2O_3,dry)	1.5	10	-	1.06	80	60
5 (Fe_2O_3,dry)	1.5	17	-	0.95	80	60
6 (Fe_2O_3,dry)	1.5	35.2	-	2.04	300	120
7 (Fe_2O_3,dry)	1.5	-	27.6	0.71	300	30
8 (Fe_2O_3,dry)	1.5	-	27.6	0.89	300	60
9 ($Fe(OH)_3$,dry)			Untreated			
10 ($Fe(OH)_3$,dry)	1.5	-	27.6	0.45	300	30
*11 ($Fe(OH)_3$,dry)	1.5	-	27.6	0.36	150	30

No. 1~5 used a tungsten stick electrode.

No. 6~11 used a stainless tube electrode.

Only *11 used 100 kHz. Others used RF (13.56 MHz).

con was added to 50 ℃ water. Fe_2O_3 was added to this solution until the ratio of Fe_2O_3 to H_2O was 0.35 to 1. The mixture was reacted with occasional shaking at room temperature during 7 days, until the color of the solution was uniform. The solution was dried at 80 ℃ for evaporation of ethanol during 3 hours and then heated in an oven during a few minutes.

A diagram of the deposition equipment and discharge electrode is shown in Fig. 1, 2a, 2b. Used electrodes were two types of tungsten stick electrodes and a stainless tube electrode. The reactor is a Pyrex double tube 320 mm high which consists of an inner tube 6 mm in diameter and an outside tube 18 mm in diameter. A tungsten stick 1 mm in diameter hangs inside of the inner tube and a stainless tube 8 mm in diameter hangs outside of the inner tube as high voltage electrode. An outside tube whose exterior was wound with copper 6 mm wide in a spiral was used as an earth electrode corresponding with the tungsten electrode. The outside tube whose exterior was wound with stainless mesh was used as an earth electrode corresponding with the stainless electrode.

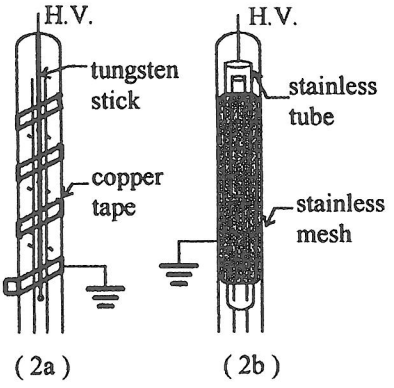

Figure 2
Electrodes of a tungsten stick electrode and a stainless tube electrode.

After we first decreased pressure to 0.1 torr and then purged the system with He, plasma was generated with RF 13.56 MHz power at atmospheric pressure. Powder was blown up inside an inner tube with the mixed gas and was coated when powder dropped between the stainless tube and the outside tube. Conditions of treatment are

Table 2
The existing ratio of elements on the surface of powder with XPS.

Sample No.	C/%	O/%	Fe/%	Si/%	-OH/%	=O/%
1 (Fe_2O_3 , wet)	25.9	56.2	10.6	7.4	Hydrolyzed TEOS	
2 (Fe_2O_3 , wet)	22.2	57.6	10.3	9.9	-	-
3 (Fe_2O_3 untreated)	16.5	66.0	17.5	0	-	-
4 (Fe_2O_3 , dry)	21.1	61.2	16.1	1.7	-	-
5 (Fe_2O_3 , dry)	9.9	64.1	24.2	1.9	-	-
6 (Fe_2O_3 , dry)	7.9	74.8	12.1	5.2	-	-
7 (Fe_2O_3 , dry)	12.5	71.2	13.5	2.8	-	-
8 (Fe_2O_3 , dry)	6.3	73.9	15.2	4.6	-	-
9 ($Fe(OH)_3$ untreated)	32.2	55.9	13.2	0	90.1	9.9
10 ($Fe(OH)_3$, dry)	11.2	70.2	14.2	4.4	70.4	29.6
11 ($Fe(OH)_3$, dry)	10.3	67.4	14.3	8.0	73.5	26.5

shown in Table 1. The silica film was characterized with high resolution SEM and XPS . In dispersibility test, after powder (0.2~0.3g) was dissolved in purified water (50 ml) with a ultrasonic wave, the solution was left in air for 4 days. We measured z-potentials of the untreated Fe_2O_3 and the treated Fe_2O_3 by the wet method and the pH of solution when powders (0.1g) of the untreated Fe_2O_3 and the treated Fe_2O_3 by the wet method were dissolved in purified water (50 ml).

3. Results and discussion

3.1 Appreciation of the treated Fe_2O_3 by wet method

The result with XPS is shown in Table 2. In the treated Fe_2O_3 by wet method, oxidation of dry plasma with O_2 decreased the existing ratio of carbon more than only hydrolysis of TEOS. Carbon was oxidized by plasma with O_2. But still about 20 % carbon at the existing ratio was left. So in the case of wet the complete oxidization of the carbon in the thin film is expected to be difficult. The results of dispersibility test showed that, after 4 days, the treated powder kept fine dispersibility but the untreated powder completely agglutinated.

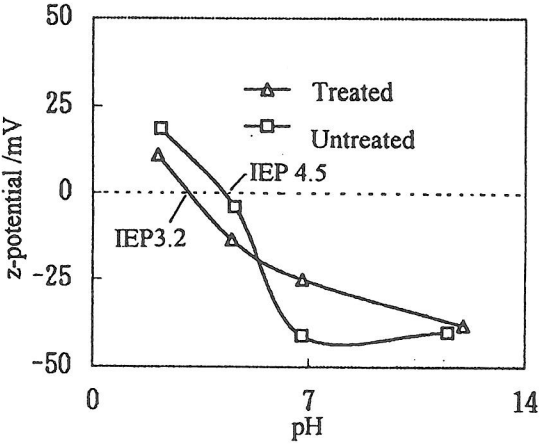

Figure 3. z-potential of Fe_2O_3 powder (untreated and treated by wet method).

The z-potential measurements of the powder, after the plasma deposition, showed that the isoelectric point was changed from pH 4.5 to pH 3.2, which had good agreement with the known value of the silica surface in Fig. 3. The improvement of the dispersibility will be attributed to this important shift of isoelectric point: the pH value of the neutral pure water (50 ml) was changed from pH 6.6 to pH 6.8. Fe_2O_3 powder is manufactured with decomposition of heat. If the decomposition of heat isn't completely performed, sulfuric acid remains in the Fe_2O_3 particle. So to change pH is because the silica film coats sulfuric acid which was left in Fe_2O_3 particle owing to incomplete decomposition of heat.

3.2 Appreciation of the treated Fe_2O_3 by dry method

Figure 4 is a SEM micrograph of Fe_2O_3 particles treated by dry method. In the

result of analysis with XPS, the dry method which used tungsten stick electrode didn't show a clear Si peak. So we used a stainless tube electrode which extended the area of the electrode, adding more discharge power. The existing ratio of Si in 300w changed from 2% to 5%. With increasing the existing ratio of Si , also the existing ratio of O atoms increased. This is because of forming SiO_2. The existing ratio of carbon was about 10 %. The dry method oxidized carbon more than the wet method. But it could not oxidize completely carbon. The result of dispersibility test showed that, after 4 days, the treated powder kept fine dispersibility but the untreated powder completely agglutinated.

With TEOS /N_2O mixture in a dry method of Fe_2O_3, the deposition rate is more than twice that of the TEOS/O_2 mixture. The bond dissociation energy of N_2O is weaker than that of O_2. The bond energy is 119.2 kpm for O_2 and 40 kpm for N_2O. So the concentration of O atoms in the TEOS/N_2O plasma must be higher than in the TEOS/O_2 plasma.

3.3 Appreciation of the treated $Fe(OH)_3$ by dry method

A SEM micrograph of $Fe(OH)_3$ particle treated by dry methods is shown in Fig. 5. We could confirm the existence of Si on the surface of $Fe(OH)_3$ particles by XPS but, after discharge, the color of powder changed from black to red-brown by oxidation. Tab. 2 shows a ratio of hydroxyl group (-OH) and double bond of O_2 (=O) from oxygen peak. The rate of hydroxyl groups decreased from 90% to 70%. We discharged by 100 kHz-100 w instead of RF (13.56 MHz) power but oxidation was not restrained. This may be because heat of discharge gathered in the reactor, so we will need to fit a water-cooling fixture up near the electrode.

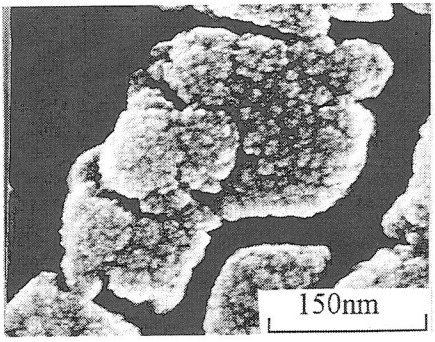

Figure 4. A SEM micrograph of Fe_2O_3 particle treated by dry method.

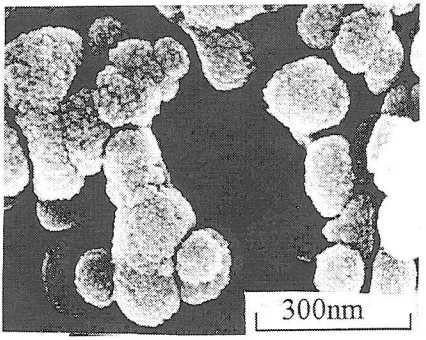

Figure 5. A SEM micrograph of $Fe(OH)_3$ particle treated by dry method.

4 Acknowledgment

We thank Mr. A.Takeda of ISI Corp. for helpful discussions and preparation of

sample by wet coating method.

5 References

(1) S.Kanazawa et.al.,J.Phys.D:Appl.Phys, 21,238(1988)
(2) T. Yokoyama et.al.,J.Phys.D:Appl.Phys, 23,374,(1990)