APPLICATION OF SINTERED TITANIUM ALLOYS TO METAL DENTURE BASES: A STUDY OF TITANIUM POWDER SHEETS FOR COMPLETE DENTURE BASE

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Abstract

The purpose of this study was the fabrication of titanium powder sheets to enable the application of sintered titanium alloys as metal denture bases. The effects of titanium particle shape and size, binder content, and plasticizer content on the surface smoothness, tensile strength and elongation of titanium powder sheets was investigated. To select a suitable ratio of powdered metal contents for application as a metal denture base, the effects of aluminum content in Ti sheets and various other powder metal contents in Ti-Al sheets on the density, sintering shrinkage, and bending strength were evaluated. Based on the results of the above experiments, we developed a mixed powder sheet composed of 83Ti-7Al-10Cr with TA-45 titanium powder (atomized, -45μm), and 8 mass% binder content.

This titanium alloy sheet had good formability and ductility. Its sintered titanium alloy had a density of 3.2g/cm³, sintering shrinkage of 3.8%, and bending strength of 403 MPa. The titanium alloy sheet is clinically acceptable for fabricating denture bases.

Key words: Titanium—Powder metallurgy—Tape casting—Metal denture base—Powder sheet

INTRODUCTION

Titanium has a high yield ratio, high melting temperature, and high affinity for oxygen. Therefore, it cannot be formed easily, and casting or joining requires an inert atmosphere. Fabrication of dental prostheses by sintering titanium alloys has advantages such as the elimination of casting defects, good yield, less segregation, and short processing time. The sintering temperature is lower than the melting point. In 1996, Kudoh suggested the possibility of applying powder metallurgy to making denture bases of sintered titanium.
alloys\(^{(3)}\). In that report, the metal powder was isostatically pressed under a load of 200 MPa to form a denture in an elastic resin mold. This method of isostatic pressing has some disadvantages, including the necessity of preparing a mold for the denture base, the requirement that the mold withstand a load of approximately 200 MPa, and the difficulty of pressing powder into a sheet of even thickness.

The development of a titanium alloy powder green sheet is useful for overcoming these drawbacks in fabricating denture bases. The purpose of this study was the production of titanium powder sheets that enabled the application of sintered titanium alloys as metal denture bases.

**MATERIALS AND METHODS**

1. **Properties of green sheets**

1) Preparation of green sheets

Four types of commercial titanium powder, listed in Table 1, were used to examine the effects of the size and shape of powder particles.

A ball mill was used to mix 50 g of titanium powder with 20 ml of distilled water (40 mass% of powder) and 0.06 g of a dispersing agent (0.12 mass% of powder; B-1 produced by Lion Co., Japan) for 12 hours as the stage of initial dispersion. Then 5.0 g of water-based binder (10 mass% of powder; A-1 produced by Lion Co., Japan) was added and mixed for another hour to prepare a slurry. At this stage, the amounts of the additives were determined based on the quantity of the powder and were expressed in terms of the outer percentage of the powder quantity, because these additives are eliminated by evaporation during sintering in later stages.

Following slurry preparation and viscosity adjustment, the slurry was placed in a sheet-forming machine (Doctor Blade equipment, DP-150, made by Tsugawa Precision Machine Co., Japan) to form a sheet of about 0.6 mm thickness. The viscosity was adjusted to between 20,000 and 40,000 cP. This sheet was dried in a constant temperature oven at 45°C for 2 hours and then heated at 110°C for 1 hour.

To examine the effects of binder amounts, we selected titanium powder of TA-45 in Table 1 and changed the amount of the binder as follows: 8 mass% of powder (B8), 12 mass% of powder (B12), 16 mass% of powder (B16), and 20 mass% of powder (B20).

The same procedure described above was adopted to prepare the green sheets. The above ball mill was used to mix 250 g of titanium powder with 40 ml of distilled water (16 mass% of powder), 2.4 g of the dispersing agent (0.96 mass% of powder; B-1 produced by Lion Co., Japan), and 0.2 g of an anti-forming agent (0.08 mass% of powder; F-2 produced by Lion Co., Japan) for 12 hours as the stage of initial dispersion. Then water-based binder (A-1, produced by Lion Co., Japan) was added and mixed for another hour to prepare a slurry.

2) Measurement of mechanical properties of green sheets

One sheet of titanium powder was cut into 4×40-mm pieces of 0.6 mm thickness; these were then tested for tensile strength with a universal testing machine (Autograph DCS-5000 by Shimadzu Inc., Japan). The gauge

<table>
<thead>
<tr>
<th>Material</th>
<th>Size Shape</th>
<th>Chemical composition (%)</th>
<th>Code</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>H  C  N  O  Mg  Si  Cl  Cr  Mn  Fe  Ni</td>
<td></td>
</tr>
<tr>
<td>TSP-350</td>
<td>−45μm pulverized</td>
<td>0.019 0.007 0.006 0.27 0.003 &lt;0.010 0.010 — 0.001 0.020 —</td>
<td>TP-45</td>
</tr>
<tr>
<td>TMP-10</td>
<td>−10μm pulverized</td>
<td>0.036 0.006 0.038 2.17 &lt;0.007 &lt;0.010 0.015 — 0.002 0.035 —</td>
<td>TP-10</td>
</tr>
<tr>
<td>TILOP-45-75</td>
<td>−75μm atomized</td>
<td>0.006 0.015 0.014 0.09 — — &lt;0.001 0.005 — 0.027 0.008 TA-75</td>
<td></td>
</tr>
<tr>
<td>TILOP-45</td>
<td>−45μm atomized</td>
<td>0.005 0.008 0.011 0.066 — — &lt;0.001 0.003 — 0.028 0.004 TA-45</td>
<td></td>
</tr>
</tbody>
</table>

All examined materials were manufactured by Sumitomo Sitix, Inc., Japan.
length was 20 mm. The crosshead speed was 50 mm/min. From the load-displacement curve, the tensile strength and the maximum elongation were calculated.

2. Properties of sintered sheets

One green sheet was cut into 4 × 40-mm pieces of 0.6 mm thickness and sintered in a vacuum furnace at 1.3 × 10⁻³ Pa at 1,050°C for 1 hour. The sheet was then cooled in the furnace to room temperature.

Three experiments were designed to examine the suitability of these sintered sheets.

1) Effect of added Al powder

Aluminum powder was added to titanium powder to control changes in dimension during sintering. Atomized titanium powder, TA-45, (45 μm or less; by Sumitomo Sitix, Inc., Japan) was mixed with atomized aluminum powder of 16–18 μm diameter (VA-1000 by Yamaishi Metals Co., Japan) to prepare powder mixtures containing 5, 10, and 15 mass% of aluminum. The aluminum powder was similar to that used by Kudoh. The mixtures were named “xAl”, where x stands for the percentage of aluminum. Thus, 0Al stands for pure titanium powder, 5Al stands for titanium powder containing 5% of aluminum, and 10Al stands for titanium powder containing 10% of aluminum.

2) Effects of annex metal powder on the Ti-Al powder mixture

To improve the strength of sintered sheets, powders of seven other metals were added by 10 mass% to the Ti-Al powder mixture. These included Sn, Cu, Co, Cr, Fe, Mn, and Zr.

Table 2 lists the properties of the powders of the other seven metals.

3) Effects of compositional changes in ternary alloys

Ternary alloys of Ti-Al-Cr and Ti-Al-Zr have been selected for use as denture bases. To investigate the effects of composition on the mechanical properties of sintered sheets, the mass percentage of aluminum in Ti-Al-Cr and Ti-Al-Zr was changed from 5.0 to 10.0, as shown in Table 3.

The following properties were determined:

1) Dimensional changes after sintering: The shrinkage percentage was determined with respect to the original length before sintering.

2) Yield strength, bending strength, and elastic modulus: A universal testing machine (Autograph DCS-5000: Shimadzu) was used to apply a three-point bending load at a crosshead speed of 1.0 mm/min with a span of 20 mm between supports. From the load-displacement curve, a value of 0.005% stress at plastic deformation was taken to be the yield strength. The bending strength was determined as the maximum stress. The elastic modulus was calculated from the load and the amount of flexure displacement.

Table 2 The properties of the powders of the other seven metals

<table>
<thead>
<tr>
<th>Powder metal</th>
<th>Material</th>
<th>Manufacturer</th>
<th>Ave. particle size (μm)</th>
<th>Particle shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>CE-1110</td>
<td>Fukuda Metal Foil and Powder Co., Ltd., Japan</td>
<td>10</td>
<td>electrolysis</td>
</tr>
<tr>
<td>Co</td>
<td>COE03PA</td>
<td>Kojundo Chemical Laboratory Co., Ltd., Japan</td>
<td>5</td>
<td>reduction</td>
</tr>
<tr>
<td>Cr</td>
<td>CRE02PA</td>
<td>Kojundo Chemical Laboratory Co., Ltd., Japan</td>
<td>10</td>
<td>pulverized</td>
</tr>
<tr>
<td>Sn</td>
<td>SN-ATW-600</td>
<td>Fukuda Metal Foil and Powder Co., Ltd., Japan</td>
<td>45</td>
<td>atomized</td>
</tr>
<tr>
<td>Fe</td>
<td>FE-5-350</td>
<td>Fukuda Metal Foil and Powder Co., Ltd., Japan</td>
<td>45</td>
<td>pulverized</td>
</tr>
<tr>
<td>Mn</td>
<td>MNE04PA</td>
<td>Kojundo Chemical Laboratory Co., Ltd., Japan</td>
<td>10</td>
<td>pulverized</td>
</tr>
<tr>
<td>Zr</td>
<td>ZRE02PA</td>
<td>Kojundo Chemical Laboratory Co., Ltd., Japan</td>
<td>10</td>
<td>pulverized</td>
</tr>
</tbody>
</table>

Table 3 Compositions of metal powder mixtures (mass%)

<table>
<thead>
<tr>
<th>Code</th>
<th>Ti</th>
<th>Al</th>
<th>Cr</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>5Al-10Cr</td>
<td>85</td>
<td>5</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>7Al-10Cr</td>
<td>83</td>
<td>7</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>10Al-10Cr</td>
<td>80</td>
<td>10</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>5Al-10Zr</td>
<td>85</td>
<td>5</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>7Al-10Zr</td>
<td>83</td>
<td>7</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>10Al-10Zr</td>
<td>80</td>
<td>10</td>
<td>0</td>
<td>10</td>
</tr>
</tbody>
</table>
(3) Structural and compositional analyses: Sintered samples of 7Al-10Cr and 5Al-10Zr were examined using an optical microscope and electron probe micro-analyzer (EPMA).

In the above measurement of each mechanical property, 5 specimens (green sheets or sintered sheets) were used for each type of measurement. An analysis of variance and a multiple-comparison test were applied to compare the statistical differences.

RESULTS

1. Mechanical properties of green sheets

1) Effects of powder size and shape
The tensile strength and elongation of green sheets for various sizes and shapes of powder particles are shown in Fig. 1. Tensile strength ranged from 0.45 to 0.56 MPa. There were no significant differences between the four types of powder (p>0.05). Elongation ranged from 2.80% to 7.80%. For pulverized powder (TP), elongation became greater with an increase in particle size. For atomized powder (TA), the particle size had no significant effect on elongation (p>0.05).

2) Effect of binder amounts
The tensile strength and elongation of green sheets of TA-45 for different binder amounts are shown in Fig. 2. The tensile strength ranged from 0.56 to 1.48 MPa and tended to increase as the amount of binder increased. The binder amounts had no significant effect on elongation (p>0.05).

2. Mechanical properties of sintered sheets

1) Effect of adding aluminum powder
(1) Dimensional changes after sintering
The dimensional changes of sintered sheets containing aluminum are listed in Fig. 3. The values ranged from −6.65% to +2.38%; negative values indicate contraction, and positive values indicate expansion.

(2) Yield strength, bending strength, and elastic modulus
The yield strength, bending strength, and elastic modulus of sintered sheets containing aluminum are shown in Fig. 4. The yield strength ranged from 64 to 554 MPa, and the bending strength ranged from 70 to 712 MPa. These values tended to decrease with greater proportions of aluminum. The elastic modulus ranged from 24 to 62 GPa, tending to decrease as more aluminum was added.

2) Effects of adding other metals to Ti-Al powder
(1) Dimensional changes after sintering
Fig. 5 lists the dimensional changes in sintered sheets that were formed by adding other metals to a Ti-Al powder. The values ranged from −4.72% to +0.26%. 10Al-10Cr and 10Al-10Sn contracted and expanded less than the alloy sheet 10Al. Green sheets containing Cu and Co demonstrated an inadequate plasticity, and these sintered sheets fell below acceptable limits.

(2) Yield strength, bending strength, and elastic modulus
The yield strength, bending strength, and elastic modulus of sintered ternary alloy
sheets are listed in Fig. 6. Yield strength ranged from 59 to 210 MPa, and whole bending strength ranged from 63 to 231 MPa. The elastic modulus ranged from 23 to 48 GPa.

3) Effects of compositional changes in ternary alloys

(1) Dimensional changes after sintering

Fig. 7 lists the dimensional changes of sintered alloy sheets. The values ranged from $-5.58\%$ to $-0.34\%$. The values for contraction were very large compared to those of the binary alloy 10Al.

(2) Yield strength, bending strength, and elastic modulus

Fig. 8 lists the yield strength, bending strength, and elastic modulus of sintered sheets containing aluminum (Ti; TA-45).
10Zr and 7Al-10Cr produced values of 433 MPa and 403 MPa. The yield strength and bending strength for other composition alloys tended to decrease with higher aluminum content.

The elastic modulus ranged from 30 to 53 GPa. The values for 5Al-10Zr and 7Al-10Cr were 52 GPa and 50 GPa. The elastic modulus for other composition alloys tended to decrease with higher aluminum content.

(3) Structural and compositional analysis

Fig. 9 shows photomicrographs of the crystal structure of sintered sheets. Fig. 10 shows surface analyses by EPMA. In any alloy containing Cr and Zr, porosity tended to increase with higher aluminum content. A surface analysis by EPMA indicated a homogeneous solution of Al and Zr in the Ti matrix for the alloy 5Al-10Zr. In 7Al-10Cr, Cr segregated.

DISCUSSION

In industry, the doctor blade method is a common technique for forming a substrate with alumina powder as a main component. A binder, water, and dispersing agent are added and mixed with the powder to form a slurry, which is then used to prepare a sheet\(^1,6,8\). While several studies have investigated the conditions for a binder and other additives, there are no reports concerning the application of this method to titanium powder.

In the present study, we conducted experiments to determine the most suitable types of titanium powder and suitable conditions for preparing sheets before sintering. Then the addition of powders of other metals was examined to adjust the mechanical properties of sintered sheets.

It was possible to prepare sheets from all
Ti-5Al-10Zr

Fig. 10 X-ray characteristic images of sintered sheets (Ti-Al-Cr and Ti-Al-Zr) by EPMA

four of the titanium powder types investigated. With TP-45 and TA-75, dispersion of titanium powder was poor in the slurry, resulting in relatively rough surfaces on unsintered and sintered sheets. For TP-10 and TA-45, the dispersion of powder in the slurry was acceptable, resulting in good surfaces.

A sheet of greater elongation seems to be preferable before sintering because more plastic deformation is desirable when molding a sheet and because the degree of recovery of the molded sheet may be relatively low. Among the four types of titanium powder, TP-45 and TA-45 resulted in relatively high tensile strength and elongation, appearing almost identical in this respect (p>0.05).

Larger amounts of binder may lead to lower density and strength of a sintered sheet. With respect to titanium powder, we determined that the minimum amount of binder required to prepare an acceptable sheet was 8 mass%.

Sintering of metal powder generally results in significant shrinkage. To ensure fit, the shrinkage of prostheses must be minimal. A sheet made of pure titanium powder exhibited 6.7% shrinkage. As shown in Fig. 3, a higher aluminum content corresponded with lower shrinkage. A sheet of 15Al exhibited values as small as 2% expansion.

Cast dental alloys exhibited 1.5% of shrinkage. Kudoh reports that sintered titanium alloys, prepared by a different method from the present technique for use in denture bases, exhibited 1.23% of shrinkage. Thus, in the present study, it appeared desirable to add aluminum to 10 mass% or more of titanium powder.

The bending strength of sintered sheets tended to decline as amounts of aluminum increased. This appears attributable to the fact that, although shrinkage was controlled, bulk density declined, and large numbers of pores contributed to a decline in flexural strength.

As described above, adding aluminum effectively controlled dimensional changes. To compensate for declines in bending strength, reduced to below 400 MPa, we tried adding other metals to Ti-Al powder mixtures.

Addition of Fe or Mn resulted in bending strengths higher than 10Al. Addition of Cr, Sn, or Zr resulted in declines. The decrease with Cr or Zr was slight, while the addition of Sn caused extreme reductions in strength. Apparently, this is because the addition of Fe or Mn resulted in significant shrinkage, increasing both bulk density and bending strength. Adding Sn caused expansion, reducing both bulk density and bending strength. Adding Cr resulted in a slight decrease in flexural strength but also in significant shrinkage control. Adding Zr also caused a slight decrease in bending strength and a slight, but insignificant, increase in shrinkage.

Ti-Al-Cr and Ti-Al-Zr are alloys that have potential for use in denture bases. A denture base requires at least 400 MPa or more of flexural yield strength. In the present study,
only 5Al-10Cr exceeded this minimum requirement. Unfortunately, this alloy shrank by 5.6% during sintering, much more than cast dental alloys\(^7\). For this reason, 5Al-10Cr is not recommended as a dental prosthesis. 5Al-10Zr and 7Al-10Cr may be second choices for use in metal denture bases, despite bending strengths slightly lower (433 MPa and 403 MPa, respectively) than normal base alloys. Because their strength still exceeds resin for use in denture bases (50–110 MPa\(^7\)), a slightly thicker sheet should meet the required strength standards for general metal denture bases, while continuing to offer a thinner form than resin bases. The titanium alloys 5Al-10Zr and 7Al-10Cr appear feasible for use as a materials for denture bases.

This study also investigated unsintered sheets to determine their moldability in forming a denture base. Fig. 11 shows a green sheet that was suction-contacted to a mold using a vacuum pack. The radius of curvature was determined at a corner between the palate-contacting portion and residual ridge slope-contacting portion by assuming the corner to be an arc. This angle corresponded to a corner of the mold of 110 degrees. The radius was determined as \(r = 1.11 \text{ mm}\) for 5Al-10Zr and 1.19 mm for 7Al-10Cr. Thus, up to around 1.2 mm, the mold surface seemed to copy well to the sheet. Since the rugae area, which likely has the smallest radius curvature on the palate, is no smaller than 2 mm, this area may copy well to a sheet of titanium alloy powder. The above radius of curvature was measured twice: immediately after suction forming and 24 hours later. We found no differences (and hence no elastic recovery) between the two measurements. These sheets are well-suited to molding.

We found unsintered sheets to be as flexible as paraffin wax, and easy to cut and machine. Such sheets can be cut to a desirable size, then placed and molded onto a refractory mold in the shape of a denture base by suction with a vacuum pack. Two or more sheets may be stacked to adjust the thickness. A dental wax instrument can be used to cut and reshape the periphery easily and precisely. A pile of such sheets may be sintered together with the mold to form a titanium alloy denture base. The present process offers advantages over casting in both labor and time, because it requires no wax or other embedded materials.

Further study is required to improve shrinkage and strength to normal levels for cast bases and to develop a suitable mold material.

**CONCLUSIONS**

We applied powder metallurgy to developing a titanium alloy sheet for use in denture bases. Green sheets were examined for particle size and shape and binder amount. Sintered sheets were examined for the effects of adding aluminum powder and other metals
to Ti-Al powder. We also studied ternary Ti-base alloys for possible use as denture bases by mixing atomized titanium powder of 45μm or less in diameter with aluminum and chromium powder and adding water-based binder by 8 mass% to form an 83-Ti-7Al-10Cr sheet. When sintered, this sheet had a density of 3.2 g/cm³, shrinkage of 3.8%, yield strength of 370 MPa, bending strength of 403 MPa, and an elastic modulus of 50 GPa. Given the physical and mechanical properties of unsintered and sintered sheets of this type, we believe that this alloy sheet has the potential for use in denture bases.

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REFERENCES


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