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研究課題名(和文) ナノレーザー蒸散加工の完全焼結ジルコニアセラミックブロックからの高精度修復物作製

研究課題名(英文) New method to make the high precise restoration from a complete sintering zirconia ceramic block by applying transpiration with a nano-laser

研究代表者

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研究成果の概要(和文)：5軸加工技術を適用したレーザー装置を組み立て、適合の良いクラウンが作製できた。さらに、クラウンの歯頸部の真円度も測定し、レーザー加工は円を正確に作製するのに、優位な方法であることが明確になった。実際に直ぐに臨床応用できるデータを得た。
以上の結果を、国際歯科材料会議2016(インドネシア)口頭発表、第71回日本歯科理工学会(2018年：大阪)でポスター発表した。さらに、2017年12月に論文をDMJ(Master Journal List掲載誌)に投稿し、2018年4月にアクセプトまでに至った。

研究成果の概要(英文)：Directly milling zirconia computer-aided design (CAD)/computer-aided manufacturing (CAM) crowns from fully sintered zirconia blocks using a 5-axis laser milling system, compared with full sintering by heating milled semi-sintered crowns, was investigated. Results of the present study suggest the superiority of the five-axis milling system in creating a zirconia prosthesis.
The above-mentioned result 2016 (Indonesia) International Dental Materials Congress, the 71st General Session of JSDMD (2018:) I announced the poster in Osaka). Furthermore, I contributed an article to DMJ (Master Journal List publication magazine) in December, 2017 and reached it by accept in April, 2018.

研究分野：補綴・理工系歯学

キーワード：レーザー加工 5軸加工 歯頸部のギャップ 新円度

1. 研究開始当初の背景

期間中に、二つの実験を行った。以下に、実験の概要と関連性を記載する。
 (1) 完全焼結ジルコニアセラミックブロックから5軸ナノレーザーで直接高精度修復物の作製
 (2) PTFEを歯冠修復材料への応用
 (1)の研究開始当初、ジルコニアセラミックからレーザーで高精度の修復物の作製する新しい方法を考えていた。実験の結果、高精度の修復物の作製方法が確立できた。そこで、次に新しい歯冠修復材料として、PTFEを考えた。(2)の実験結果から、PTFEが歯冠修復材料として優秀であることを証明できた。
 次の実験として、PTFEからレーザーを用いて高精度の修復物を作製する実験を予定している。

(1) 完全焼結ジルコニアセラミックブロックから5軸ナノレーザーで直接高精度修復物の作製

弾性係数を大幅に向上させた高強度セラミックスが開発された。このビッカース硬度が1200~2000の硬度を有するため、コア材であるコーピングの材料として注目を集め、CAD/CAMシステムによるセラミックスの加工技術の開発がなされ、一般に普及している。

現在は、半焼結のジルコニアセラミックブロックをCAD/CAMシステムで切削してコーピングを作製し、再び電気炉で本焼結する方法(6時間)が一般化している。このような複雑な工程を必要とするのは、焼結体の硬度(1200VH以上)が高過ぎるため、切削機械での加工ができないからである。また、半焼結ブロックを本焼結するとき生ずる焼成収縮を補正して作製しなければならない。本研究は全く新しいレーザービームを照射し、被照射面に物質が蒸散する大きなエネルギーを短時間(ナノ秒)で与えることにより加工する方法である。この方法により、従来の半焼結ブロックを切削し、再び再焼結する時間が不要となり(作製時間が1/10)、焼成収縮も補正する行程も必要なくなる、かつ高精度の修復物を作製する。

(2) PTFEを歯冠修復材料への応用

ポリテトラフルオロエチレン(PTFE)は、化学的に安定で、人間に無毒で、熱に高度耐性化して、化学製品で、とても低い摩擦係数を有する。このPTFEを歯冠修復材料に応用できるように、硬さ、着色テスト、磨耗試験、細菌付着試験を行った。結果、PTFEが歯冠修復材料として、優秀であることを明確にする。

二つの実験を各々、2.研究目的、3.研究の方法、4.研究成果を順に記載していく。

(1) 完全焼結ジルコニアセラミックブロックから5軸ナノレーザーで直接高精度修復物の作製

2. 研究の目的

In the present study, we developed a five-axis laser milling system for a zirconia prosthesis to keep the excellent dimensional accuracy of the advantage of the milled substructure without long sintering time, and evaluated the accuracy of complete zirconia crowns milled by three- and five-axis laser milling systems, compared with crowns fully sintered by

heating mechanically milled semi-sintered crowns.

3. 研究の方法

The materials used were fully sintered zirconia blocks (i.e., fully sintered blocks obtained by heating milled semi-sintered zirconia blocks; Aadva Zirconia Disk ST, Lot no. 1608241, GC Co., Tokyo, Japan) and semi-sintered zirconia blocks (Fig. 1), which shrink 19.808% by volume with full sintering according to the manufacturer's information.

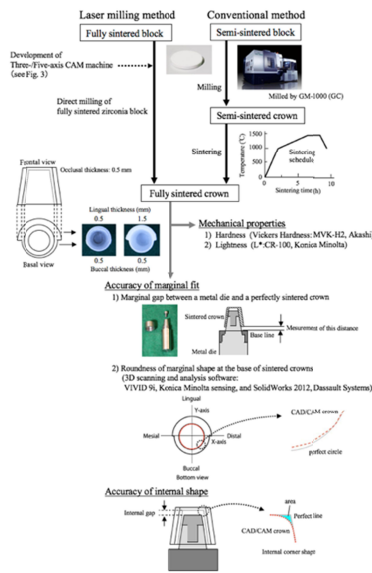


Fig. 1 Schematic representation of the experimental flow

Development of laser milling machines for the direct milling of fully sintered zirconia blocks

We first developed a three-axis laser milling machine for a zirconia prosthesis. This laser milling machine was a fiber semiconductor laser (Nd:YVO₄ laser; wavelength of 1064 nm) with average output of 20 W (AC power supply; 100 V, 50 Hz), pulse energy of 1 mJ/pulse, M2 value of 1.3, and resolution of 40 μm. The laser processing speed for zirconia milling was 500 mm/min. The known weakness of three-axis milling relates to the milling of specimens in the longitudinal direction of the prosthesis. Indeed, a brief test revealed this weakness. We therefore developed and constructed a five-axis milling machine that can create a zirconia prosthesis suitable for clinical use. Specifications of the five-axis milling machine were basically the same as those of the three-axis milling machine except for the number of axes and the movement of the machines.

CAM of semi-sintered zirconia crowns

Ten specimens in three sizes for each heating schedule were prepared by milling from semi-sintered zirconia blocks with a CAD/CAM machine (GM-1000, GC Co., Tokyo, Japan) (Fig. 1). Three-dimensional CAD software (Power SHAPE2015, Delcam Co. Ltd, Birmingham, England) was used to design the specimens and CAM software (DentMILL2011, Delcam Co. Ltd, Birmingham,

England) was used to mill the specimens. Fully sintered crowns were fabricated from semi-sintered milling crowns following a heating schedule (to 1000 °C for 2 h and to 1450 °C for 4.5 h) or by rapid heating (to 1450 °C for 1 h) (Fig. 1). The thickness of the cement layer of each specimen under the condition of a fully sintered zirconia crown was set as 0 μm. *Surface observations made using a scanning electron microscope*

The surface geometry of the semi-sintered zirconia specimens and fully sintered zirconia crowns (sintered under rapid or normal heating) was observed under a scanning electron microscope (JSM-6365F, JEOL Ltd., Tokyo, Japan) at a magnification of ×10,000 and an accelerating voltage of 5.0 kV.

Mechanical properties of zirconia crowns
Accuracy of zirconia crowns

a) Marginal gap

An *in vitro* study was undertaken to compare the vertical marginal accuracy of CAD/CAM zirconia crowns. Crowns were prepared in two sizes (i.e., there were six specimens for each group) with a lingual thickness of 0.5 or 1.5 mm, buccal thickness of 0.5 mm and occlusal thickness of 0.5 mm (i.e., the dimensions of complete crowns) (Fig. 1). The internal dimensions of the crown specimens were set the same as for the metal die abutment tooth, which meant that the cement layer was set as 0 μm. Zirconia crowns were seated on metal dies made of stainless steel (SUS303, Japan MECC Co. Ltd., Tokyo, Japan), and the accuracy of fit was evaluated by measuring the gap between the base line on the die and the margins of the specimen at four specific sites using a measuring microscope (STM6, Olympus Co., Tokyo, Japan) with accuracy of 1 μm (Figs 1 and 2).

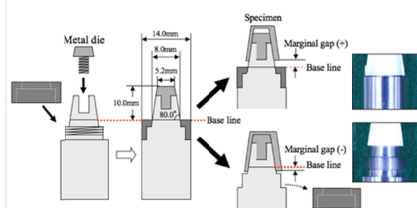


Fig. 2 Metal dies for assessing the marginal fit of zirconia crowns

b) Roundness of the marginal shape at the base

Three-dimensional data of the fully sintered zirconia crowns were obtained using a three-dimensional digital scanner (VIVID 9i, Konica Minolta Co. Ltd, Tokyo, Japan), and three-dimensional images were constructed using three-dimensional CAD software (SolidWorks 2012, Dassault Systèmes SolidWorks Co, Vélizy-Villacoublay, France) to analyze the round shape at the base of the crowns (Fig. 1). A reference plane including three points on the base of the crown was set. The origin was set at the center of gravity (G) of a triangle consisting of

these three points on the base of the crown on the reference plane.

The X-axis was defined as the line passing through point G parallel to the medial-distal line of the crown containing the points of the buccal (0.5 mm thick) and lingual (0.5, 1.0, and 1.5 mm thick) borders. The Y-axis was set as the orthogonal axis of the X-axis including point G. The coordinates (xi, yi) of 20 points on the internal surface of the base (internal margin) of the crown on the XY plane (the reference plane) were obtained to estimate the roundness and roundness error of the marginal shape of the crown.

Roundness was estimated employing the least-squares circle method, which uses a circle that separates the roundness profile of an object by separating the sum of the total area into equal amounts inside and outside:

$$f = \frac{\{(x-x_i)^2 + (y-y_i)^2 - R^2\} + \{(x-x_i)^2 + (y-y_i)^2 - r^2\}}{2}$$

where R is the radius of the least-squares circumscribed circle and r is the radius of the least-squares inscribed circle. A perfect circle has a diameter of 8.0 mm and roundness of 0.00. *Internal shape of zirconia crowns*

4. 研究成果

Three- and five-axis laser milling machines for a zirconia prosthesis

Figure 3 shows the appearance of the developed three- and five-axis laser milling systems and a schematic representation of the movement for three- and five-axis laser irradiation. In the case of the three-axis laser milling system, irradiation of the zirconia block shifted through three-axis motion of the block stage (Fig. 3A). In the case of the five-axis laser milling system, the zirconia block was fixed on a rotating stage and three-axis motion of the stage was combined with rotation of the specimen and rotation of the laser converging optical unit (Fig. 3B).

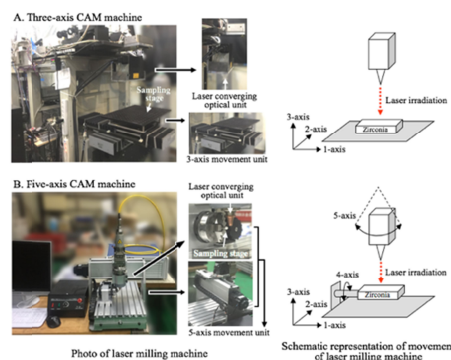


Fig. 3 Laser milling machine for producing zirconia crowns directly from fully sintered zirconia blocks

Mechanical properties of zirconia crowns

The Vickers hardness test revealed that the hardness values of zirconia specimens in laser milled and conventional specimens were almost the same (three-axis, 1518.6-1545.6 Hv1.0; five-axis, 1523.9-1530.4 Hv1.0; conventional, 1530.0-1546.0 Hv1.0),

whereas the hardness of the chalk-like semi-sintered specimens was extremely low (69.4-72.3 Hv1.0) (Fig. 4A). The lightness value (L^*) was highest for chalk-like semi-sintered specimens (100.1-100.6) followed by laser milled and conventional specimens, with values being similar (three-axis, 84.1-84.3; five-axis, 84.3-84.4; conventional, 83.4-83.8) (Fig. 4B).

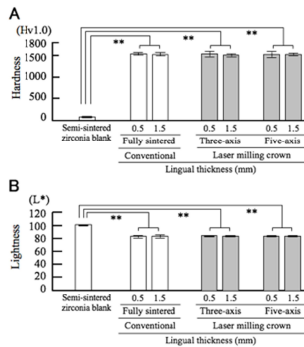


Fig. 4 Mechanical properties of zirconia crowns
A. Hardness, B. Lightness
n=6 for each experimental condition. *P<0.05, **P<0.01.
Data were analyzed in a Tukey test to determine which differences were statistically significant.

Accuracy of the marginal fit

The accuracy of the marginal fit was estimated from the marginal gap, which is the distance between the base line of the metal die and the margin of the crown (Fig. 2). The order of the marginal gap of crowns by creating method was three-axis milling > conventional > five-axis milling system. The order of crown by lingual thickness was 1.5 mm > 0.5 mm in the conventional group, and almost the same for the direct milling system (Fig. 5). **Roundness of the internal marginal shape** Distortion of the internal marginal shape at the base of zirconia crowns is shown as a superimposition over a perfect circle with a diameter of 8 mm (Fig. 5). The diameter of crowns in all groups was 8.0 mm. However, the buccal side (0.5 mm thickness) of the conventional crown with lingual thickness of 1.5 mm was constricted on the inward side, which

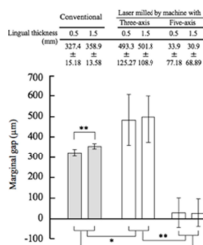


Fig. 5 Marginal gap between the fully sintered zirconia crown and the metal die
n=6 for each experimental condition. *P<0.05, **P<0.01.
Data were analyzed in a Tukey test to determine which differences were statistically significant.

but by the roundness (Fig. 6 and Table 1). Crowns with lingual thicknesses of 0.5 and 1.5 mm directly milled from fully-sintered zirconia blocks with three- and five-axis laser milling machines were almost perfect

circles (Fig. 6).

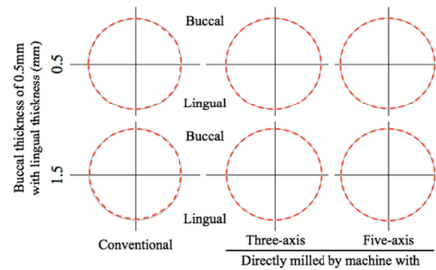


Fig. 6 Internal marginal shape at the base of the fully sintered zirconia crowns

The distortion of marginal shapes of crowns was reflected by the roundness. The values of roundness of marginal shapes of laser-milled crowns having the two lingual thicknesses were almost the same, while conventional crowns had larger thickness values (order of roundness by lingual thickness, 1.5 mm > 0.5 mm).

Internal shape of zirconia crowns

Observation of the internal corner shape of zirconia crowns reveals the corner roundness of crowns milled by the three-axis milling machine and produced conventionally, while the crowns milled by the five-axis milling machine had a sharp corner edge. The internal gap of zirconia crowns in three-axis milling groups had large variance, and there was thus no statistical significance between three-axis and conventional groups. Meanwhile, the internal gap in the five-axis group was almost zero.

CONCLUSION

Results of the present study show that Direct milling specimens had an extremely low distortion of shape and high dimensional accuracy; however, the disadvantage of three-axis laser milling was roundness of the internal corner of crowns. Five-axis milling overcame this weakness, and realized excellent accuracy.

We conclude that five-axis milling systems perform well in creating a zirconia prosthesis with precise dimensions and shape all over the prosthesis, leading to excellent accuracy.

This paper was accepted to Dental Materials Journal.

インパクトファクター 1.073 (2016年)



(2) PTFE を歯冠修復材料への応用

2. 研究の目的

Polytetrafluoroethylene (PTFE) is a

hydrophobic molecule with excellent dielectric properties and one of the lowest coefficients of friction of any solid, which results in reduced friction, wear and energy consumption in machinery, industrial and medical devices, and cookware. These applications in medical and dental fields use its difficulty in adhesive property, which is also useful for maintenance of good oral hygiene, however prevent PTFE from application to prosthesis.

3. 研究の方法

To evaluate the physical properties of PTFE (composed of at least 20000 C₂F₄ monomer units linked into very long unbranched chains (molecular weight; millions to ten million). melting point; 327 °C, glass transition temperature; 130 °C, density; 2.1-2.3g cm⁻³, Fluoro Coat Co. Ltd., Kawagoe, Japan) as a dental material, we prepared specimens (10mm x 10mm x 2mm) of porcelain (VITA VM[®]13, VITA Zahnfabrik H. Rauter GmbH & Co. KG, Bad Säckingen, Germany) according to the manufacturer's instruction, gold alloy (YP GOLD type III, Yamakin Co. Ltd., Osaka, Japan), bovine tooth (mandibular incisor, Yokohama Edible Meat Public Corporation, Yokohama, Japan), and composite resin (CR; Ceramage, Shofu Inc., Kyoto, Japan) according to the manufacturer's instruction for comparison. (Fig. 1)

4. 研究成果

Before measurement of each physical property, the surface roughness (Ra and Rz) of each specimen was evaluated (Fig. 1). The surface roughness values for porcelain, gold alloy, bovine tooth, and CR were almost the same, and were much lower than that of the PTFE specimens. The Ra and Rz values of the zirconia antagonist were also high, falling between the values for PTFE and the other specimens (Table 1).

The worn volume of PTFE and porcelain was almost the same, and was approximately 1/2 that of gold alloy, 1/3 that of bovine tooth, and 1/9 that of CR

Table 1 Surface roughness of specimens and zirconia antagonist

	Surface roughness (μm)	
	Ra	Rz
Zirconia antagonist	0.45 ^{a,c,d,e} (0.097)	3.64 ^{b,c,d,e} (1.133)
PTFE	0.59 ^{b,c,d,e} (0.107)	7.47 ^{b,c,d,e} (0.699)
Porcelain	0.12 ^a (0.044)	1.83 ^a (0.727)
Gold alloy	0.19 ^a (0.031)	2.30 ^a (0.349)
Bovine tooth	0.18 ^a (0.031)	1.55 ^a (0.304)
Composite resin	0.18 ^a (0.066)	2.11 ^a (1.202)

n=6 for each experiment. Superscript letters denote statistically significant differences (p<0.01) within each measurement item compared to a) PTFE; b) porcelain; c) gold alloy; d) bovine tooth; e) composite resin.

(Table 2A). However, the maximum depth of the worn cavity of PTFE was approximately 1/2 that of porcelain and gold alloy, 1/3 that of bovine tooth, and 1/6 that of CR (Table 2A). Wear of the zirconia antagonist, porcelain, and gold alloy was almost the same, approximately 1/3 that of bovine tooth, and 1/6 that of CR (Table 2B). Dynamic friction during the wear test was much lower in PTFE than in the other specimens, which were approximately 1/5-

1/6 of the value exhibited by PTFE (Table 2A).

The Vickers hardness test revealed that porcelain (540HV)>bovine tooth (283HV) >gold alloy (270HV)>CR (65HV)>PTFE (4.8HV). PTFE was therefore an extremely soft material (Table 2A). The results of the wear and hardness tests indicated that PTFE exhibited low hardness and low wear with low friction (Table 2A), while the physical properties of gold alloy and bovine tooth were almost identical to each other (Table 2A).

Table 2 Wear and Vickers hardness of specimens and zirconia antagonist

A. Specimens	Wear test			Vickers hardness (HV1.0)
	volume (mm ³)	depth (mm)	friction (N)	
PTFE	0.006 ^{a,d,e} (0.0011)	0.013 ^{b,c,d,e} (0.0024)	0.37 ^{a,b,c,d,e} (0.030)	4.8 ^a (0.45)
Porcelain	0.005 ^{a,d,e} (0.0013)	0.027 ^{b,c,d,e} (0.0036)	2.12 ^a (0.089)	539.7 ^b (20.24)
Gold alloy	0.012 ^{b,c,d,e} (0.0014)	0.027 ^{b,c,d,e} (0.0011)	1.90 ^{b,c,d,e} (0.047)	270.1 ^a (1.92)
Bovine tooth	0.017 ^{b,c,d,e} (0.0021)	0.047 ^{b,c,d,e} (0.0039)	2.07 ^a (0.350)	282.7 ^a (12.01)
Composite resin	0.056 ^{b,c,d,e} (0.0128)	0.077 ^{b,c,d,e} (0.0036)	2.15 ^a (0.158)	64.6 ^a (1.88)

n=6 for each experiment. Superscript letters denote statistically significant differences (p<0.01) within each measurement item compared to a) PTFE; b) porcelain; c) gold alloy; d) bovine tooth; e) composite resin.

B. Zirconia antagonist	Wear of antagonist against each specimen (mm ³)				Vickers hardness (HV1.0)
	PTFE	Porcelain	Gold alloy	Bovine tooth	
	0.059 ^{a,c} (0.0046)	0.056 ^{a,c} (0.0337)	0.059 ^{a,c} (0.0273)	0.179 ^{b,c,d,e} (0.0434)	0.365 ^{b,c,d,e} (0.0460)
				Composite resin	1437.9 (39.70)

n=6 for each experiment. Superscript letters denote statistically significant differences (p<0.01) compared to a) PTFE; b) porcelain; c) gold alloy; d) bovine tooth; e) composite resin.

The coloration test revealed that PTFE and porcelain exhibited extremely low coloration compared with bovine tooth and CR (Fig. 3A,B). In PTFE and the prosthesis material specimens, the order of coloration was curry>coffee>tea, in contrast with bovine tooth, in which the

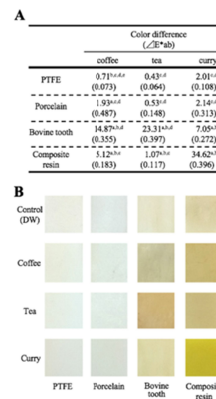


Fig. 3 Coloration with food and drink. A. Color difference, B. Coloration of each specimen. n=6 for each experimental condition. Superscript letters denote statistically significant differences (p<0.01) within each drink/food compared to a) PTFE; b) porcelain; c) bovine tooth; d) composite resin.

order of coloration was tea>coffee>curry.

The bacterial adhesion test using *S. mutans* and *S. sanguinis* revealed similar tendencies in PTFE and the prosthesis material specimens, all of which recorded lower bacterial adhesion than bovine tooth. The order of adhesion tendency was bovine tooth>CR >porcelain>gold alloy>PTFE (Table 3).

Bacteria adhesion of specimens

	Mitochondrial activity of bacteria attached to specimen (% of bovine tooth)	
	<i>S. mutans</i>	<i>S. sanguinis</i>
PTFE	3.40 ^{a,c} (0.61)	0.82 ^{a,c} (1.03)
Porcelain	35.11 ^{a,d} (6.17)	17.11 ^{a,d} (8.82)

ポスター, 亀田 剛, 岡 俊哉, 大熊一夫, 第70回日本歯科理工学会, 2018

6. 研究組織
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CONCLUSION

We conclude that PTFE has the potential to be an excellent material for clinical use as a material/component of prosthesis and dental instruments/devices.

This paper was accepted to Dental Materials Journal.
インパクトファクター 1.073 (2016年)

Dental Materials Journal

Decision Letter (DMJ2018-088.R3)

From: chiefdmj@gmail.com
To: tkameda@ngt.ndu.ac.jp
CC:
Subject: Dental Materials Journal - Decision on Manuscript ID DMJ2018-088.R3
Body: 15-May-2018

Dear Dr. KAMEDA:

It is a pleasure to accept your manuscript entitled "Polytetrafluoroethylene (PTFE): a resin material for possible use in dental prostheses and devices" in its current form for publication in the Dental Materials Journal.

Thank you for your fine contribution. On behalf of the Editors of the Dental Materials Journal, we look forward to your continued contributions to the Journal.

Sincerely,
Prof. Osamu Suzuki
Editor in Chief, Dental Materials Journal
chiefdmj@gmail.com

Date Sent: 15-May-2018

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(1)の実験から、高精度の修復物のレーザーによる作製方法が確立できた。そこで、次に新しい歯冠修復材料として、従来の歯料における加工では難しいPTFEの応用を考え、(2)の実験結果から、PTFEが歯冠修復材料として優秀であることが証明できた。
次の実験として、PTFEからレーザーを用いて高精度の修復物を作製する実験を予定している。

5. 主な発表論文等
(研究代表者、研究分担者及び連携研究者には下線)

[雑誌論文](計 2件)

1. Dental Materials Journal, accept、2018, 査読あり
Five-axis laser milling system that realizes more accurate zirconia CAD/CAM crowns by direct milling from fully sintered blocks,
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2. Dental Materials Journal, accept、2018, 査読あり
Polytetrafluoroethylene (PTFE) : a resin material for possible use in dental prostheses and device
Kameda T, Ohkuma K, Oka S

[学会発表](計 2件)

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2. 5軸レーザーCAM装置により完全焼結したZrO₂ブロックから作製したCAD/CAMクラウンの適合性,