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Relationship between the process parameters and the saturation point in electrophoretic deposition

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Abstract

We used the electrophoretic deposition (EPD) process to fabricate a composite with glass frit and investigated the EPD parameters to find the optimum deposition time by understanding the relationship between the process parameters of zeta potential (ZP), pH, deposition yield and saturation point in a slurry. A binder and a dispersing agent were mixed properly with glass frit (0.2–25 μm, d_{50} = 8.77 μm) in an ethyl alcohol medium for the preparation of the slurry. The pH and ZP were in an inverse relationship to each other due to the generation of H_3O^+ ions with the addition of the dispersing agent in the slurry. The acidic nature of the slurry resulted in a decrease of the pH and an increase of the ZP. Otherwise, the pH increased with the addition of the glass frit in the slurry because H_3O^+ ions were absorbed on the glass frit. Therefore, the OH^- ions correspondingly increased. The saturation point of EPD was strongly correlated with the variation of the pH in the slurry; this is caused by a chemical reaction between the ethyl alcohol and the ions that make up the glass frit. An adjustment of the pH variation and the saturation point in the slurry can be established with respect to the optimum deposition time in the slurry.

Keywords: Electrophoretic deposition; Glass powder; pH; Saturation point; Zeta potential

1. Introduction

The electrophoretic deposition (EPD) method has been widely applied for the coating and infiltration in ceramic areas because the process is economically viable considering the lower cost of the raw materials and considering that the processing timing is fast comparing to other deposition techniques [1–3]. The EPD provides suitable means of fabricating ceramic–matrix composites that are reinforced with fibers [3–5] and for fabricating porous layers as membranes [6], laminated structures [7] and thermal barrier coatings [8] due to their advantages of less limited substrate shapes and the capability to scale-up to high rates of production.

A number of the EPD have been used to fabricate the composite using glass frit [9–11] but noticed that the optimum deposition time for controlling the deposition yield and the layer was rarely considered [11,12]. Reasons for setting the deposition time were not mentioned as well [9,10,13–15]. In addition, the adjustment of the voltage during the deposition process is very difficult if used to control the porosity and the shape of the deposition layer [10,11]. Therefore, understanding the relationship among processing factors in EPD method can contribute to acquire optimum condition of infiltration and coating for fabricating glass composite.

To explain the origin of the potential drop over the deposit during the EPD process for an efficient process operation and the optimum deposition time, a number of studies have investigated the origin of ion transport and related theories using an electrostatic double layer [16–19]. Some suggest that ions move with particles in a slurry and that this is related to the thickness of the electrostatic double layer and to the magnitude of the surface potential of the particles. Furthermore, several papers have focused on other parameters, such as the behavior of differently sized powders during the EPD process [20], the effect of the suspension's composition [21], and the concentration of the material [22] for an effective fabrication or deposition. However, given that these studies were based on the deposition of single-crystal material such as Al_2O_3 [16–19,21] and MgO [22], the saturation point of glass frit during the EPD

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process was not directly addressed. As glass frit is a multi-component system which contains more than one oxide element, it is important to analyze the parameters of the deposition of glass frit when it is used in the EPD process.

The main purpose of this study is to find a correlation between the process parameters for an optimum deposition time during the EPD process regardless of the raw materials or the purpose of the deposition. We investigated the internal state of a type of slurry by specifically preparing the slurry, and we succeeded in the deposition using the optimum slurry condition. The optimum deposition time during the EPD process is established considering the saturation point of the deposition yield, which occurs under the optimum slurry condition. The internal characteristics of the slurry were investigated to evaluate the effect of the raw materials that make up the slurry, in this case glass frit, a dispersing agent and a binder, all of which were tested at various ratios. The establishment of the optimum deposition time was determined from the relationship among the pH, zeta potential (ZP), and the saturation point of the deposition and the leaching ions.

2. Experimental procedure

The glass frit used for EPD process was $7SiO_2$–$9B_2O_3$–$18Al_2O_3$–46ZnO–7MgO–$4.5Na_2O$–8.5CaO system in this study. The approximate size of the glass frit was 0.2–25 μm (d_{50} = 8.77 μm), and a dispersing agent (DISPERBYK-103, BYK Additives and Instruments, Germany) and a binder (Butvar B-98, Solutia, USA) were dispersed in ethyl alcohol (95.0%, Sigma–Aldrich, USA) with the glass frit to improve the dispersibility and adhesive property. The slurry was dispersed properly using an ultrasonic bath (JAC-2010, Kodo Technical Research Co. Ltd., Korea) for 5 min, with a subsequent dispersion process conducted by means of mixing with a magnetic stirrer for 30 min to improve the dispersion of the glass frit in the slurry. EPD experiments were performed at room temperature at a constant voltage of 80 V using a DC supply (OPE-1501DI, ODA Technologies Co. Ltd., Korea). At this voltage, the current was maintained at 0.1–0.2 mA. The distance between the stainless-steel square-shaped electrodes was 1.5 cm.

To investigate the effect of the raw materials and the internal characteristics of the slurry, glass frit, a dispersing agent and a binder were added to ethyl alcohol at various ratios while simultaneously measuring the pH and ZP with a Zeta-meter (Zetaprobe analyzer, Colloidal Dynamics Inc., USA). The optimum slurry condition was chosen after considering the deposition yield and the layer characteristics of fifteen types of slurry conditions. The optimum slurry was used to find the relationship between the process parameters so as to determine the optimum deposition time in the EPD process. The deposition weight was continuously measured every 30 min during the process to obtain the maximum deposition yield and saturation point. The pH was measured by a portable pH meter (CP-401, Elmetron, Poland) for continuous measurements from inside the EPD bath to analyze how the pH varied. An ICP-OES device (Optima 7300DV, PerkinElmer Inc., USA) was used to examine the amount of leaching ions by comparing the results 5 min and 300 min after the slurry was manufactured to understand the cause of the saturation point and the variation of the pH during the EPD process.

3. Results and discussion

Two results able to predict the relationship between the parameters and the optimum deposition time were obtained by the EPD experiments. The first is the characteristics of slurry as influenced by the effect of the raw materials, and the second is the variation of the slurry characteristics, in this case the pH, ZP and deposition yield during the EPD process. The glass frit was deposited on the cathode which had a positive ZP value due to the presence of H_3O^+ ions. The H_3O^+ ions are greater in number compared to the OH^- ions in the slurry because the dispersing agent, which is acidic, generated H_3O^+ ions to create an acidic slurry with a positive ZP.

The pH and ZP with the variation of the glass frit content showed an inverse relationship (in Fig. 1). This result was in accordance with several previous studies [4,23,24]. The ZP shows a tendency to decrease with an increase in the frit content, whereas the pH increases inversely (neutralization). The increased pH with the addition of glass frit is related to the frit absorbing the H_3O^+ ions. Therefore, the OH^- ions increased relatively and the pH became neutral. In contrast, the ZP, which is the potential difference, was lower than before because the number of absorbed H_3O^+ ions on each piece of glass frit was decreased by the increase in the surface area due to the addition of the glass frit. This weakens the surface charge layer based on the electric double layer [25]. Fig. 2 shows this procedure, in which the number of adsorbed ions decreased after the addition of the glass frit, leading to the variation of the pH and the ZP.

The binder does not affect the pH, as shown in Fig. 3, because the binder is not associated with the ion generation and the adsorption in the slurry. However, Van der Waals force arises due to the long linear polymer, which is generated by the binder [26,27]. Hence, the glass frit is dispersed by the Van der Waals force. Eventually, the number of ions that are adsorbed on each piece of glass frit can be reduced, as shown in Fig. 4,

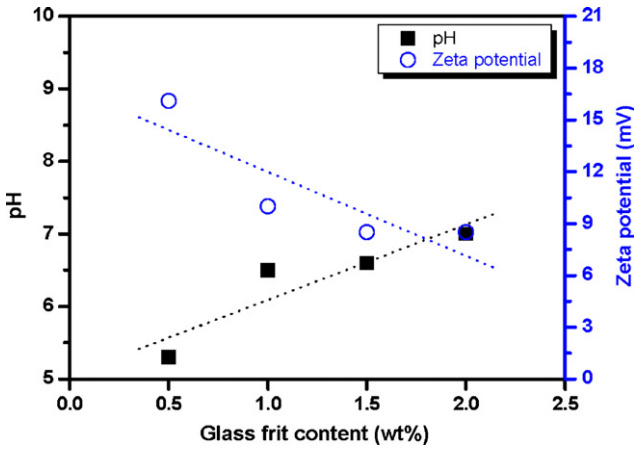

Fig. 1. Relationship between the pH and ZP with the glass frit content.

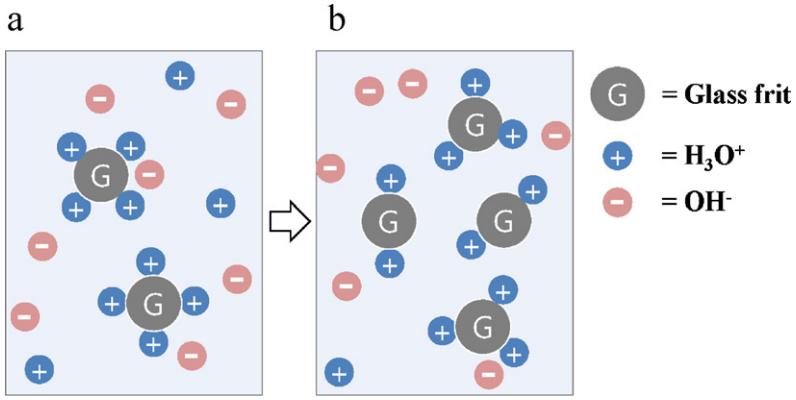

Fig. 2. Variation of adsorbed ions with the addition of glass frit: the initial state (a) and after the addition of the glass frit (b).

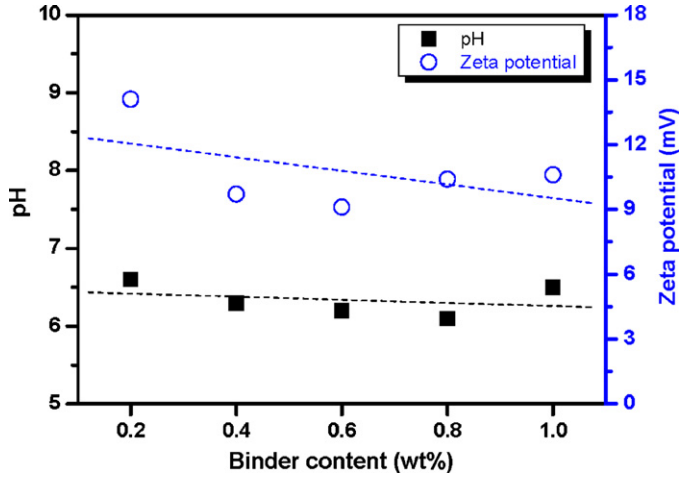

Fig. 3. Relationship between the pH and ZP with the binder content.

which reduces the shearing force and correspondingly the ZP. Thus, the slurry was stable with a binder content of at least 0.4 wt%. However, the appropriate binder content should be considered because excess binder causes aggregation and precipitation of the glass frit [27].

The ZP shows a tendency to increase with an addition of the dispersing agent content, but the pH decreases conversely (acidification) (in Fig. 5). This occurs because H_3O^+ ions are generated due to the addition of the dispersing agent in the slurry, which leads to the decrease in the pH (acidification). The ZP was increased by the increased number of absorbed H_3O^+ ions on each piece of glass frit, as additional absorbed H_3O^+ ions lead to a higher surface charge layer via the electric double layer [25]. Fig. 6 shows the variation of the number of H_3O^+ ions in the slurry, comparing the initial state and the state after the addition of the dispersing agent. The ions adsorbed on the glass frit surface also increase due to the increase in the number of H_3O^+ ions in the slurry.

It was possible to control the pH and the ZP of the slurry, as shown in Figs. 1, 3 and 5. These results show how one can maintain or control the ZP and pH value with the addition of a dispersing agent and/or a binder according to the amount of powder in the slurry. Table 1 summarizes the slurry conditions with various ratios of the contents, including the ZP, which is related to the electrophoretic velocity of the glass frit [21,25]. Therefore, the No. 1 slurry was selected for the optimum slurry condition as it had the highest ZP, and it was used to fabricate the glass composite for the investigation of the relationship between the process parameters.

Fig. 7 shows SEM images of the deposition layer (a) and surface (b) using the optimum slurry condition for a processing time of 1 h. Although the glass frit was deposited successfully on the substrate using the EPD process, the saturation point was reached while increasing the amount of the deposition weight. The deposition weight increased continuously to about 200 min on the substrate while the deposition rate was decreased from

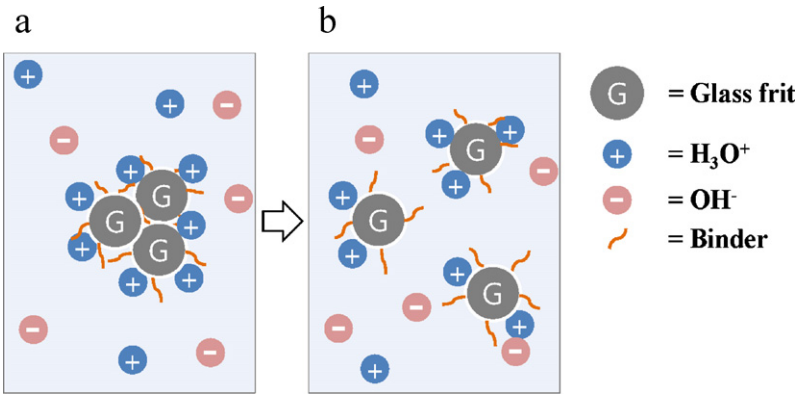

Fig. 4. Dispersion of the glass frit by the addition of the binder: the initial state (a) and after adding the binder (b).

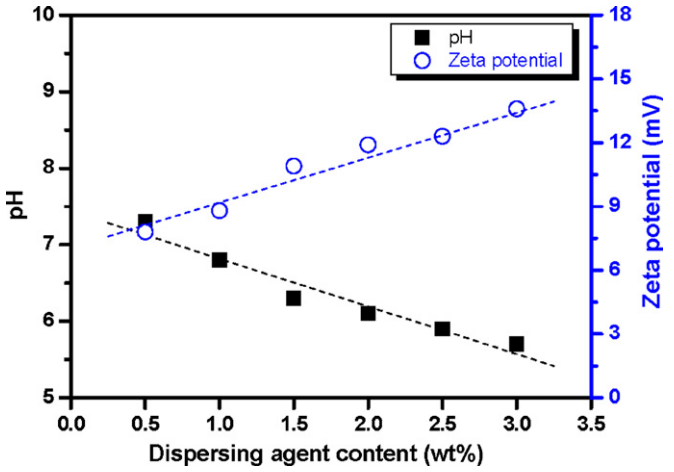

Fig. 5. Relationship between the pH and ZP with the dispersing agent content.

200 to 240 min. The maximum saturation was reached in 240 min (in Fig. 8).

In Fig. 9, the pH of the slurry (powder) increased sharply from the initial time to 15 min, finally becoming stable after 50 min. However, the initial pH of the slurry with the dispersing agent was 5.1 due to the increase in the number of H_3O^+ ions which were generated by the dispersing agent. However, it became continuously alkaline during the 300 min experiment. The pH of the slurry with the dispersing agent during the EPD process changed from 5.1 to 8.9, but the pH started to decrease after 180 min (in Fig. 9). This acid changing point is correlated well with the saturation starting point, at around 200 min (in Fig. 8).

The relationship between the peak point of the pH during the EPD process and the starting point of saturation is explained by means of ICP-OES (in Table 2). The glass frit ions were leached from the glass frit surface continuously during the 300 min experiment. As a result, a chemical reaction occurred between the glass frit surface and the ethyl alcohol. When the glass frit ions are leached in the slurry, the H_3O^+ ions in the ethyl alcohol are absorbed onto the glass frit surface. Therefore, the H_3O^+ ions in the slurry decreased correspondingly and the pH increased in the alkaline direction, as shown in Fig. 9.

Why the glass frit caused a chemical reaction with the ethyl alcohol can be determined by examining the residual water in the ethyl alcohol [28,29]. It has been proposed that in ethyl alcohol, oxide surfaces acquire charges in a similar way to water via ion exchange reactions [30–32]. The reaction between a glass frit surface and ethyl alcohol has been described in terms of two chemical reactions [29].

Table 1
Slurry conditions at various content ratios.

No.	Change factors	Composition (wt%)				ZP (mV)
		Ethyl alcohol	Powder	Dispersing agent	Binder	
1	Glass frit	96.3	0.5	3.0	0.2	16.1
2	Glass frit	95.8	1.0	3.0	0.2	10
3	Glass frit	95.3	1.5	3.0	0.2	8.5
4	Glass frit	94.8	2.0	3.0	0.2	8.5
5	Dispersing agent	98.8	0.5	0.5	0.2	7.8
6	Dispersing agent	98.3	0.5	1.0	0.2	8.8
7	Dispersing agent	97.8	0.5	1.5	0.2	10.9
8	Dispersing agent	97.3	0.5	2.0	0.2	11.9
9	Dispersing agent	96.8	0.5	2.5	0.2	12.3
10	Dispersing agent	96.3	0.5	3.0	0.2	13.6
11	Binder	96.3	0.5	3.0	0.2	14.1
12	Binder	96.1	0.5	3.0	0.4	9.7
13	Binder	95.9	0.5	3.0	0.6	9.1
14	Binder	95.7	0.5	3.0	0.8	10.4
15	Binder	95.5	0.5	3.0	1.0	10.6

(a) Alkalis are released into slurry on account of an ion exchange with protons from the slurry.

$$\equiv Si{-}OR + H_2O \rightleftarrows Si{-}OH + R^+ + OH^- \quad (1)$$

(b) Silica is released into slurry as the siloxane bonds in the glass are attacked by the hydroxyl ions from the slurry.

$$\equiv Si{-}O{-} + H_2O \rightleftarrows Si{-}OH + OH^- \quad (2)$$

Ion exchange between alkalis and silica arise due to these two chemical reactions, and the pH also increases due to the generation of OH^- ions. Therefore, the variation of the pH will be influenced by the amount of adsorbed H_3O^+ and the generation of OH^- ions, the glass frit composition, the solvent type and the chemical reactions on the surfaces of the glass frit. However, the number of OH^- ions which can be involved in the ionic cloud around the glass frit increases gradually during the

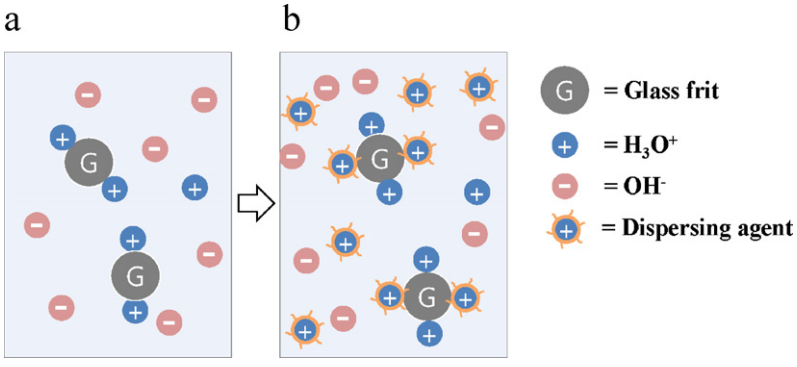

Fig. 6. Increase in the H_3O^+ ions generated by the addition of the dispersing agent: the initial state (a) and the state after adding the dispersing agent (b).

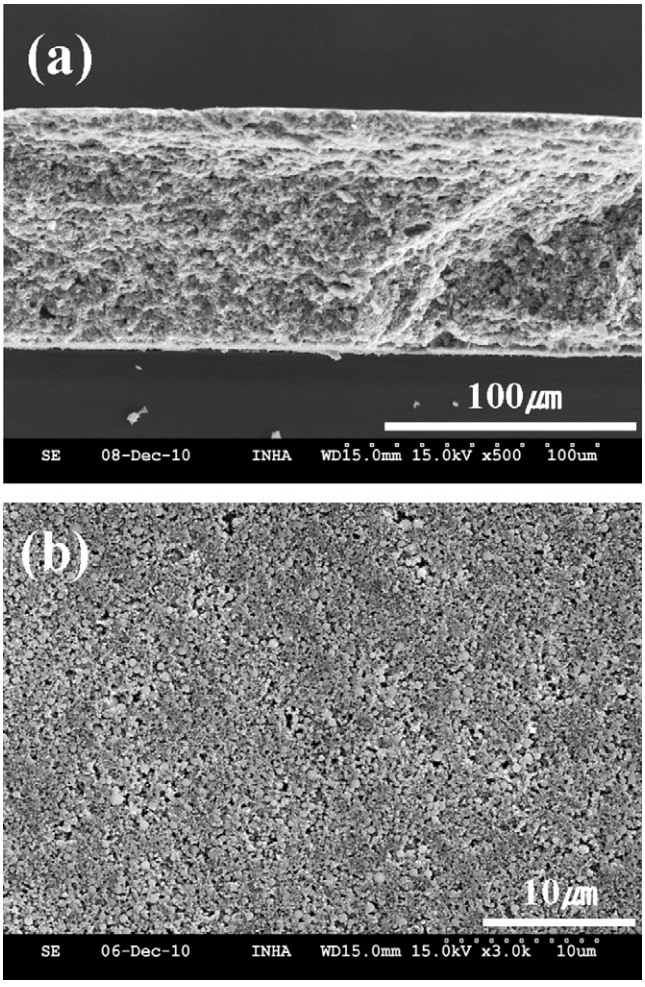

Fig. 7. Deposition layer (a) and surface of the glass frit on the layer (b).

EPD process due to the chemical reactions between the ethyl alcohol and the glass frit [19,33]. Therefore, the ZP of the electric double layer with the glass frit will decrease. Finally, because the glass frit does not have a high enough ZP to move to the cathode substrate, the saturation point is reached.

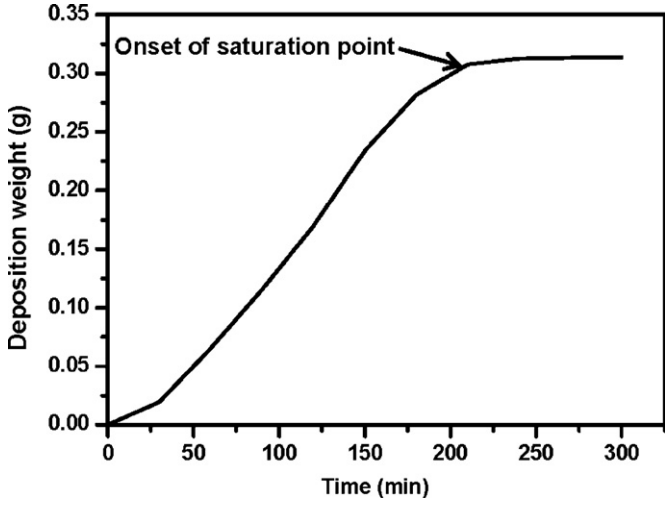

Fig. 8. Saturation point of deposition as a function of the deposition time.

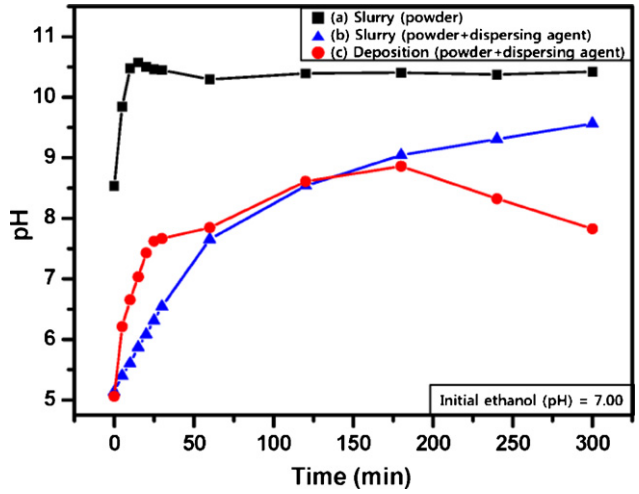

Fig. 9. pH variation of the slurry with (a) powder (b) powder and dispersing agent and (c) powder and dispersing agent during the EPD process.

Table 2
Changes in the content of ions leaching from the glass frit in the slurry.

Leaching concentration (mg/L)							
Composition (mol%)	Zn	Mg	Na	B	Ca	Si	Al
	51.1	6.74	4.55	7.28	8.47	5.79	16.07
After 5 min	1.1	0.38	4.1	3.3	2.6	1.0	0.2
After 300 min	199.7	185.2	110.1	62.4	19.3	4.0	3.7

Depending on the cause of the variation of the pH and the deposition saturation point, the deposition time can be controlled by changes in the glass frit composition, the amount of glass frit, the H_3O^+ions, and the generation of the OH^- ions in the slurry. Based on these results, when the glass frit is added to the slurry used with the EPD process, an understanding of the relationship between the leaching ions from the glass frit surface and the pH variation during the process can allow one to determine an efficient EPD process considering the saturation time.

4. Conclusion

The ZP and pH of slurry can be controlled by understating the effect of the raw materials that make up the slurry. This suggests that maintaining and controlling of the proper ZP, which is related to the electrophoretic velocity of the powder, is possible. To establish the optimum deposition time, the relationship between the saturation point and the pH of the slurry was confirmed by examining the ions leaching from the glass frit surface. The glass frit ions leached from the frit surface owing to a chemical reaction between the glass frit surface and the ethyl alcohol that existed in the mix. Thus, H_3O^+ ions were absorbed on the glass frit surface. However, the quantity of OH^- ions increased gradually during the EPD process on account of the chemical reactions. Therefore, the ionic cloud around the glass frit included numerous OH^- ions, which weakened the ZP and saturation point. Given this result, we could predict the saturation point of the deposition by

analyzing the ions leaching into the slurry, which affected the pH, through which we could control the deposition time by changing the glass frit composition, the amount of glass frit or the solvent type.

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