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Electrophoretic coagulation behavior of ferroelectric barium titanate powders in mixed solutions of alcohol and acetylacetone

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Although the deposition of $BaTiO_3$, known as a ferroelectric compound with spontaneous dipole moments, has never occurred in either propanol and acetylacetone, these mixtures were found to enhance the deposition of the powders on a cathode. The present study carried out the systematic investigation of the solution-mixing effect of propanol and acetylacetone on the electrophoretic deposition of $BaTiO_3$. The optimum mixing ratio for the deposition was 50–70 vol% of propanol, while a depressed migration of $BaTiO_3$ powders was observed in the mixed solutions. Therefore, it was considered that the enhanced deposition was attributed to the coagulation of the $BaTiO_3$ powders on the cathode. The deposition characteristics varied with the kind of alcohol used showed that a more highly enhanced deposition was achieved with alcohols having longer side-chains such as octanol. An intertwinement between the side-chains in the alcohols was considered to have an effect on the coagulation of the $BaTiO_3$ powders.

1. Introduction

Electrophoretic deposition (EPD), a colloidal process with the accumulation of finely dispersed powders from suspensions onto substrates in a dc electric field, is an attractive means for the forming of functional ceramic films because of its technological variability and tractability. The application of EPD to ferroelectric $BaTiO_3$ (BT) films has recently gained much attention [1–9] because of a variety of applications to electronic devices such as high permittivity capacitors, ultrasonic sensors and actuators. However, some difficulties in the electrophoretically film-formation of BT have been pointed out, since the EPD of BT is limited to a few poisonous solutions; diethylene glycol dimethylether, 1-nitropropane and pyridine. Recently, alternative solutions have been developed as an effective suspension medium for the EPD of BT [2–9]. Nagai *et al.* have found that the mixed solutions of ethanol (EtOH) and acetylacetone (Acac) are effective for the EPD of BT [2], and succeeded in electrophoretically fabricating ferroelectric BT thick films with a thickness of 10 to 70 μm using the mixed solutions. However, the mixing effect of the two solutions has not yet been established in detail. In the present study, the solution-mixing effect has been systematically investigated using various kinds of alcohols. This paper deals with the EPD characteristics of BT in the mixed solutions of propanol (PrOH) instead of EtOH to Acac. In addition, the effect of alcohols in the mixed solutions on the EPD of BT will be discussed.

2. Experimental

Considering their practical uses, commercial BT powders (>98% Kanto Kagaku, Inc.) were used as raw materials. The commercial powders were first pre-heated at 700°C for 1 h in air prior to the electrophoretic treatments for removal of any adsorbed gases. The obtained powders were sufficiently ground to an average size of 1–2 μm in diameter with a ball-mill, which was measured by a scanning electron microscope. In the present study, Acac and the primary alcohols of reagent grade were used as-received.

The BT powders were ultrasonically dispersed for 180 s in mixed solutions with different mixing ratios of PrOH to Acac, and left for another 30 s without any ultrasonic vibration. The concentrations of the dispersed powders were at 10 g/L. Two flat Pt plate electrodes were set in the suspensions containing the BT powders at a working distance of 3 mm. The electrodes were cleaned prior to the use by sonicating in acetone followed by rinsing with distilled-deionized water. EPDs were carried out by applying a dc voltage of 120 V between the two electrodes with an area of 1.2 cm^2 on which the BT powders had accumulated.

The deposited amounts of BT were determined by weighting the deposits after drying over night at temperatures above the boiling points of solutions used. A commercial electrophoresis cell (Mitamurariken Kogyo, Inc.) was used to measure the velocities of the BT powders in the suspensions. The migration velocities were estimated by measuring the migrating time of the BT powders for a distance of 80 μm in an electric field of 30–60 V/cm.

3. Results and discussion

3.1. EPD characteristics of BT in mixed PrOH-Acac solutions

Although the migration of the BT powders toward the cathode was observed in PrOH, Acac, and their mixture solutions with PrOH:Acac = 50:50 in vol%, the BT powders were only deposited in the mixed solutions. Deposits were not obtained in either PrOH or Acac solutions. Thus, the results showed that not only EtOH but also PrOH were effective additive solutions to Acac for the EPD of BT. It was also observed that the deposits uniformly formed thick films of BT on the electrodes. The thickness of the films was adjusted to 10–70 μm using the experimental conditions such as the applied voltage.

Fig. 1 shows the dependence of the deposited amount of BT on the mixing ratio of PrOH to Acac. A large amount of deposition was observed in the range of 50 to 70 vol% PrOH, and the amount gradually decreased below 50 vol% and beyond 70 vol% PrOH. A similar bell-shaped dependence has been observed in the previous study [2]. When EtOH was added to Acac, the amount was almost independent of the mixing ratio between 20 to 80 vol% of EtOH. According to the previous study [2], free protons can be produced by the keto-enol equilibrium reaction of Acac with alcohol. BT powders have been considered to have migrated with the protons released from Acac in the mixed solutions. In the present study, the electrophoretic experiments were carried out in the solutions with a small amount of hydrochloric acid (HCl) instead of Acac in order to investigate the effect of protons on the EPD of BT. The PrOH-HCl solutions led to the migration of the BT powders toward cathode similar to that in the PrOH-Acac solutions. Table I compares the results in the PrOH-HCl solutions with those in the PrOH-Acac solutions. The amount of BT deposited in an electric field of 200 V/cm in the former solution was ca. 0.5% of that in the latter solution. A large current was present in the PrOH-HCl solutions, and the evolution of hydrogen gas which causes poor EPD was observed. The reduced amount of deposits was, therefore, ascribed to the large quantity of hydrogen gas evolved during the EPD. The current flow could be lowered by using a lower applied voltage. However, no satisfactory EPD was achieved in the PrOH-HCl solutions. This result indicates that coagulation of BT powders on the cathode was hardly promoted in the low electric field. From these results, it is understood that the mixed PrOH- or EtOH-Acac solutions provided favorable conditions for the EPD of BT.

TABLE I Amounts of BaTiO$_3$ deposited on cathode in propanol-HCl and propanol-acetylacetone solutions under various electric fields, respectively

Suspension media	Electric field (V/cm)	Amount of deposit (mg/cm^2)
Propanol (20 ml)–HCl (0.1 ml)	3.3	0.66
	66	0.87
	200	0.33
Propanol (10 ml)–Acetylacetone (10 ml)	200	6.0

The electrophoretic depositions were carried out for 3 min.

Fig. 2 shows the effect of the applied voltage on the migration velocity of the BT powders in the mixed PrOH-Acac solutions. The measurements were made

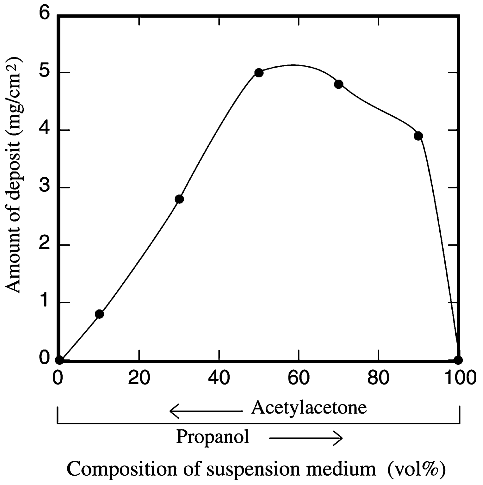

Figure 1 Amount of deposited BaTiO$_3$ powders as a function of composition of suspension medium.

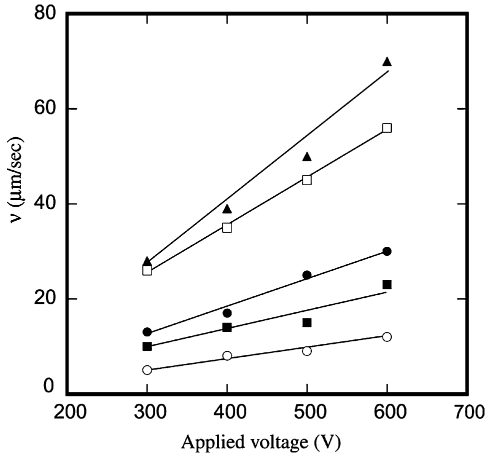

Figure 2 Applied voltage dependences of migration velocity of BaTiO$_3$ powders in mixed solution of propanol (PrOH) to acetylacetone (Acac). The mixing ratios of PrOH:Acac in vol% were as follows: 100:0 (●), 75:25 (○), 50:50 (■), 25:75 (□) and 0:100 (▲), respectively.

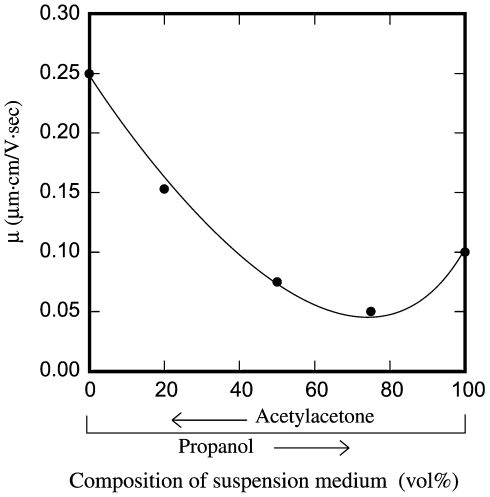

Figure 3 Electrophoretic mobility of $BaTiO_3$ powders as a function of mixing ratio of propanol and acetylacetone in suspension medium.

using various mixing ratios of PrOH to Acac. As the applied voltage was increased, the migration velocity was monotonically increased. The increasing ratio was dependent on the mixing ratio. A higher migration velocity was obtained in pure Acac without the addition of PrOH. From the obtained migration velocities, the electrohpretic mobilities of the BT powders were calculated using

$$M = (v \times A)/(I \times r),$$

where M is the electrophoretic mobility, v is the migration velocity, A is the cross section area of the cell perpendicular to the direction of the dc electric field, I is the current flow and r is the resistivity of the suspension. In the calculations, the values obtained with the applied voltage of 600 V were used. Fig. 3 shows their estimated electrophoretic mobilities. A maximum value for the electrophoretic mobilities was obtained in pure Acac, indicating that the BT powders were most drifting in pure Acac. As the mixing ratio of PrOH increased, the electrophoretic mobility gradually decreased and became a minimum value for the mixing ratio between 50 to 75 vol% around which the EPD was highly enhanced. From these results, it is clear that the mixed PrOH-Acac solutions are effective in coagulating BT powders on the cathode after discharge.

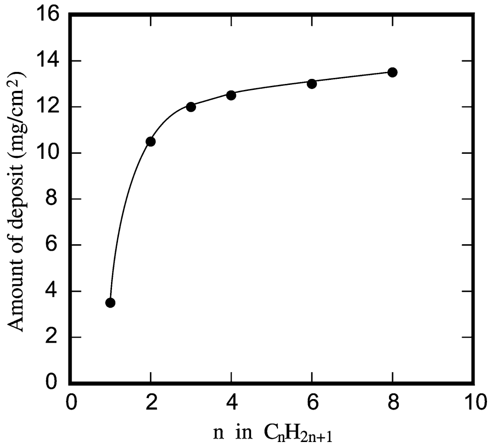

Figure 4 Amount of deposit as a function of number of carbons in alcohols used.

4. Effect of alcohol in suspension medium on EPD of BT

Fig. 4 shows the amount of the deposit as a function of the number (n) of carbons in alcohols involved in the suspensions. The concentration and composition of the suspensions were 15 g/L and the constant vol% of alcohol:Acac = 1:1, respectively. As the carbon number in the alcohols increased, the deposited amount increased to a constant value above $n = 4$, corresponding to butanol. When the alcohol with a long side-chain such as octanol was involved in the suspensions, the migration of the BT powders was obviously depressed because of the high viscosity of the suspensions. Therefore, it was clear that the addition of alcohol had an effect on the coagulation of the discharged BT powders on the cathode. Mizuguchi et al. have succeeded in promoting the coagulation of Al_2O_3 powders by adding nitrocellulose with a long side-chain to the suspensions [10]. The addition effect of nitrocellulose has been considered to be due to an intertwinement between the side-chain in the nitrocelluloses adsorbed on the Al_2O_3 powders. In considering the present system, it would be assumed that the alcohols are adsorbed on the BT powders. Therefore, a similar effect can be expected in the EPD using alcohols with long side-chains. Since the present EPD is, however, more complicated than the previous EPD, further detailed studies are needed in order to deeply understand the role of alcohol on the enhanced EPD characteristics.

5. Conclusions

In the present study, the EPD characteristics of the BT powders in the mixed PrOH-Acac solutions were systematically investigated. Despite the fact that both the pure PrOH and pure Acac were ineffective solutions for the EPD of BT, a large amount of BT was deposited on the cathode in the mixed solutions. An enhanced EPD was obtained in the range of 50 to 70 vol% PrOH in which the electrophoretic mobility of the BT powders was depressed. The origin of the enhancement was considered to be the coagulation of the discharged BT powders on the cathode. The coagulation of BT was highly promoted with alcohols with long side-chains such as octanol. This was probably due to an intertwinement between the side-chains in the alcohols.

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