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Development of New Titanium Coating Material (CaTiO₃-aC) with Modified Thermal Decomposition Method

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Abstract: We developed a novel method for titanium coating material using modified thermal decomposition technique, specifically focusing on presence of CaTiO₃ and carbon C. Two layers of thin film coating composed of CaTiO₃-amorphous carbon compound (CaTiO₃-aC) and hydroxyapatite (HA) were generated on titanium surface. In this method, ratios of Ca/P as well as Ca/Ti, sintering temperature and sintering velocity were carefully planned. Within crystal structure of CaTiO₃ granules, 4 atomic % of carbon in amorphous state was included. By our method, inclusion of carbon in HA suggested formation of carbonate apatite. Regarding with attachment-detachment experiment at titanium surface, adhesion strength was 2.5 times stronger in CaTiO₃-aC/HA coating substrate as compared to HA only coating material. Results of the novel developed modified thermal decomposition method suggested that the 2 layers biomaterial composed of CaTiO₃-aC (0.6 μm) and carbonate apatite-included HA (2.4 μm) can be used as a coating material on titanium surface.

Key words: Biomaterial, Titanium, Carbon, HA, Coating material, CaTiO₃-aC

Introduction

Titanium implant has now been used in the clinics after reforming its surface with several methods such as blasting. Although titanium implant possesses excellent mechanical strength and biocompatibility, affinity to living bone is very low due to its bioinert feature¹. On the other hand, hydroxyapatite (HA) has excellent bone conductivity with osteogenic tissue, and thus has been widely used as a filling material²⁻⁴. Thus HA is generally used as a coating material to improve bone conductivity of metal materials such as titanium and its alloys, stainless steel, and Co-Cr-Mo alloys^{1,5,6}. Plasma-sprayed HA coating of titanium implant is one of the most commonly used methods in the clinics⁷⁻¹⁰. However, there are many shortcomings of this method. The plasma method is performed at high surface temperature (1200 °C), and coating film is thick (50 μm) and is easy to detach^{6,7,11,12}. It has also been known that bone bonding ability decreases in coatings performed with this method. Moreover, HA coating formed by plasma method consists of α-TCP, and its chemical bonding ability

with titanium is weak. There are also concerns of resorption in biological environment^{9,13,14}.

To solve these problems, development of a different method other than direct plasma-sprayed HA coating to implant substrate is necessary. Conditions for development of such a method include:

a thin HA layer without α-TCP, and similar level of crystal structure and components with living body from a perspective of biological affinity, necessity of development of a material with possible thinnest but strongest ability of adhesion at interface between HA and titanium substrate, and this adhesive material should have biological affinity with long-term bioactivity in living bone.

Herein, we report development of a film-like new titanium coating material containing CaTiO₃ and carbon with modified thermal decomposition method.

Ukegawa performed plasma coating of HA at titanium implant surface and examined bone bonding ability¹⁰. Although presence of perovskite (CaTiO₃)-like substrate was reported as an adhesive interposition material (between TiO₂-HA), structure as well as its involvement in adhesion was unknown at the time.

Preparation of perovskite (CaTiO₃) is normally made by dry method. Thus it could not be synthesized other than powder

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particles, and its film coating type was not possible. Zhou and Akao⁶⁾ have reported excellent bone-conductivity of HA coating by thermal decomposition method using 2 layers of coating method composed of HA and a film compound, which consists of perovskite (CaTiO₃) as a main component. We focused carbon in organic solvent of the liquid used in thermal decomposition method. This carbon has been known to improve wetness of metal¹⁵⁾. Thus we developed modified thermal decomposition method, considering that by providing existence of carbon in addition to CaTiO₃ within crystal structure of adhesive material, adhesive strength would increase. We named our new material as CaTiO₃-amorphous carbon (aC) compound.

In this study, we used CaTiO₃-aC as coating material and examined adhesive strength with titanium.

Material and Methods

1. Preparation of CaTiO₃-aC as well as coating solution

Highly pure CaCO₃ was heated at 1050 °C in normal air for 2 hours, and CaO was obtained.

28.8 gram of 2-ethyl hexanic acid (CH₃ (CH₂)₃CH (C₂H₅) COOH) was put into 100 ml conical flask. While it is being heated from 100 °C to 120 °C, 3.36 gram of this calcium oxide powder was gradually added and 2-ethyl hexane calcium ([CH₃ (CH₂)₃CH(C₂H₅) COO]₂Ca) solution was prepared.

After cooling, it was dissolved by adding 48 gram of 1-butanol (CH₃ (CH₂)₃OH), and followed by addition of 170 gram of titanium tetraisopropoxide (Ti [OCH (CH₃)₂]). Then well stirring was performed, and about 110 ml of stock application solution was prepared. The stock solution had a specific gravity of 0.92, and was clear, yellowish brown viscose material. CaTiO₃-aC application solution was obtained by diluting the stock solution 3 times (mass ratio) with 2-propanol (CH₃CH (OH) CH₃).

For HA solution, it was prepared following the similar method mentioned above. 2-ethyl hexane calcium ([CH₃ (CH₂)₃CH (C₂H₅) COO]₂Ca) was dissolved in 42 g of 1-butanol (CH₃ (CH₂)₃OH). Then 10.7 gram of bis (2-ethylhexyl) phosphate ([CH₃ (CH₂)₃CH (C₂H₅) CH₂O]₂POOH) and 2.9 gram of distilled water were added, followed by well stirring. Finally 100 ml of the solution was prepared. This solution was clear, viscose liquid and had a specific gravity of 0.89. Hydroxyapatite (HA) application solution was obtained by diluting the stock solution 2 times with 2-propanol (CH₃CH (OH) CH₃).

2. Preparation and analysis of test pieces of each titanium coating plate

Etching of JIS2 type titanium plate with 0.7 mm thickness and 35 mm angle was performed by boiling it in 6N HCl solution for 15 minutes. Then it was rinsed one time in tap water and 3 times in distilled water, and then was dried at 60°C.

The titanium plate was soaked in each of the above C and HA application solutions for 5 minutes. The materials were then slowly

pulled up in vertical direction, and dried 10 minutes at room temperature and 20 minutes at 110 °C. The material was then quickly heated at 650°C in a firing furnace for 10 minutes, followed by rapid cooling.

Basic handling of the coating method:

1 layer coating method with CaTiO₃-aC is repeated 3 times as mentioned in method 2 (including soaking the titanium plate in CaTiO₃-aC application solution, firing as well as rapid cooling).

1 layer coating method with HA is repeated 10 times as mentioned in method 2 (including soaking the titanium plate in HA application solution, firing as well as rapid cooling).

Preparation and examination of the powder for carbon analysis

Test piece of 1 layer coating with CaTiO₃-aC was prepared, and distribution state of carbon within CaTiO₃-aC was observed by TEM as well as EF-TEM (Energy Filtered TEM). TEM observation sample was prepared as follows: Surface of the sample was shaved by scratching with a diamond pen. Shaved powder particles were dispersed in ethanol, followed by dropping on micro grid (a grid attached to a plastic film with carbon-coated micro hole) and drying. For EF-TEM analysis, JEM-3010 (speed voltage 300 kV) was used (JEOL co. Ltd., Tokyo, Japan).

Using the same material, EELS (Electron Energy-Loss Spectroscopy) analysis was performed. This method provides element analysis of the sample through passing of an electronic energy spectrum. For EELS analysis, JEM-2200FS was used (JEOL co. Ltd., Tokyo, Japan).

Measurement and analysis of the layer thickness as well as cross-sectional observation

After preparation of test piece of 1 layer coating with CaTiO₃-aC, 1 layer of HA coating was performed on it. Then these 2 types of coating (CaTiO₃-aC /HA- CaTiO₃-aC /HA) were repeated, and a test piece of 4 layers coating was prepared (hereafter called as test piece of 4 layers coating). For performing cross-sectional SEM analysis of the 4 layers coating test piece, it was processed with cross-sectional polisher (JEOL SM-09010). Then it was observed and analyzed with SEM (JEOL JSM-7000F)-EDX(ED-2300F). And taking mass increase and theoretical density of the piece into account (CaTiO₃: 4.04g/cm³, HA: 3.16g/cm³), thickness of each of CaTiO₃-aC and HA layer was calculated.

Measurement of adherence strength

Etching of grade 2 titanium plate with 15 × 15 × 0.7 mm³ size was performed by boiling it in 6N HCl solution for 20 minutes. Then it was rinsed 3 times in distilled water. Roughness of etching surface of the titanium plate (Ra) measured by a touch-needle type diamond surface roughness calculator was 2.5 mm. Using

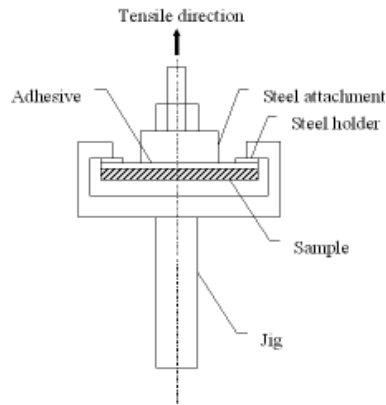


Figure 1. Model of device for pull-up strength test between titanium and coating material based on JIS A 6909:2003.

this titanium plate, first test piece of 1 layer coating with CaTiO₃-aC was prepared, then 1 layer of HA coating was added. At this step test piece of 2 layers with CaTiO₃-aC/HA coating (hereafter called as test piece of 2 layers coating) was prepared. As controls each of test pieces of 1 layer coating with CaTiO₃-aC or HA was prepared using the same titanium plate. Adhesive strengths of film layers of these 3 test pieces were measured by a standard method (JIS A6909: 2003, architectural coating material). Coating plate was attached to steel table by 2 liquid type epoxy adhesive agent (araldite) and fixed for 24 hours at room temperature. Pull up strength test was performed at a 0.1 mm/min of crosshead speed using universal test machine (Autograph AK-100KG, Shimadzu Co. Ltd., Tokyo, Japan)(Figure 1). The measurement was repeated 6 times.

Results

Distribution state of carbon-included CaTiO₃-C

At high power magnification of TEM image, granule of coated CaTiO₃-aC showed micro crystal structure with diameter of 10-20nm. Aggregates of these micro crystals resulted in formation of multicrystals (Figure 2). Electronic diffraction data showed that crystal system of CaTiO₃-aC belongs to the orthorhombic system (JCPDS-International Centre for Diffraction Data) (Figure 2, right down inset).

At EELS analysis, type of element within CaTiO₃-aC was clarified (Figure 3). Carbon (C) peak in addition to Ca, Ti and O peaks suggested that C element included in CaTiO₃-aC coating material (Figure 3).

At TEM image of CaTiO₃-aC and element mapping with EF-TEM as well as color mapping of these analysis, C, Ca, Ti and O distributions were observed (Figure 4). Though Ca, Ti and O distributed in all area, C was localized indefinitely. Right down color mapping image also confirmed indefinite distribution of carbon (Figure 4). All these analysis indicated that C existed in an indefinite form within multicrystals of CaTiO₃-aC coating

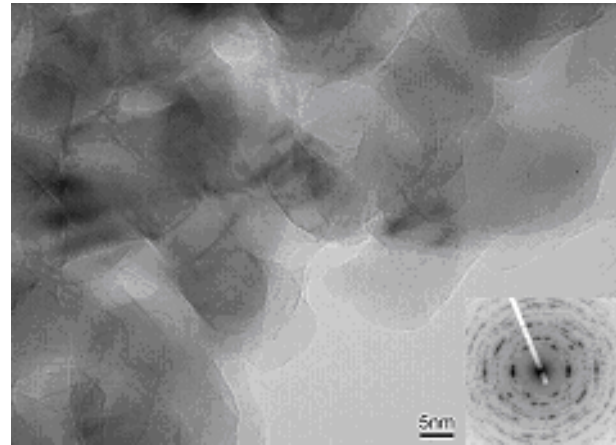


Figure 2. High-power TEM magnification image and electron diffraction pattern of CaTiO₃-aC coating powder. At high-power TEM magnification image, coated CaTiO₃-aC was shown as conglomerated multicrystals of clustered microcrystals. At electron diffraction pattern (right down inset), CaTiO₃-aC crystal system belongs to the orthorhombic system (JCPDS-International Centre for Diffraction Data).

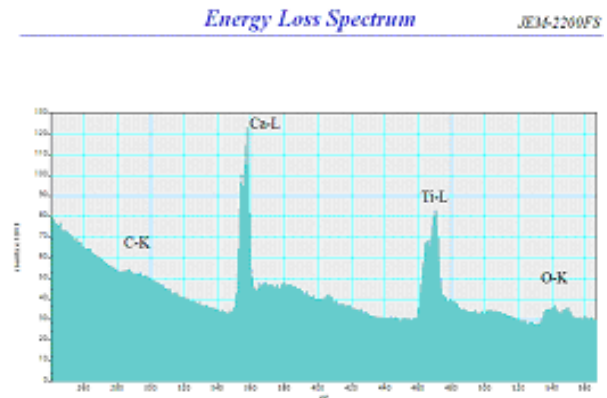


Figure 3 Element analysis of CaTiO₃-aC by EELS. Carbon (C) peak in addition to Ca, Ti and O peaks suggested that C element included in CaTiO₃-aC coating material.

material.

Cross-sectional observation of 4 layers coating material and quantitative analysis of the elements at the each layer

At cross-sectional analysis of 4 layers coating material with SEM, 4 layers structure of CaTiO₃-aC/HA/CaTiO₃-aC/HA was observed on the titanium base (Figure 5). From mass increase and theoretical density of the CaTiO₃ (4.04g/cm³), thickness of CaTiO₃-aC film layer was calculated to be 0.6 ± 0.1μm. Similarly, from mass increase and theoretical density of the HA (3.16g/cm³), thickness of HA film layer was calculated to be 2.4 ± 0.4 μm.

Next quantitative examination of C at CaTiO₃-aC layer was performed by element analysis of each of the coated 4 layers (Figure 6, Table 1). Measurement of element ratio (atomic %) at CaTiO₃-aC layers was described as follows: As shown in composition image (reflect electron image) of figure 6, asterisk mark (*) shows irradiation center of electronic beams at EDS analysis. As shown in this image, enlargement of electron beams

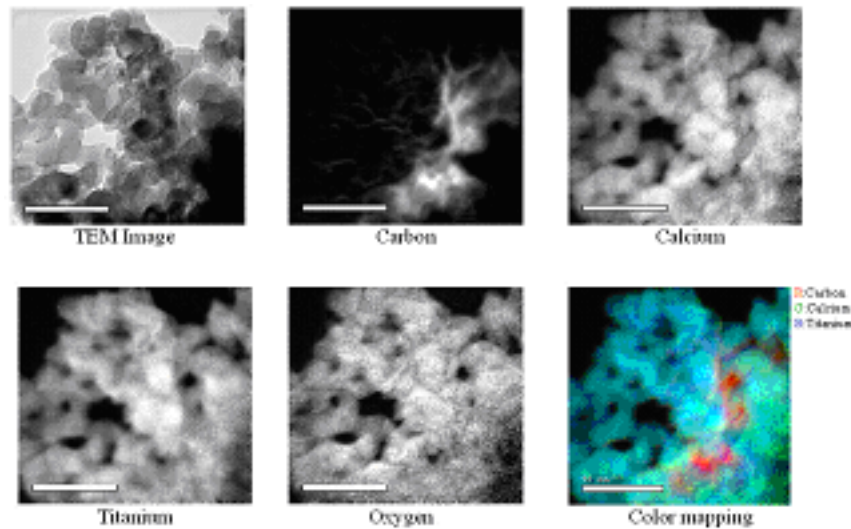


Figure 4 TEM image of CaTiO₃-C, element mapping with EF-TEM and color mapping of these elements. Though Ca, Ti and O distributed in all area, C was localized only at some areas. Right down color mapping image also confirmed indefinite distribution of carbon. C, red; Ca, green; Ti, blue.

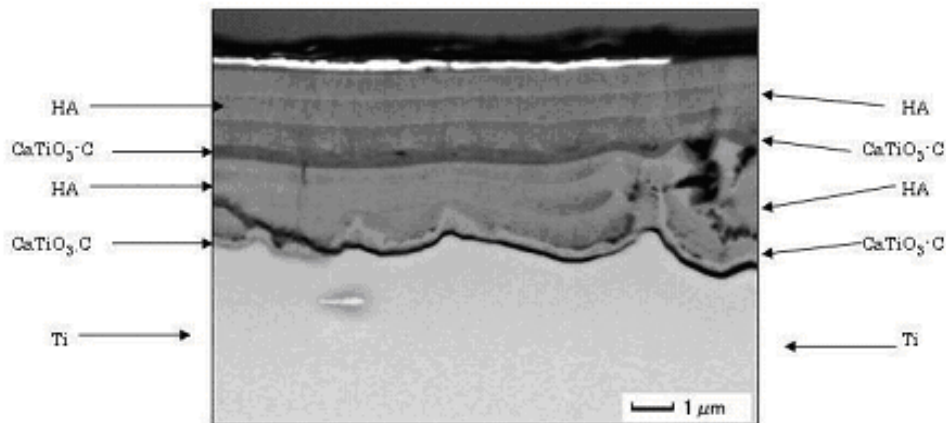


Figure 5. Cross-sectional analysis of 4 layers (CaTiO₃-aC/HA/CaTiO₃-aC/HA) coating material (about 5mm) at titanium surface border (SEM, reflect electron image). From mass increase and theoretical density of the CaTiO₃ (4.04g/cm³), thickness of CaTiO₃-aC film layer was calculated to be $0.6 \pm 0.1 \mu\text{m}$. Similarly, from mass increase and theoretical density of the HA (3.16g/cm³), thickness of HA film layer was calculated to be $2.4 \pm 0.4 \mu\text{m}$.

is circular with a diameter of about 1mm from center of each irradiation. Because results of element analysis at each of point 040 (CaTiO₃-aC layer-second layer), point 042 (HA layer-first layer) and point 043 (CaTiO₃-aC layer-first layer) also include information from adjacent layers, pure measurement of each element ratio could not be done. Element ratio of CaTiO₃-aC was considered to be calculated more precisely in the second layer of CaTiO₃-aC (point 040) than in the first layer of CaTiO₃-aC (point 043) because frequency of sintering of the previous one is less than the latter one. However, results of Ca, O, P and C element analysis were considered to consist of components of adjacent HA layer. Since Ti was not included in HA, result of Ti element analysis (8.57 atomic %) was considered to represent only component of CaTiO₃-aC layer. Because C should not exist at the

point 045 (Ti base), the calculated value of 5.81% was considered as background. Thus subtraction of this carbon ratio (5.81%) from the carbon ratio of 9.67% at point 040 will give us the actual ratio of carbon (3.86%) at this area. When similar calculations are done for O and Ca, actual ratios for O (58.18-0=58.18) and Ca (16.48-0.84=15.64) (atomic%) will be obtained. From these findings, element ratios of CaTiO₃-aC (atomic%) were found to be as 15.64 for Ca, 8.57 for Ti, 58.18 for O, and 3.86 for C. Our results demonstrated that this novel compound consists of about 4 atomic% carbon.

Likewise as shown in table 1, mass% of C at point 040 is 4.97 mass%, and when the background level of Ti base (point 045) was subtracted from this ratio, the actual ratio was found to be 3~4 mass%.

Elemental analysis by SEM+EDS

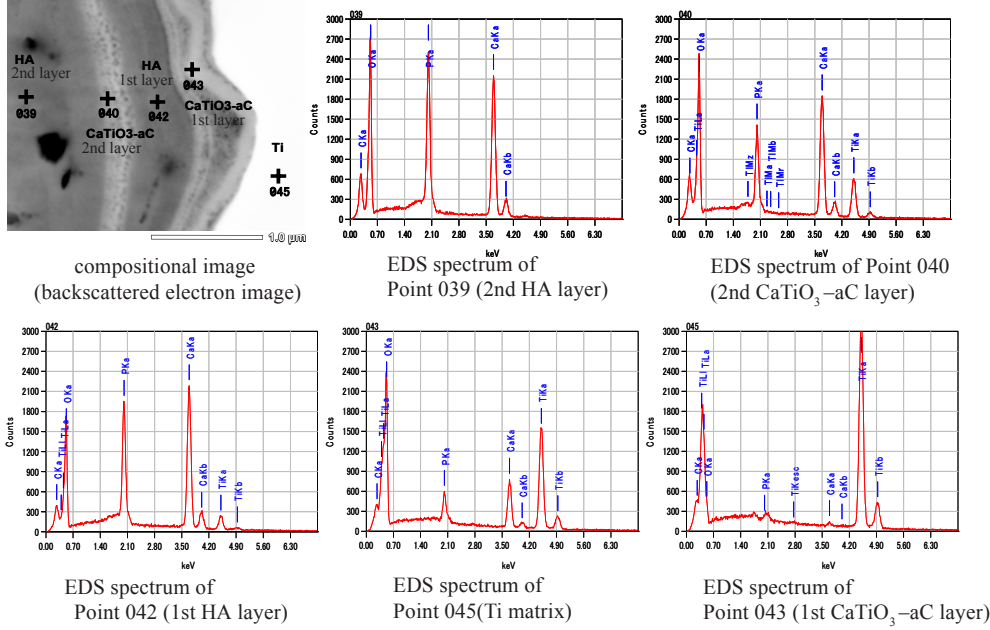


Figure 6. Element analysis at each layer of 4 layers coating material. Element analysis by SEM+EDS. Composition image (reflect electron image). X-ray spectrum. Ti:Ti matrix containing measurement point 045, CaTiO₃-aC 1st layer: containing measurement point 043, HA 1st layer: containing measurement point 042, CaTiO₃-aC 2nd layer: containing measurement point 040, HA 2nd layer: containing measurement point 039.

Table 1: Density of each layer element (Figure 5,6) by SEM+EDS (standardless method)

	C	O	P	Ca	Ti
Ti matrix	1.53 mass%	0 mass%	0.13 mass%	0.73 mass%	97.61 mass%
45	5.81 at. %	0 at. %	0.19 at. %	0.84 at. %	93.16 at. %
CaTiO ₃ -aC layer (1st)	1.63 mass%	39.6 mass%	3.01 mass%	10.33 mass%	45.43 mass%
43	3.46 at. %	63.24 at. %	2.48 at. %	6.59 at. %	24.23 at. %
HA layer (1st)	2.82 mass%	34.19 mass%	16.09 mass%	39.51 mass%	7.39 mass%
42	5.82 at. %	53.01 at. %	12.89 at. %	24.46 at. %	3.83 at. %
CaTiO ₃ -aC layer (2nd)	4.97 mass%	39.81 mass%	9.41 mass%	28.25 mass%	17.56 mass%
40	9.67 at. %	58.18 at. %	7.10 at. %	16.48 at. %	8.57 at. %
HA layer (2nd)	6.98 mass%	41.20 mass%	17.94 mass%	33.88 mass%	0 mass%
39	12.68 at. %	56.22 at. %	12.65 at. %	18.45 at. %	0 at. %
Ti :Ti (TP35), H:< 0.013,O: <0.20, N:< 0.05, Fe:< 0.25(JIS H 4600-1979)					
Density of element for ideal materials.					
	C	O	P	Ca	Ti
CaTiO ₃	0 mass%	35.3 mass%	0 mass%	29.47 mass%	35.23 mass%
	0 at. %	60 at. %	0 at. %	20 at. %	20 at. %
Ca ₁₀ (PO ₄) ₆ (OH) ₂	0 mass%	38.70 mass%	17.02 mass%	44.06 mass%	0 mass%
	0 at. %	56.41 at. %	12.82 at. %	25.64 at. %	0 at. %

On the other hand, at the second HA layer (point 039), because Ti is 0%, element ratio calculated at HA layer is highly likely to

be pure. Thus when background of Ti base (point 045) is subtracted, element ratios are found to be 17.61 for Ca (18.45-

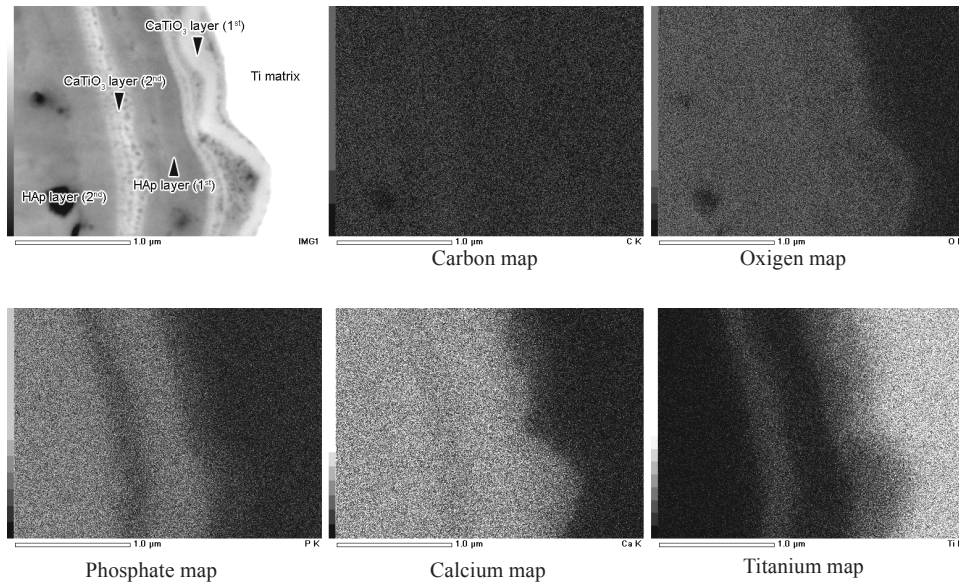


Figure 7. EDS analysis at 4 layers coating. Existence of high-density carbon at CaTiO₃-aC layer was confirmed.

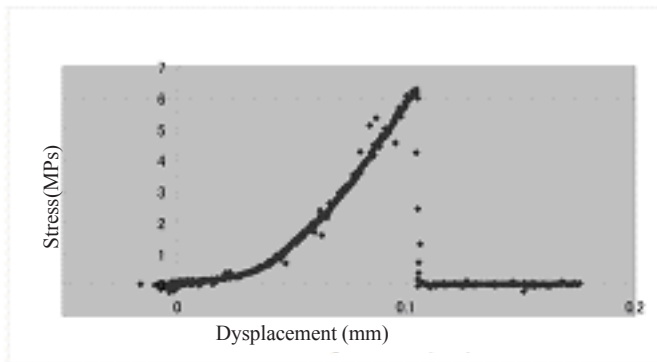


Figure 8. Stress curve plot of pull up strength test of 1 layer CaTiO₃-aC coating.

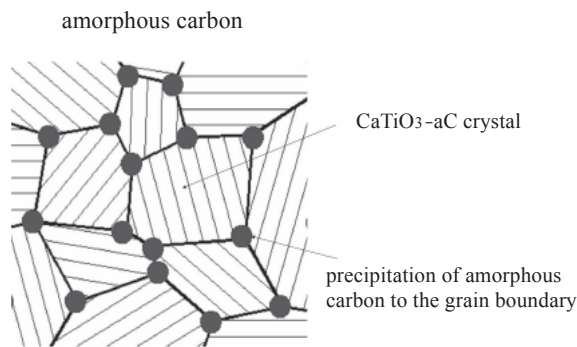


Figure 9. Expected structure of CaTiO₃-aC complex

0.84), 12.46 for P (12.65-0.19), 56.22 for O (56.22-0), and 6.87 for C (12.68-5.81) atomic%). This result suggests that HA prepared by the current method includes a large quantity of carbon and possesses characteristics of carbonate apatite.

Moreover at cross-sectional image, EDS analysis showed that though P at CaTiO₃-aC layer decreased, peaks of Ca, Ti and O

Table 2. Adhesive strength between the coating and titanium.
Sample: 1 layer coated CaTiO₃-C, 2 layer coated CaTiO₃-C/HA, 1 layer coated HA. Adhesive strength (MPa), Surface roughness (Ra).

Sample	Adhesive strength (MPa)	Surface roughness (Ra)
CaTiO ₃ -C, 1 Layer Coating	6.3 ± 0.7	2.5 ± 0.5
CaTiO ₃ -C/HA, 2 Layer Coating	4.9 ± 0.6	2.5 ± 0.5
HA 1 Layer Coating	2.0 ± 0.4	2.5 ± 0.5

were high, and the layer of CaTiO₃-aC interpositioned between the inside and outside HA layers consisted of high density carbon (Figure 7).

Adherence strength of Ti base and coating materials

From result of pull up strength test of 1 layer CaTiO₃-aC coating method, stress curve plotted is shown in figure 8. Results of adhesive strength test between each coating layer and Ti base material were found to be 3 times higher for CaTiO₃-aC alone (6.3 MPa) and 2.5 times stronger for CaTiO₃-aC-interpositioned HA coating (4.9 MPa) as compared to HA coating alone (2.0 MPa) (Table 2). This result suggests that CaTiO₃-aC functions for improvement of the adhesive strength between Ti and HA.

Discussion

1. Characteristics of titanium coating material (CaTiO₃-aC) prepared by modified thermal decomposition method

Recently perovskite (CaTiO₃) and similar materials have been paid attention due to their use as an adhesive substrate for titanium coating material^{6,10}, as well as their novel biomaterial characteristics with high bone conductivity ability¹⁶⁻²⁰. And

development of an insoluble HA coating method instead of plasma-sprayed coating has been rushed. Within CaTiO₃ coating method, only 50nm of ultra-thin layer can be done by ion sputtering¹⁷⁻²⁰, and thus regarding with absence/presence of bone conductivity, opinions are not constant. Therefore thermal decomposition method took attention of the researchers⁶.

In this study, we developed a modified thermal decomposition method for HA and CaTiO₃ coating. This modification resulted in formation of a novel compound (CaTiO₃-aC) for the coating, which consists of carbon in addition to perovskite (CaTiO₃). Our results clarified the following facts:

Thickness of CaTiO₃-aC ($0.6 \pm 0.1 \mu\text{m}$) and HA ($2.4 \pm 0.4 \mu\text{m}$) layers is extremely thin.

Since CaTiO₃-aC is composed of granules with a size of 10-20 nm and the carbon is indefinitely localized, the carbon was considered to be in an amorphous state.

Content of amorphous carbon within CaTiO₃-aC coating is about 4mol%. Besides HA layer also consists of carbon. Thus HA layer was considered to have characteristics of carbonate apatite.

When CaTiO₃-aC was used as a bonding material between titanium and HA, the adhesive strength was 3 times stronger as compared to HA alone coating.

Furthermore our group has also examined physicochemical analysis and bone conductivity of the novel material.

According to study of Okauchi et al. (preparation in press), following facts were clarified: Both CaTiO₃-Ca and HA was found to have minus charge; Solubility of CaTiO₃-aC was 1/10 of HA.

Likewise, according to study of Andrea et al. (unpublished data) and Inoue et al. (preparation in press), no cytotoxicity of CaTiO₃-aC was detected. And following facts were made clear:

CaTiO₃-aC had similar level of bone conductivity with HA;

CaTiO₃-aC was involved in calcification reaction in appropriate cellular environment.

Moreover, Zhou and Akao showed that pore of titanium plate coated with double layer of CaTiO₃ and HA by thermal decomposition method had similar bone binding power as compared to HA only coating in an animal study⁶.

All these studies and our current data suggest that CaTiO₃-aC prepared by modified thermal decomposition method is an excellent material for using both as implant coating or adhesive material for HA coating.

Zhou and Akao reported for the first time coating method of perovskite (CaTiO₃) and HA⁶. Calcium titanate generally known as perovskite (CaTiO₃) has a cancellus cuboidal crystal structure. Within this crystal structure, 1 calcium ion at the center, 8 titanium ions at the peak and 12 oxygen ions mainly at the periphery are located. Though it is prepared as particular form by sintering with dry method at 1200 °C, it has been known that it cannot be made as film type and does not contain carbon. Therefore, we considered

that CaTiO₃ coating material at the current study should not be called as perovskite. Rather synthesis of a novel compound named as CaTiO₃-aC was suggested.

Mechanism for improvement of adhesive strength at the border of titanium and CaTiO₃-aC remains unknown at this point. Generally it has been known that the higher the energy at metal surface, the better wetness with liquid occurs. Carbon has been reported to increase this surface energy¹⁵. And both metal and carbon are hydrophobic and shows good concordance. Therefore, one possible explanation for higher adherence strength of CaTiO₃-aC-interpositioned HA coated titanium than HA alone-coated titanium in adherence strength test could be increased adhesion due to enhanced wetness depending on carbon presence.

What kind of form does carbon have within CaTiO₃-aC compound? Our analysis showed that carbon existed in an indefinite form within CaTiO₃ crystal. The carbon atom was suggested to be in amorphous state without crystallizing (Figure 9).

2. Differences between modified thermal decomposition and general thermal decomposition methods

In conventional thermal decomposition method, a solution with equal Ca/Ti composition ratio (1) in CaTiO₃ solution of the material is prepared. Using this ratio, only CaTiO₃ can be formed, and amorphous carbon does not exist. In our modified thermal decomposition method, Ca/Ti ratio in the solution was kept between 1.01~1.10. Thus more Ca in the solution had reaction with TiO₂, and plenty of nano-level calcium titanate-amorphous carbon (CaTiO₃-aC) was generated by sintering.

On the other hand, Ca/P was mixed within HA solution of the material with a theoretical ratio of 1.67. When this ratio was used, in plasma-sprayed method (high temperature), CaO and α -TCP included HA is synthesized. Thus this formation was considered to advance resorption of HA. However, in our modified method, Ca/P ratio was prepared in a range between 1.75~1.85. In this case, as reported by Zhou and Akao⁶, about 30% of β -TCP included HA is synthesized, and CO₃ replaces with PO₄, which then results in formation of a small quantity of carbonate apatite. Generally hydroxyapatite in the body has been known to contain low resorptive β -TCP rather than small quantity of carbonate apatite or α -TCP. According to comparative experiment of the HA solubility sintering at 650 °C and 1200 °C by Okauchi et al (unpublished data), solubility of HA sintered at 650 °C was lower as compared to its sintering at 1200 °C. Moreover solubility of CaTiO₃-aC as compared to HA both sintered at 650 °C CaTiO₃-aC was lower. Thus these results suggest that resorption of 2 layers of CaTiO₃-aC/HA in the body is late, and the bone conductivity is expected to be kept for a long period.

In the current modified thermal decomposition method, the sintering temperature was limited to 650 °C. At temperatures less than 500 °C, generation of CO₂ becomes easy, and CaCO₃ is

formed, which decreases crystallization and then bonding ability of HA. At high temperatures, titanium base has been known to become fragile¹⁷⁻²⁰. Moreover, in the current modified method, a rapid heating (20-200 °C/minute) was made as an absolute condition. Due to rapid heating, O₂ supply will not be enough, which gives rise to incomplete burning. Thus carbon within the organic solvent will remain in CaTiO₃ crystal in an amorphous state. As mentioned above, this amorphous carbon was considered to improve wetness at Ti surface border and contribute to increase of adhesive strength between Ti and HA.

In conclusion, the novel developed coating material (CaTiO₃-aC) can be used for various purposes such as titanium implant coating substrate or by itself as a new biomaterial.

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