Development of an Electrophoretic Sol-Gel Coating Process for Porous Metals

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An electrophoretic sol-gel coating process was developed for applying to surface modification of metallic materials with complicated shapes such as porous metals. In this process, sol-gel transformation is directly induced on the substrates. In the present work, the formation of TiO$_2$ coating layer on SUS 304 substrates is discussed as a practical example of the coating process. The colloidal particles derived from hydrolysis of titanium tetraisopropoxide in ethanol can be deflocculated using a small amount of CaCl$_2$ to form a transparent solution. When a dc voltage of 1–5 V was applied between the substrate (cathode) and counter electrode in this solution, the gel film was formed on the substrate. After subsequent water-soaking and annealing processes, the coating layers with no cracking were obtained successfully on the substrate. As the results of X-ray photoelectron spectroscopy, the coating layers were found to consist of TiO$_2$ doped with Ca$^{2+}$ ions.

Keywords: porous metals, coating, electrophoresis, sol-gel process, deflocculation

1. Introduction

Many types of porous metals are being investigated very actively for applying in various industries. In order to establish practical applications of the porous metals, the surface modification that enhances their functions will be important as well as morphology control of the porous bodies. For example, a barrier coating is required for the materials utilized in corrosive environments. For filter application, the catalysts and sub-catalysts must coat on the surface of the open pores. The coatings with superior biocompatibility and bioactivity will be useful for medical applications. However, homogeneous coating layers are difficult to be formed efficiently on the materials with complicated shapes such as deep and continuous pores.

In order to form ceramic coating layers on conductive substrates, including metals, flex and glass substrates coated with ITO, electrophoretic deposition processes using various colloidal solutions have been developed and its achievements have become a center of attraction. In most of these processes, the colloidal particles electrophorese directly to deposit on the substrates.

By contrast, the coating processes using homogeneous sols (not colloidal solutions) are also worth examining for porous metals because densified and homogeneous coatings can be obtained. These processes are also expected to be applied for precision surface treatment of minute components. Recently, the present authors have proposed an electrophoretic deposition process for forming ceramic coating layers on porous metals. In this process, sol-gel transformation is induced on an electrode (substrate) by using homogeneous sols as the electrophoresis medium. The sols can be prepared by deflocculating colloidal solutions formed by hydrolysis of metal alkoxides using appropriate agents. After the deposition, the ceramic layers can be obtained by annealing under suitable conditions.

As a practical example of this coating process, the formation of TiO$_2$ layer on SUS 304 substrates is investigated. Because anatase-type TiO$_2$ has a superior biocompatibility, the coating layer is expected to provide superior biocompatibility to the porous bodies of SUS 304. However, the details in process conditions for obtaining the coating layers with high quality remains still unclear in the present situation. The present paper discusses the relationships of several process conditions with physical and chemical states of the coating layer on SUS 304 substrates in order to develop novel coating process for metallic materials with complicated shapes such as porous metals.

2. Experimental Procedure

2.1 Preparation and characterization of sols

TiO$_2$ that was derived from titanium tetraisopropoxide was selected for the coating material. The designated concentrations of titanium tetraisopropoxide (50 mol/m$^3$) and water (200–1000 mol/m$^3$) were dissolved separately into several solvents including methanol, ethanol and 2-propanol. Then, these solutions were mixed in order to induce hydrolysis reaction of titanium tetraisopropoxide at 30°C. The colloidal solutions of the condensation products that were formed by the hydrolysis reaction were aged using a stirrer for 3.6 ks. Thereafter, the colloidal solutions were deflocculated using a small amount (~1 mol/m$^3$) of agents such as CaCl$_2$ in order to prepare transparent sols of the precursor.

Before the deflocculation, the zeta potential of the colloidal particles was measured by the rotating prism method using micro-electrophoresis equipment at 20°C in order to determine electrophoresis condition for the deposition process. Furthermore, thermogravimetry–differential thermal analysis (TG-DTA) was performed after drying the particles. The constituent phases of the particles were identified using X-ray diffraction (XRD) before and after annealing process.

2.2 Electrophoretic sol-gel coating process

Plates and lotus-type porous bodies of SUS 304 were employed as the substrate materials for the electrophoretic deposition process. The electrophoretic coating on the substrates was performed using a SUS 304 plate as the counter electrode, as shown in Fig. 1. The applied voltage between the substrate and counter electrode was varied in the range of 1–5 V with a dc power supply. In the case of coating on the porous bodies, the evacuation treatment was con-
ducted before the electrophoretic process, in order to fill the continuous pores of the substrate materials with the sol. After the deposition process, the specimens were dried. Then, subsequent water-soaking process was conducted at 20°C for 3.6 ks for some specimens, in order to facilitate to remove residual alkoxy groups. Finally, the specimens were annealed under various conditions. After these processes, the coating layer on the specimens was observed using optical microscopy (OM), scanning electron microscopy (SEM). Furthermore, the coating layer was characterized using X-ray photoelectron spectroscopy (XPS). Thickness of the coating layers was measured with a contact probe method.

3. Results and Discussion

3.1 Preparation of sols for electrophoretic process

The colloidal solutions were obtained successfully by mixing the solutions of titanium tetraisopropoxide and water using methanol, ethanol and 2-propanol as the solvents. The colloidal particles synthesized in these solutions are agglomerations of the condensation products of titanium alkoxides. Figure 2 shows the zeta potential of the colloidal particles in these solutions measured by the rotating prism method using micro-electrophoresis equipment at 20°C. The colloidal particles exhibit positive zeta potential values that become low in order of methanol > ethanol > 2-propanol. The magnitude of zeta potential of the colloidal particles seems to be related to the dielectric constant of the solvents.

When the electrophoresis of the condensation products is performed, some agents for increasing zeta potential of the colloidal particles are desirable to dissolve into the solutions. In the present work, metal chlorides such as CaCl₂ are selected as the agents. The variation in zeta potential of the colloidal particles in ethanol due to the addition of CaCl₂ (100 mol/m³) is also shown in Fig. 2. The zeta potential of the colloidal particles tends to increase positively by the addition of CaCl₂. Furthermore, the addition of CaCl₂ induced an interesting phenomenon in the ethanol solutions. Although the colloidal dispersion in these solutions was maintained just after the addition of CaCl₂, the deflocculation completed to obtain transparent solutions (sols) after 1–1.5 ks. The condensation products of titanium alkoxides are considered to be charged positively in the sols even after the deflocculation. The colloidal particles (agglomerates of the condensation products) are considered to dissolve into ethanol due to a strong repulsive force between the condensation products that is induced electrically by increasing positive charge. The deflocculation can be also achieved by the addition of other metal chlorides that release multi-valent cations.

However, the deflocculation using metal chlorides was induced only in the ethanol solutions, but not in the methanol and 2-propanol ones. The solvent effect on deflocculation can be interpreted from agglomerate state of the condensation products and dielectric constant of the solvents. When the hydrolysis of titanium tetraisopropoxide is performed in alcohols, the exchange of alkoxy groups is considered to occur. In fact, the DTA curves of the reaction products obtained in several alcohols suggest difference in residual alkoxy groups of the condensation products depending on the type of alcohol, as shown in Fig. 3. The reactivity of the alkoxy is sensitively changed by the exchange of alkoxy groups. In the present case, it was confirmed that the reactivity becomes high in order of methanol > ethanol > 2-propanol. Because the condensation products synthesized in methanol exhibit relatively strong agglomeration, the deflocculation is considered to be hardly achieved using CaCl₂. By contrast, the dielectric constant of solvent
becomes to the influential factor in determining deflocculation ability of the agents when 2-propanol is used as the solvent. The charge of the condensation products is rarely controlled using the agents in 2-propanol due to its low dielectric constant. Consequently, the deflocculation is difficult to be induced in 2-propanol. The deflocculated sols prepared in ethanol using CaCl$_2$ were utilized for the electrophoretic deposition process in this work.

3.2 Preliminary investigation for annealing process

In order to synthesize TiO$_2$ from the condensation products that are formed by the hydrolysis reaction, the specimens are required to be annealed under suitable conditions. The annealing behavior of the products was preliminary investigated after drying the colloidal particles that were prepared in ethanol without deflocculation.

Figure 4(a) shows experimental results of TG-DTA analysis for the condensation products synthesized in ethanol. Decrease in weight of the specimen due to dehydration is observed below $\sim$120°C. Thereafter, the pyrolysis of residual alkoxy groups seems to occur in the temperature range of 200–400°C. Because the exothermic reactions corresponding to the pyrolysis are detected at 200–300°C and 360–400°C, two types of residual alkoxy groups are suggested to exist in the condensation product. From the result of TG-DTA analysis, the residual alkoxy groups are found to be removed by annealing above $\sim$400°C.

Furthermore, the annealing behavior of the product is changed when the water-soaking treatment is subsequently performed. Figure 4(b) shows TG-DTA curves of the specimen after water-soaking for 3.6 ks. The exothermic reactions are also finished at $\sim$400°C. In addition, the reaction heat that

![Fig. 4 TG-DTA curves of the condensation products synthesized in ethanol. (a) as-prepared, (b) after water-soaking treatment.](image)

Fig. 5 XRD patterns of the condensation products synthesized in ethanol. (a) as-prepared, (b) after annealing at 400°C for 3.6 ks, (c) after annealing at 600°C for 3.6 ks.

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Fig. 6 Variation in current during the electrophoretic coating process at 30°C under the applied voltage of 5 V (200 mol/m$^3$ H$_2$O).

![Fig. 6 Variation in current during the electrophoretic coating process at 30°C under the applied voltage of 5 V (200 mol/m$^3$ H$_2$O).](image)
is released due to pyrolysis of the residual alkoxy groups significantly decreases by the water-soaking treatment. The residual alkoxy groups seem to be hydrolyzed additionally during the subsequent water-soaking process. The water-soaking treatment is considered to facilitate to remove residual alkoxy groups from the condensation products.

In order to determine annealing condition of the specimens, it must take the crystal type of TiO$_2$ obtained by annealing into account as well as the removal of residual alkoxy groups. Figures 5(a)–(c) show XRD patterns of the water-soaked specimens before and after annealing at 400°C.
and 600°C for 3.6 ks respectively. In the XRD pattern of the specimen before annealing, only halo patterns are observed (Fig. 5(a)). When the annealing was performed at 400°C, the specimens are found to contain anatase-type TiO$_2$ (Fig. 5(b)). However, trace of rutile-type TiO$_2$ can be observed in the specimens annealed at 600°C (Fig. 5(c)). Therefore, the condensation products should be annealed 400–500°C in order to obtain anatase-type TiO$_2$ without rutile formation. From the results of these preliminary investigations, the water-soaking and subsequent annealing are decided to be performed after the electrophoretic coating process for plates and lotus-type porous bodies of SUS 304.

3.3 Electrophoretic coating process using the transparent sols

The electrophoretic deposition for SUS 304 substrates was conducted in the sols (solvent: ethanol) deflocculated using 1 mol/m$^3$ CaCl$_2$. The concentration of H$_2$O in ethanol was set as being 200 (equivalent to alkoxide groups in titanium tetraisopropoxide) and 1000 mol/m$^3$. Figure 6 shows the variation in current during the electrophoretic deposition process (200 mol/m$^3$ H$_2$O, applied voltage: 5 V). The electrolytic current was induced under the applied voltage. Furthermore, the condensation products deposited successfully to form gel film on the substrate (cathode). The current decreases significantly with increasing deposition time. Because the current is related to kinetics of the electrode reactions, the deposition rate is considered to decrease with increasing deposition time.

Figures 7(a) and (b) show the SUS 304 plates after electrophoretic coating under the applied voltages of 1–5 V for 7.2 ks. When the electrophoretic deposition was conducted in the sol with 1000 mol/m$^3$ H$_2$O, transparent gel films were formed on the substrate. However, the films cracked and peeled off during subsequent drying process, as shown in Fig. 7(a). In this case, the gas generation due to electrolysis of H$_2$O can occur on the electrodes. The gas generation was likely to deteriorate the adhesion of deposited films on the substrates, and results in the fracture of the films during subsequent drying process.

By contrast, the films with particular interference color$^7$ were obtained when the sols with 200 mol/m$^3$ H$_2$O were used for the deposition process, as shown in Fig. 7(b). The coating layer seems to grow homogeneously under the applied voltage was 4–5 V. According to the measurement for thickness of the coating layer after drying using a contact probe method, their thickness reached 150–200 nm when the deposition was performed at 5 V for 7.2 ks, as shown in Fig. 8. In addition, no crack formation in the coating layer was induced during the drying process when the sols with 200 mol/m$^3$ H$_2$O were used for the deposition process. Therefore, H$_2$O concentration in the sols is one of the important factors in determining quality of coatings formed during this deposition process.

3.4 Characterization of the coating layer formed on SUS 304 substrates

After the coating process, the water-soaking and subsequent annealing processes were performed. No crack formation was observed in the specimens prepared using the sols with 200 mol/m$^3$ H$_2$O with OM and SEM after annealing at 400°C for 3.6 ks.

In order to clarify the chemical state of the coating layer, the XPS analysis of the specimens with and without water-soaking was performed after annealing at 400°C for 3.6 ks. The chemical shift of Ti$_2$p$_{3/2}$ and Ti$_2$p$_{1/2}$ spectra clearly indicates that the constituent phase of the coating layer is TiO$_2$ (Fig. 9(a)). Furthermore, Ca$^{2+}$ ions are clarified to be doped successfully into the TiO$_2$ coating layer as shown in Fig. 9(b). The doping of Ca$^{2+}$ ions in the coating layer is expected to enhance their biocompatibility and bioactivity.$^9$ There was no difference in Ti$_2$p and Ca$_2$p spectra between the specimens with and without water-soaking process. However, the feature of C$_1$s spectrum is clearly different depending on the difference in the after-treatments. The coating layer without water-soaking prior to the annealing process contains a trace of impurity carbon that is derived from residual alkoxide groups even after annealing at 400°C for 3.6 ks as shown in Fig. 9(c). However, the impurity carbon can be removed sufficiently by combining water-soaking and annealing process. The water-soaking process is found to facilitate to remove residual alkoxide groups in the coating layers.

This process can be also applied for the lotus-type porous bodies of SUS 304. Figure 10 shows the cross-sectional OM micrograph of a porous body after the coating process. The specimen was cut using an electric discharge machining equipment before the OM observation. The particular interference color on the pore surface clearly indicates that the coating layer was formed even on inner surface of the open pores. The coating on the porous bodies of SUS 304 was accomplished successfully using the electrophoretic sol-gel deposition process.

The electrophoretic coating process that is developed in this work can be applied to other coating materials if the sols of the precursor are deflocculated sufficiently. The deflocculation is considered to be one of the important points for forming homogeneous coating layers on the substrate materials that have complicated shapes by this process.

4. Conclusions

In the present work, an electrophoretic sol-gel coating process was investigated for forming ceramic layers on the metallic materials with complicated shapes such as porous metals. The formation of TiO$_2$ coating layer on SUS 304 substrates was examined as an example of this process. The main results obtained in this work are summarized below:

1. The colloidal particles that are synthesized by the hydrolysis reaction of titanium tetraisopropoxide exhibit a positive zeta potential in alcohol solvents. By the addition of metal chlorides with multi-valent cations such as CaCl$_2$, the zeta potential of the colloidal particles in ethanol increases positively and the particles are deflocculated sufficiently to form a transparent sol.

2. The electrophoretic coating process on plates and lotus-type porous bodies of SUS 304 is performed successfully by using the sols prepared by the deflocculation of the colloidal solutions. H$_2$O concentration in the sols...
influences significantly on the quality of coatings after drying.

(3) The coating layer that is composed of anatase-type TiO$_2$ can be obtained by the water-soaking and subsequent annealing at 400°C for 3.6 ks. The cations that are derived from the deflocculation agents, such as Ca$^{2+}$, can be doped into the coating layers through the coating process.

REFERENCES