Dental Titanium Casting Researches in China

Z. M. Yan¹, T. W. Guo², Y. M. Zhang² and Z. C. Li³

¹Department of Prosthodontics, The PLA 160th Hospital, Jiaozuo. 454003, P.R. China
²Department of Prosthodontics, Stomatological College, Fourth military Medical University, Xi’an, 710032, P.R. China
³Xibei Nor-ferrous Metals Institute, Xi’an, 710000, P.R. China

Titanium is an ideal material for use in prosthodontics because of its biocompatibility, corrosion resistance, and mechanical strength combined with its lightweight. Recently the use of titanium and titanium alloys for fixed restorations has increased substantially, mainly due to the improvement of techniques for the casting titanium and its alloys. This article reviewed the studies on titanium casting techniques in China. The rapid developments of the Chinese titanium industry make a good condition for doing researches on dental titanium castings. Now researches on dental titanium casting in China are very active and fast. In 1995 the first titanium casting machine was developed and worked well, by use of which titanium denture frameworks, titanium denture bases, titanium crowns and bridges and titanium-porcelain restorations could be made successfully. To expand the applications of titanium alloys as dental prosthodontic materials, TiZr alloy and TAMZ alloy for dental uses were also developed. Their physical and mechanical properties are better than pure titanium and their biocompatibilities are excellent. In order to solve problems of polishing and finishing of titanium castings, a series of surface treatment techniques and procedures were developed recently, including sandblasting, chemical dipping, mechanical polishing, chemical polishing, electrochemical polishing, and anodizing of titanium castings, which make the surface treatments of the titanium castings more easy and more efficient and have improved the surface qualities of the dental titanium castings.

(Received June 19, 2002; Accepted July 19, 2002)

Keywords: titanium, titanium alloys, dental casting technique

1. Introduction

Ni–Cr alloy, stainless steel and Co–Cr alloys have been paid more and more attention for their toxic elements, which may cause allergy, monstrosity and carcinoma. Titanium with excellent biocompatibility and high strength/weight ratio is thought to be the main prosthodontic metal material in 21st century. In China titanium stored in the earth comprises one third of storage in the world, and rapidly developments of the Chinese titanium industry make a good condition for doing research on dental titanium casting.

In 1995 the first titanium-casting machine was developed in China. From 1989 to 1998, twelve dental titanium casting machines made in Japan, Italy, Germany and America respectively were introduced into several cities in China, such as Beijing, Shanghai, Taiyuan and so on. Some of them still worked well now. Titanium denture frameworks, titanium denture bases, titanium crowns and bridges and titanium-porcelain restorations can be made by use of dental casting techniques.

2. The Developments of Dental Titanium Casting Machine in China

The first as-service titanium casting machine, Mode LZ-II pressure-suction—centrifugal dental titanium casting machine was developed by college of stomatology, fourth military university and JIANXI machinery manufactory in 1995. Through experimentation it was shown that the casting rate of the dental casting machine was 98 percent, the thickness of reactive layers of the casting was from 50 to 75µm, the surface micro-hardness of the castings was from 400 to 450HV, and porosity in the casting was ranked from 0 to 1. By using the dental titanium casting system, removable partial denture frameworks, complete denture bases and crowns were fabricated successfully. Since 1995, the dental titanium casting machine have been used in department of Prosthodontics, college of stomatology, fourth military university for 5 years, by which 625 dental titanium castings were made. The rate of fracture of titanium clasps for one to three year’s recall was only 3 percent. The dental casting system had been introduced into many cities in China, such as Tianjin, Nanjing, Shanghai, and Shenzhen, etc.

3. Developments of New Titanium Alloys for Dental Purposes

Pure titanium is suitable for making the crowns because the strengths of the titanium are fairly comparable to type III gold alloy. However the strength of pure titanium is not suitable for making many kinds of dentures, such as the denture bases, the clasps and so on. The Ti6Al4V alloy with higher strength than pure titanium, but the toxic element vanadium restrained the use of it. To expand the applications of titanium alloys as dental prosthodontic materials, it is necessary to develop new titanium alloy with excellent biocompatibility and better strengths.

3.1 TiZr alloys

The element Zirconium belongs to the vital group, non-toxic to human body. TiZr alloy was developed in 1998 in China.

Table 1 shows the composition of the TiZr alloy (mass%). Table 2 and Table 3 show that TiZr alloy has higher tensile strength than TA2, and higher yield strength than TA2 and IV gold alloy. These properties of the alloy resulted in stronger retentive forces than IV gold alloy for dental uses.
3.2 TAMZ alloy

3.2.1 The composition and mechanical properties of the TAMZ alloy

Table 4 and Table 5 show the composition and mechanical properties of TAMZ alloy.

3.2.2 Evaluation of TAMZ alloy biocompatibility

(1) Cytotoxicity test

According to ISO standard, the filter diffusion test is designed to demonstrate the activity of succinate dehydrogenase of culture cells, which is fast, suitable and reliable for evaluating the cytotoxicity. The results showed that the filters with fibroblasts in negative control group were stained dark blue, while the filters of positive control group had unstained zone. Comparing with the negative control, the filters in experimental groups had showed no difference significantly in staining intensity and diameter. Based on the standard of ISO, the TAMZ alloy presented noncytotoxicity and scored as 0 rank.

(2) Hemolysis test

Hemolysis test is used to evaluate the acute hemolytic activity of materials, which contact to bones or tissues permanently in vitro. Based on the standard of China, this test estimated the extent of soluble hemoglobin from red blood cells after the experimental materials contacting with blood. The results showed that the hemolytic value of the new alloy was about 0.15%, which is in accordance with the minimum standard of less than 5%. It is indicated that the TAMZ alloy has significant low level of hemolytic activity.

(3) Mucous membrane irritation test

Mucous membrane irritation test has been suggested as one of the necessary tests to evaluate the biocompatibility of dental prosthetic appliances. In the study, golden hamsters were selected for histocompatible assessment by inserting and fixing test discs in the cheek pouch. As revealed from morphological and histopathological examinations, none of the new titanium alloys presented significant alterations in mucosal epithelium and connected tissue such as inflammation or hyperkeratosis. It is seemed that the TAMZ alloy has no affection on oral mucous membrane.

4. The Surface Treatments of the Dental Titanium Castings

Titanium dentures, including removable partial titanium denture frameworks, titanium complete denture bases and crowns, have some advantages, such as, good fitness, excellent elasticity of the clasps that enable the tips of clasps extended into the concave of the abutments in depth of 0.75 mm and easily seated in and removed of the dentures. However the problems of polishing and finishing of them due to its lower heat-conductivity and higher chemical reactivity, which has not been solved successfully, have impeded the applications of dental titanium restorations in prosthodontics. In order to improve the methods of surface finishing of titanium castings efficiently, a series of surface processing techniques of titanium castings have developed.

4.1 Sandblasting of titanium castings

The dental titanium castings were sandblasted with 80–110 µm grain sized aluminum oxide for 30 to 60 s. The results shows that the optimum emission pressure is 4.5 MPa and the suitable distance from the nozzle to the specimens was 10 to 20 mm. The α-case layer of the hard reactive layers on the titanium castings can be removed after sandblasting, but the layers rich in silicon and phosphorus, and the dendritic crystal structures were remained, which may be removed with chemical processing. Figures 1 and 2 show the metallographical structures of titanium casting before and after sandblasting respectively.

4.2 Chemical dipping of titanium castings

The remained surface reacted layers of titanium castings after sandblasting were removed completely by using a special chemical dipping methods, as shown in Fig. 3. The immersing solution contained 3 to 5% hydrofluoric acid and 30% nitric acid. The optimum immersing time is 60 to 90 s at the temperature of 50 to 60 °C which do not affected the fitness of the dentures.

4.3 Mechanical polishing of titanium castings

The titanium casting can be polished with dental electrical handpiece by using carborundum, diamond and carbor-boron grinding materials, of which the latter two materials were more effective and more efficient because they are hard and have good heat conductivity.

4.4 Barrel polishing of titanium castings

Barrel polishing is a more efficient method than polishing by hand. In 1997 a new dental barrel polishing machine was developed. The grinding materials mainly contained alumina shaped in trigon, abnormity, column and conglobation. After titanium castings were polished in the barrel polishing machine at the velocity of 450 to 650 rpm for 30 to 45 min, the
Table 4 Composition of the TAMZ alloy (mass%).

<table>
<thead>
<tr>
<th>Composition</th>
<th>Ti</th>
<th>Zr</th>
<th>Mo</th>
<th>Al</th>
<th>Fe</th>
<th>Si</th>
<th>C</th>
<th>N</th>
<th>H</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass Bal</td>
<td>1–3</td>
<td>1–2.5</td>
<td>2–3</td>
<td>0.3</td>
<td>0.15</td>
<td>0.1</td>
<td>0.05</td>
<td>0.015</td>
<td>0.15</td>
<td></td>
</tr>
</tbody>
</table>

Table 5 Main mechanical properties of the TAMZ alloy.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Tensile strengths (MPa)</th>
<th>Elongation (%)</th>
<th>Yield strengths (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TAMZ</td>
<td>800</td>
<td>15</td>
<td>730</td>
</tr>
<tr>
<td>Ti6Al4V</td>
<td>896</td>
<td>10</td>
<td>392</td>
</tr>
<tr>
<td>Ti5Al12.5Fe</td>
<td>942</td>
<td>15.5</td>
<td>445</td>
</tr>
</tbody>
</table>

4.5 The electrochemical polishing of titanium castings

The mechanism of electrochemical polishing is a processing of anode, which is resulted in improving the surface micro-geometrical figuration and the lightness of the electrolytically polished metals. Dental titanium castings could be electrolytically polished in a non-aqueous electrolyte. The surface roughness decreased below to 0.45 µm. The bulk volume changes of the castings are acceptable for dental clinic uses.

4.6 Coloration of titanium castings by Anodization

A layer film of oxidized titanium is formed on the titanium castings when they are anodized in oxidative solutions. Anodized titanium shows different color due to the interference of lights. Titanium castings were anodized in 0.5 kmol·m⁻³ sulfuric acid and 0.2 kmol·m⁻³-phosphate acid electrolyte at different voltages. Anodized at 10 V and 45 V respectively, the colors of the titanium castings appear in two brilliant goldish yellow colors. The goldish yellow colors may be used to improve the esthetics of titanium dentures, which is probably acceptable to the patients. Coloration of titanium denture frameworks by anodization is easy and serviceable to enhance the aesthetics of titanium dentures.

The corrosion resistance and the color stability of anodized titanium in oral environment were also investigated recently. The results show that the corrosion resistance is superior significantly to that of the unanodized titanium, and the color stability of the anodized titanium is acceptable for clinic uses.

The procedure of the anodizing of titanium is shown as follows:

Titanium castings → Chemical dipping → Washing → Connection → Washing → Anodization → Washing → Hot water processing → Dryness → Finishing.