

Preparation and Impurity Control of the BaTiO₃ Coatings by Micro Arc Oxidation Method

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BaTiO₃ coatings were prepared by micro arc oxidation (MAO) method. Only Ba(OH)₂ was dissolved in the electrolyte and process time was less than 30 min. Commercial purity Ba(OH)₂ (97%) containing BaCO₃ as impurity was used in preparing the electrolyte. XRD showed that the coating was composed of largely BaTiO₃, and in some process conditions, small quantity of impurity, BaCO₃, was characterized in the coating layer. The quantity of BaCO₃ could be controlled to negligible quantity by regulating the applied voltage and duration time of the MAO process.

Keywords: BaTiO₃, micro arc oxidation (MAO), BaCO₃, impurity control

1. Introduction

Micro arc oxidation (MAO) method can produce thick ceramic coating layers on the so called 'valve metals' like Ti, Al, Mg, Ta, etc., using the plasma made by arc discharge over the break-down voltage.¹⁻⁴⁾ These ceramic coatings can be used as heat, corrosion, and wear resistant layers of the metallic substrate. Also, titania coatings on Ti can enhance the biocompatibility of the Ti implants.⁵⁾

Another important feature of micro arc oxidation is that it can synthesize more complex ceramic compounds other than simple oxide of the substrate metal.⁶⁻⁹⁾ Some researchers have investigated the synthesis of perovskite-type coating layers on Ti substrate, as BaTiO₃⁶⁻⁸⁾ and SrTiO₃.⁹⁾ Among them, BaTiO₃ is the promising one due to its piezoelectric, ferroelectric, and optoelectric properties. The advantage of MAO method compared with the conventional thermal synthesis processes of BaTiO₃ is that it can produce thick BaTiO₃ layers in relatively short time scale by simply applying voltage of ~100 V to the Ti substrate immersed in the electrolyte containing Ba²⁺ ion. Usually, solutions containing Ba(OH)₂ · 8H₂O or Ba(CH₃COO)₂ were used as electrolytes. Although using high purity raw materials, the solubility of CO₂ gas into the solutions containing Ba(OH)₂ · 8H₂O is high and BaCO₃ is composed during the process, and hot ammonia water is used for cleaning the specimen after coating to

minimize BaCO₃ formation. Also, in some process conditions, suspended powders are attached to the coating layer during the arc discharge.¹⁰⁾ So, impurity particles in the electrolyte can be trapped in the coating.

In this investigation, Ba(OH)₂ · 8H₂O of 97% purity, containing BaCO₃ powders for impurity, was used as raw material. The suspended powders can be trapped in the oxide layers during the MAO process. So, the process conditions for reducing BaCO₃ in the BaTiO₃ coating were studied by varying process variables like maximum applied voltage and duration time of the MAO process.

2. Experimental

Pure Ti of grade 1 was used in this investigation as the substrate for BaTiO₃ coating. Ti plate was cut to 10 × 10 × 1 dimension, polished to #1500 emery paper, and rinsed by acetone, ethyl alcohol, and distilled water using ultrasonic cleaner.

The electrolyte was prepared by dissolving Ba(OH)₂ · 8H₂O (97% purity) into the distilled water and heated to 80 °C. The concentration of the solution was 0.5 M. The reason for heating the solution to 80 °C is that the solubility of Ba(OH)₂ · 8H₂O is not sufficient to synthesize BaTiO₃ at around room temperatures and increases abruptly around 80 °C. Throughout the oxidation process, the temperature of the solution was held at 80 °C. As sufficient concentration of Ba(OH)₂ · 8H₂O could be achieved by heating the solution, there was no need to add acetic acid to form Ba(CH₃COO)₂. Also, in this investi-

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gation, NaOH was not added to the solution, which was usually used to set the pH of the solution around ~14.⁸⁾

The solution of 80 °C dissolved 0.5 M of Ba(OH)₂ · 8H₂O completely, and some insoluble impurities were suspended in it. By filtration and XRD, the insoluble impurities were found to be mainly BaCO₃. A DC power supply (maximum voltage and current: 500 V and 2 A, Analog Research Systems Co., Korea) was used in this investigation. DC pulse (on-off mode) with 50% duty and 100 Hz frequency was applied and the maximum applied voltage of the pulse was varied. Process duration time was also controlled to minimize the impurity powder attachment. The prepared coatings were characterized using XRD.

3. Results

The condition of treatment is listed in table 1. In MAO process, arc starting voltage and other critical voltage values (e.g. the minimum potential needed to form BaTiO₃) are affected by the chemical species and concentration. The maximum voltage of the pulse used in this investigation was higher than prior works in the literature,^{6,8)} and this is due to the difference of chemical species and concentration of the electrolytes. Another reason is due to the fact that the primary concern of this

investigation is to discover the appropriate process conditions to minimize the attachment of the impurity BaCO₃ in the raw materials and consequently suggest some process conditions of low cost using relatively low purity materials. So, sufficiently high voltages are applied to form BaTiO₃. Fig. 1 shows the XRD results of the BaTiO₃ synthesis MAO process. In the figure, BaTiO₃ peaks are found at all process conditions tried. With the increment of applied voltage and duration time, the intensity of peaks from Ti substrate decreases while the intensity of peaks from formed BaTiO₃ layers increases. Peaks from TiO₂ were not characterized. Schreckenbach et al.⁶⁾ studied the distribution of BaTiO₃ and other titania phases and discovered that the majority of the coating layers was BaTiO₃ and only small portion of passivating titania layers was found in the vicinity of the coating layers/Ti substrate interface. So, considering the thickness of the coatings and fraction of the titania phases, peaks by titania phases would be difficult to characterize, although some peaks from the Ti substrate are still found in the condition 4 in table 1.

Some peaks by BaCO₃ are found in process condition 3 and 4. Although it is difficult and somewhat ambiguous to discriminate the BaCO₃ peaks from the ground noise level and determine the existence of those peaks, there exists an inclination that the peaks from BaCO₃ become clear and show higher intensity by increasing the applied voltage and process duration time. So, it can be found that the amount of impurity particles attached and trapped in the coating layer also increases with the increment of applied voltage and duration time. So, for the suggestion of the appropriate process conditions with low BaCO₃ level, it is necessary to take more experiment with various duration time and applied voltage level.

Table 1. Process conditions for BaTiO₃ synthesis.

Process condition	Max. voltage (V)	Duration time (min)
1	85	5
2	100	5
3	100	30
4	160	5

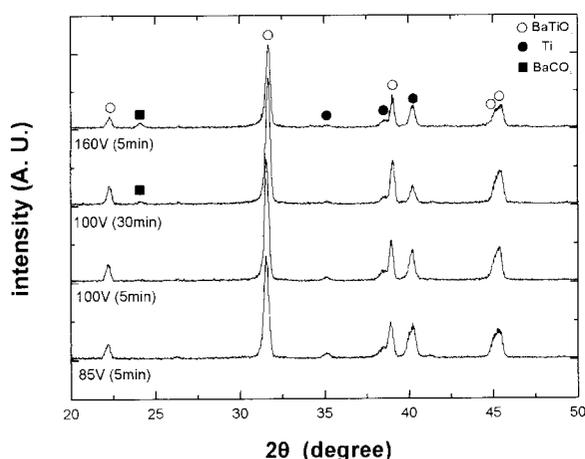


Fig. 1. XRD results of BaTiO₃ synthesis.

4. Discussions

In Figs. 2~4, XRD results of various process time and applied voltage are suggested. In Fig. 2, when applied voltage is 85 V, peaks from BaCO₃ can be found in the process time of 15 min. When applied voltage is 100 V, BaCO₃ peaks are found in every process time tested, as shown in fig. 3. It is notable that for the process time of 5 min, BaCO₃ peaks can be found in Fig. 3, while not found in Fig. 1. Although the criterion of peak existence is qualitative in this investigation, the results from all other process conditions are clear, except for 100 V-5min. From Figs. 1~3, it can be concluded that the attachment of BaCO₃ increases with the increment of applied voltage and process time. For 85 V, BaCO₃ is not formed when process time is 5 or 10 min. However, when the applied voltage is 100 V, the characterization

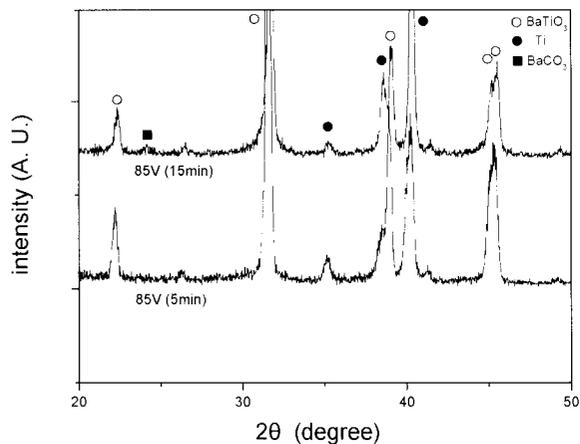


Fig. 2. Characterization of BaCO₃ peaks for the applied voltage of 85V with process time 5 and 15min.

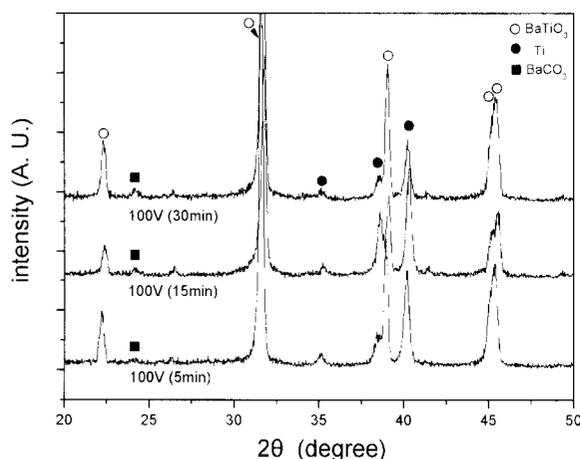


Fig. 3. Characterization of BaCO₃ peaks for the applied voltage of 100V with process time 5, 15, and 30min.

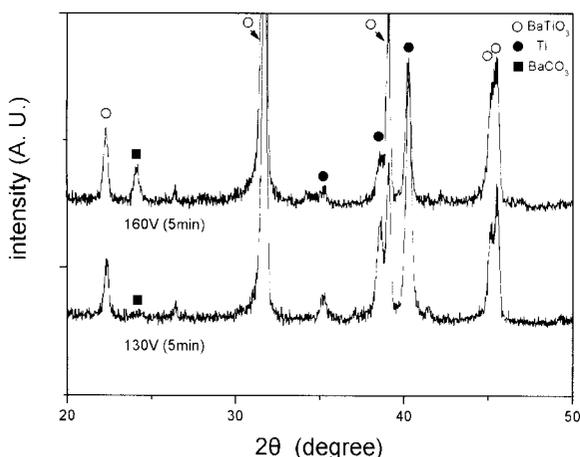


Fig. 4. Characterization of BaCO₃ peaks for the applied voltage of 130V and 160V with process time 5min.

Table 2. Optimization of MAO process for reducing attachment of BaCO₃.

Applied voltage	Process time		
	5min	15min	30min
85V	×	○	-
100V	○	○	○
130V	○	-	-
160V	○	-	-

* × : negligible quantity in the XRD characterization
 ○ : characterized, - : not tested

of BaCO₃ is somewhat unclear for process time of 5 min. So, for the higher applied time, BaCO₃ is expected to be characterized within 5min's process time. In Fig. 4, XRD results of applied voltages of 130 and 160 V, and process time of 5 min are drawn. As expected, BaCO₃ peaks are clear in the figure. In all the process conditions tried, BaTiO₃ is the dominant phase and the fraction of residual titania is negligible. The attachment of BaCO₃ increases by increasing applied voltage and process time. So, to minimize the attachment of BaCO₃, selection of lower applied voltage and shorter process time would be favorable. In table 2, process conditions for minimizing the BaCO₃ are summarized.

5. Conclusions

The synthesis of BaTiO₃ and minimization of impurity BaCO₃ were investigated. By heating to 80 °C, sufficient amount of Ba(OH)₂ · 8H₂O (97% purity) could be dissolved in the electrolyte. By controlling maximum applied voltage and process time, the attachment of impurity BaCO₃ could be controlled. In the XRD results, as the applied voltage and process time increase, peaks from BaCO₃ become clear. To minimize the attachment of BaCO₃ in the electrolyte, selection of lower applied voltage and shorter process time would be favorable.

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