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Surface Modification of Molding Silica Gel Using Dielectric Barrier Discharge

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In order to lower the reproduction cost of molding silica gel used for dehumidifier, a surface treatment of the molding silica gel was performed using an optimized dielectric barrier discharge in CF_4 atmosphere. After the surface treatment, the surface characterizations such as fluorine content and endothermic reactions were carried out. The results showed that the optimized dielectric barrier discharged plasma could effectively modify the surface of molding silica gel and achieve replacement of -OH groups by $-CF_n$ or -F groups. It was also found that the endothermic reaction on the plasma-treated molding silica gel shifted to the low temperature side and its property was maintained even after the reproduction use at least 3 times.

Key words: silica gel, molding silica gel, surface treatment, dielectric barrier discharge

1. INTRODUCTION

Silica gel made up of micro-pore works as an excellent adsorption material and therefore molding silica gels are widely applied to dehumidifiers. However, in such dehumidifiers, it is desired to lower the operation cost including the reproduction cost of the molding silica gels. When the molding silica gel is reproduced after use, a large electric power for the heating processes is demanded. Water molecules adsorbed by a weak Van der Waals interaction between the adsorbed molecules on silica gel begin to be dehydrated at around 50℃. In contrast, the heating process carried out at elevated temperature around 150℃ is necessary to dehydrate water molecules formed by a strong chemical adsorption between the silica gel surface (-OH groups) and water molecules. Therefore, a heating system which is possible to generate the hot wind of approximately 150℃ is generally equipped in the dehumidifier. If there is a molding silica gel that can be reproduced at lower temperature, the operating cost of the dehumidifier will become low. In order to lower the temperature for the reproduction, it is necessary to change the surface characteristics of the molding silica gel.

In a previous report [1], as a basic study, we performed surface treatments of powdery silica gels using a dielectric barrier discharge in CF_4 atmosphere. The results showed that the dielectric barrier discharge could form a low energy surface by introduction of $-CF_n$ (n=1-3) or -F groups on the surface of silica gel. It was also found that the endothermic reaction on silica gel obtained by a brief surface treatment was located at the low temperature side in comparison with those obtained using a radio-frequency (rf) plasma [2-4]. Thus, we showed that the surface treatment technique using the dielectric barrier discharge was a powerful technique for preparing the low energy surface on the powdery silica gel. However, it was not clear whether the dielectric barrier discharge could be applied to the surface treatment of the molding silica gel or not. The molding silica gel has a three dimensional and complex structure. On the other hand, the dielectric barrier discharge used for the surface treatment of the powdery silica gel was generated by a parallel electrode system where the powdery silica gels were inserted between an electrode (upper electrode) and a dielectric layer made of quartz glass. Therefore, in the case where the conventional dielectric barrier discharge source is applied to the surface treatment of the molding silica gel, the only partial fractions opposite to the upper electrode are modified. The inner surface of the molding silica gel, in which the dielectric barrier discharge is never generated, is not modified.

In this study, we first constructed a new dielectric barrier discharge device that performs a superior surface treatment of the molding silica gel. Using the optimized dielectric barrier discharge source, the surface treatments of molding silica gels were performed for 5, 10, 20 and 30min. The surface characterizations such as fluorine content and endothermic reactions were carried out using an energy dispersive X-ray (EDX) and a differential scanning calorimeter (DSC), respectively. Finally, it was discussed how long the formed low energy surface could be maintained.

2. EXPERIMENTS AND METHODS

Figure 1 shows the structure of the molding silica gel used in the typical dehumidifier. The molding silica gel obtained from Seibu-Giken Corporation is made up of powdery silica gels whose particle diameters are from 0.07 to 0.14 mm and alumina (Al_2O_3) as filler, and is constructed from a number of pieces with a semi-cylindrical shape. As mentioned in Sec. 1, in the case where a conventional dielectric barrier discharge source is applied to the surface treatment, the only top fractions of the molding silica gel inserted between an upper electrode and a dielectric layer are modified. The inner surface and the inclined plane of the semi-cylinder can't be modified.

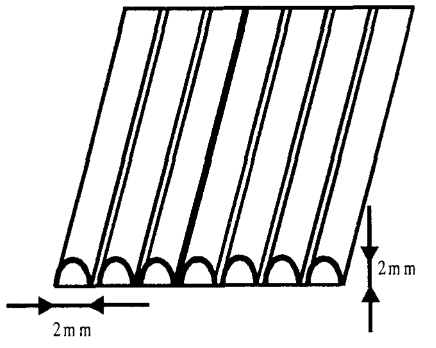

Fig. 1 Structure of molding silica gel.

An optimized surface treatment system is shown in Fig. 2. A molding silica gel with a width of 40mm and 65mm in length was inserted between two quartz glass disks sandwiched between two electrodes made of stainless steel with a diameter of 70mm. Each quartz glass had a thickness of 1mm and a diameter of 100mm. Two electrodes were earthed and cooled by passing the cooling water of around 13℃ through the inside of them. A rod shaped electrode made of stainless steel with a diameter of 1mm and 80mm in length was used for applying high voltage. As shown in Fig.2, the rod shaped electrodes were arranged at the inner side and the inclined plane of the semi-cylinder. Here, it is noted that the molding silica gel is a dielectric material together with the quartz glass. The presence of the dielectric materials leads to the formation of a large number of short-lived micro-discharges [5-6]. An accumulation of charge starts in the area where the micro-discharge reaches the dielectric material. This leads to the reduction of the electric field in a discharge gap, and therefore the discharge is choked. In our optimized dielectric barrier discharge source, a number of short-lived micro- discharges are produced at narrow gap regions formed between the rod shaped electrode, the surface of molding silica gel and the surface of quartz glass disk.

The dielectric barrier discharge was operated applying the pseudo sinusoidal wave of which maximum value was 7kV and frequency was around 8kHz. CF_4 gas (99.99%) controlled by a mass flow controller entered into the chamber from the upper side of the chamber, in which a flow rate was kept at 1.2l/min. All experiments reported here were made under atmospheric pressure. The discharge voltage was measured using a high voltage probe, and the measurement of the discharge current was carried out using a Rogowski coil. The discharge power was obtained by integration of the product of discharge voltage and discharge current for a period of pseudo sinusoidal wave.

After the plasma surface treatments for 5, 10, 20 and 30 min, the surface characterizations of the molding silica gels were performed. The existence of the treated fluorine on the molding silica gel was evaluated using EDX (EDAX DX-4 spectrometer, Philips). The endothermic character of the treated surface was investigated using DSC. In this measurement, water vapor was first adsorbed on the treated molding silica gel surface and thereafter the pulverized silica gels of 15mg in weight were sampled for the respective DSC measurements.

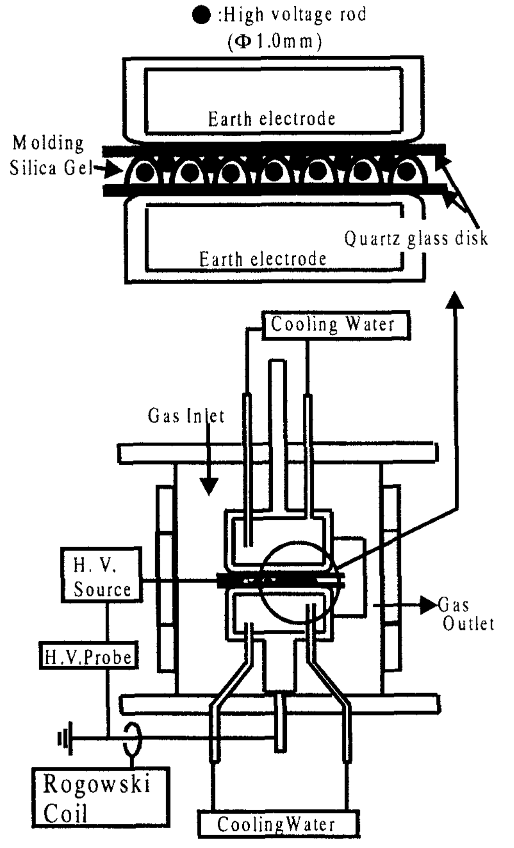

Fig. 2 Schematic diagram of experimental apparatus.

3. RESULTS AND DISCUSSIONS

Figure 3 shows waveforms of discharge voltage and discharge current in dielectric barrier discharge in CF_4 atmosphere. When the discharge voltage was 7kV, the obtained current value and the discharge power were much higher than those obtained in a previous surface treatment using a conventional dielectric barrier discharge source [1]. Therefore, in order to adjust the discharge power to a previous power value of 15W, the discharge voltage was set to 5.5kV, which allow us to compare the treatment ability using an optimized discharge source with that using a conventional discharge source. As can be seen from Fig. 3, the discharge current consists of the displacement current due to capacitance of dielectric materials and current pulses brought by the short lived micro-discharges. This indicates that the micro-discharge formation is terminated within an extremely short time (~10ns) and therefore a thermal equilibrium is not achieved. Thus, even on the optimized dielectric barrier discharge source, it is confirmed that the micro-discharge in a non-equilibrium condition was produced.

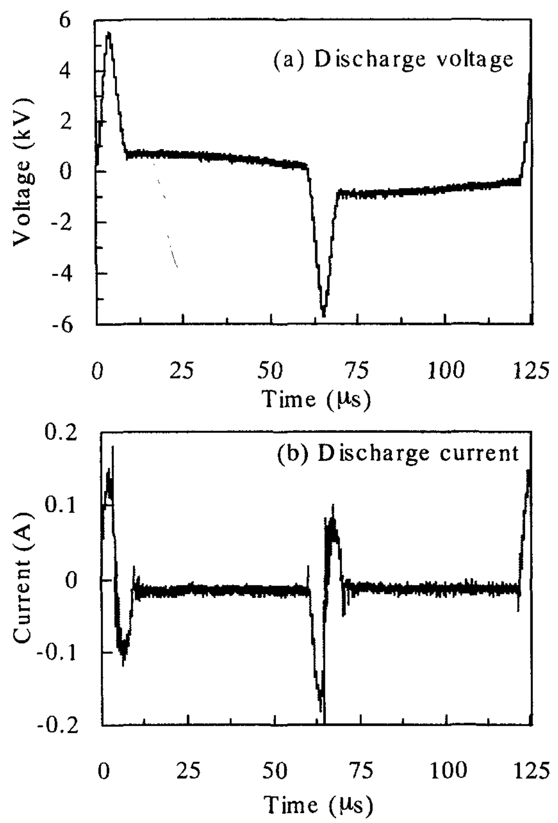

Fig. 3 Waveforms of discharge voltage and current.

Figure 4 shows the EDX spectra of the parent and the molding silica gels treated for 5, 10, 20 and 30min using the optimized dielectric barrier discharge source. In this figure, Si and O are due to the principal constituent of silica gel, and Al is from the filler. F is of new groups bonded to the surface of the molding silica gel, which may be brought by replacement of -OH groups by $-CF_n$ or -F groups[2]. The peaks around 0.3kV associated with carbon atom are confirmed. Although their peaks may also be of CF_n bonds, the EDX measurement reported

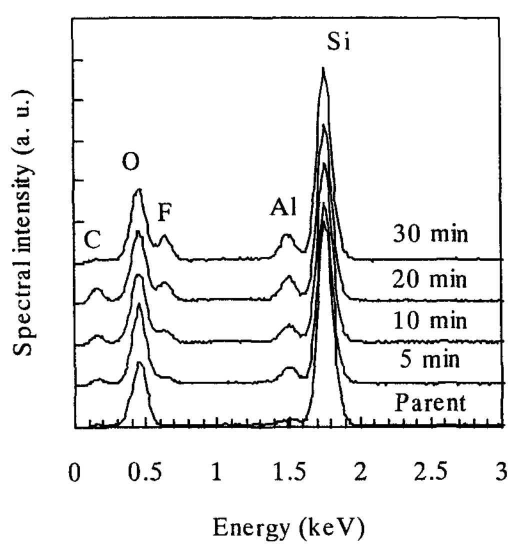

Fig. 4 EDX spectra of the parent and plasma-treated silica gels for 5, 10, 20 and 30min.

here was impossible to identify clearly because a sticking agent on a sample stage for fixation of silica gel contained carbon atom[1]. Figure 5 shows the variation of fluorine content against the plasma treatment time. It can be seen from this figure that the fluorine content increases with the increase of treatment time. Thus, changing the treatment time, the amount of replacement by $-CF_n$ or -F groups can be controlled. On the other hand, in the case where the surface treatment of the molding silica gel was performed for 30min using a conventional dielectric barrier discharge source, the fluorine content was less than 0.5%.

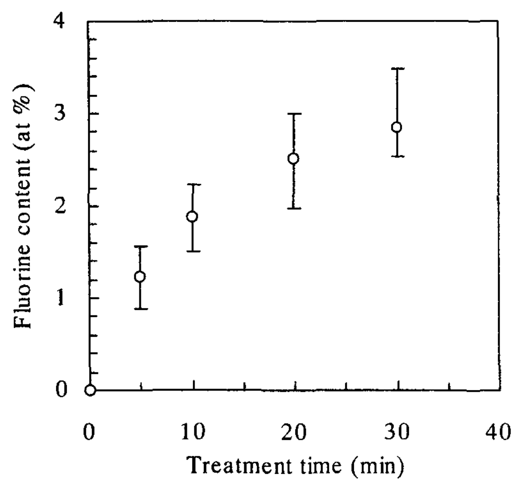

Fig. 5 Variation of fluorine content against the plasma treatment time.

Figure 6 shows DSC profiles of the parent and plasma-treated molding silica gels. The ordinate means an endothermic heat change of the adsorbed water vapor. Each measurement was carried out at a heating rate of 10℃/min. Also, in order to indicate the amount of scatter in measured values obtained by 4 times samplings, the typical difference between minimum and maximum values is shown by the vertical and horizontal error bars. The amount of scatter is relatively small, which suggests that the optimized dielectric barrier discharge source could uniformly modify the surface of molding silica gel. In the case where the surface treatment was performed for 30min using a conventional discharge source, the obtained DSC profile was the almost same as that obtained from the parent one, which would be brought by fact that the surface modification wasn't achieved except the partial fractions opposite to the upper electrode.

From Fig. 6, it is found that the endothermic reaction of plasma-treated silica gel was located at lower temperature side in comparison with that of the parent one. The value of minimum heat flow on the reaction curve gives us an index of the dehydrated temperature. The dehydrated temperature obtained by the treated molding silica gel becomes low with the increase of the treatment time. The dehydrated temperatures for the cases of 5, 10, 20 and 30 min are 80, 77, 74 and 69℃, respectively, while the value of the parent one is 89℃.

Also, the quantum of the adsorbed water vapor decreases with the increase of plasma treatment time. That is, the more the low energy surface is formed, the more the quantum of the adsorbed water vapor decreases. This indicates that the chemical adsorption between the silica gel surface (-OH groups) and water molecules is not dominant but Van der Waals interaction between the adsorbed water molecules will be. In consequence, the adsorbed water vapor is dehydrated at low temperature, indicating that the hydrophobic character of molding silica gel is enhanced in a sense. Thus, the surface treatment technique decreases both the dehydrated temperature on the molding silica gel and the quantum of the adsorbed water vapor. In an actual case, it is desired that an optimum value of fluorine content will be selected in consideration of economical balance between the dehydrated temperature and the quantum of adsorbed water vapor.

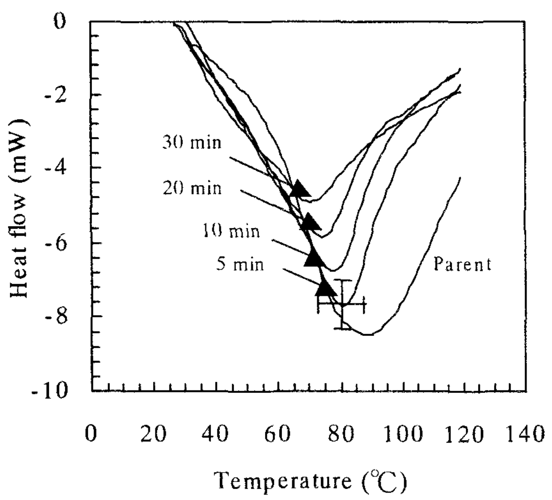

Fig. 6 DSC profiles of the parent and plasma-treated silica gels for 5, 10, 20 and 30min.

By the way, the dehydrated temperatures obtained on the powdery silica gels treated for 5, 10 and 15min were 77.6, 71.2 and 58.3℃ respectively while that obtained on the parent one was 93℃[1]. As compared with the results obtained on the powdery silica gel using a conventional dielectric barrier discharge source, it seems that the shift quantity of the dehydrated temperature obtained on the molding silica gel using an optimized dielectric barrier discharge is small. However, a decreasing ratio of the dehydrated temperature for the case of equal fluorine content is almost the same. For example, a fluorine content of the powdery silica gel treated for 10min was 2.1at%, in which case a decreasing ratio of the dehydrated temperature to the parent value was 23%. On the other hand, a fluorine content of the molding silica gel treated for 30min was 2.7at%; in this case, a lowering ratio was 22%. Thus, in the case where the fluorine contents obtained on the powdery and molding silica gels were the almost same, the decreasing ratio is equal. However, the treatment time to prepare the low energy surface on the molding silica gel is longer than that on the powdery silica gel. This tendency will be improved by the increase of discharge power and a diameter of rod electrode which adjusts a gap length. Studies in such directions are in progress.

Thus, it was found that an optimized dielectric barrier discharge source could uniformly modify the surface of the molding silica gel. However, one of the interesting characteristics of the treated molding silica gel is how long the formed low energy surface is maintained. From this viewpoint, we repeated the DSC measurement on the same sample used in the first DSC measurement. Figure 7 shows DSC profiles obtained by 3 times measurements on the same sample. In this case, the molding silica gel treated for 20min was used. As can be seen from this figure, the second and the third profiles corresponds to that obtained from the first measurement within a close range indicated by the horizontal and vertical error bars shown in Fig. 6. Thus, it was corroborated that the treated molding silica gel could stand the reproduction use at least 3 times.

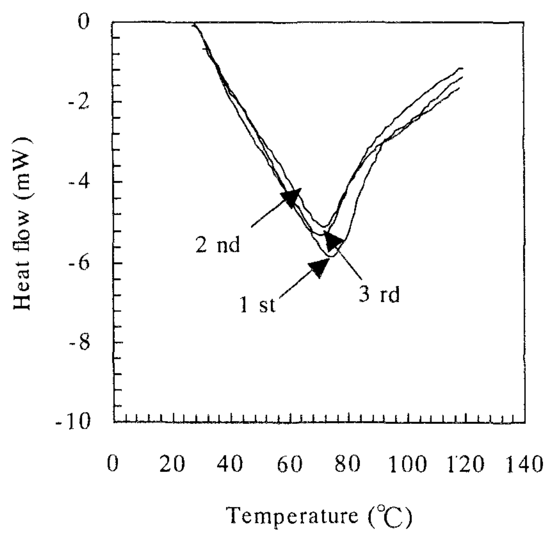

Fig. 7 DSC profiles obtained by 3 times measurements on the same sample. The molding silica gel treated for 20min was used.

4. CONCLUSION

In order to modify the surface of molding silica gel with a three dimensional and complex structure, we first constructed a new dielectric barrier discharge source with better the surface treatment of the molding silica gels. The treated molding silica gels were characterized using EDX and DSC. The results showed that the optimized dielectric barrier discharge in CF_4 atmosphere could uniformly modify the surface of the molding silica gel. The modified surface of the molding silica gel had a low energy surface brought by fact that the replacement of -OH groups by $-CF_n$ or -F groups was achieved. As a proof, the endothermic reaction on the plasma-treated molding silica gel shifted to the low temperature side compared with that on the parent one. It was also confirmed that the treated molding silica gel could stand the reproduction use at least 3 times. Thus, it was investigated that the optimized dielectric barrier discharge source could prepare the molding silica gel whose reproduction cost would be lowered.

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