CASTING OF TITANIUM ALLOYS FOR DENTAL APPLICATIONS

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ABSTRACT

In dentistry, gold-based noble metal alloys have traditionally been cast into various types of dental prostheses, such as partial dentures, crowns, and bridges. More recently, less expensive dental alloys with base-metal elements, such as Co-Cr and Ni-Cr, have been used. Titanium is considered to be an attractive alternative to these traditional dental alloys because of its remarkable lack of toxicity and its mechanical properties that resemble those of hard and extra-hard casting gold. However, casting titanium to make dental prostheses has been hampered because of its high melting point, low density, and high chemical reactivity; these characteristics make it difficult to carry out traditional dental casting processes. Over the last 15 years, pioneering researchers and clinicians have tried to overcome the problems associated with casting titanium dental appliances. The Department of Biomaterials Science at Baylor College of Dentistry has also investigated the feasibility of making titanium a viable choice for dental applications. The topics addressed in this presentation include: titanium alloys studied, casting performance, machinability, wear resistance, electrochemical behavior, biocompatibility, quality of casting, and veneering with dental porcelain.

Key words: Titanium casting, titanium alloys, machinability, wear

INTRODUCTION

Alloys that are used for dental prostheses must possess certain properties, such as good biocompatibility, ease of casting and finishing, minimal solidification shrinkage, minimum reactivity with the mold materials, good wear resistance, and excellent corrosion resistance. Gold and gold alloys have been used in dentistry as restorative materials for many years. The American National Standards Institute/American Dental Association (ANSI/ADA) has grouped gold casting alloys into four types for different uses, based on the minimum amounts of gold they contain. Although most dental crowns and bridgeworks are presently made with less expensive alloys, the ANSI/ADA specification has served as a general baseline for designing and selecting other types of casting alloys for dental applications. When investigators in Japan first begin studying the use of titanium in dentistry in the 1970s, they selected commercially pure (CP) titanium for their initial evaluation because the strengths of dental gold alloys and CP titanium are fairly comparable.

There are currently several hundred alloys available that are specifically made for fabricating cast dental prostheses. More than half of these metals are designed for all-metal crowns, bridges, onlays, and inlays. Since 1989, the ADA has stipulated that casting alloys may have any composition as long as they meet certain requirements for toxicity, tarnish, yield strength, and elongation [1]. Besides gold alloys, base metal alloys are used extensively. Conventionally cast Co-Cr alloy (mainly for partial denture frameworks, which have almost replaced cast gold alloy frameworks) and Ni-Cr alloy (for crowns and bridges and porcelain-
fused-to metal restorations have been used) [2]. Interest in titanium as a casting metal for dental appliances grew because it offered favorable properties, particularly excellent biocompatibility and low cost compared to gold. Titanium also possesses high strength, stiffness and ductility, and good corrosion resistance.

While titanium holds much promise for dentistry, the casting process had to be considerably adapted from both titanium industrial casting and from dental casting of conventionally used alloys. The particular properties of titanium make it difficult to cast: high melting point, low density, and high chemical reactivity with gases such as oxygen, hydrogen, and nitrogen. Some of the modifications in casting technology required for titanium include selecting heat sources high enough for fusing titanium; isolating the molten metal from air; developing an investment material that reacts very little or does not react at all with the molten titanium; and finding new ideas for delivering the molten metal into the mold at the desired velocity. There are currently more than 10 different casting machines intended for dental titanium casting. Melting is carried out under an inert gas (usually argon); electric arc or high-frequency induction melting methods are used; and differential gas pressure or centrifugal casting methods are employed to pour the molten metal into the mold. MgO investment material was found to be the least reactive with molten titanium. By using various combinations of these techniques, the present casting machines can produce acceptable castings that are nearly comparable to conventionally cast dental alloys.

Thus, the technology is in place for performing acceptable titanium casting; however, further work must be done to improve the properties of the cast metal. The purpose of our work in this area for the last six years has been to continue the development of titanium casting so that this metal will become a viable choice for dentists and prosthodontists.

STUDIES PERFORMED

Titanium alloys studied

We have spent a great deal of time studying titanium alloys. Although experiments on certain properties of cast CP titanium are encouraging, the low yield strength of pure titanium may prevent its application in high load-bearing areas. Thus, we looked to β-phase titanium alloys for improved strength. Some β-phase alloys could be good candidates for dental casting alloys because they may have lower fusion temperatures than other titanium alloys [3]. In selecting β-stabilizing elements, we chose the β-eutectoid type, some of which could potentially reduce the fusion temperature. The elements chosen in varying compositions were Ag, Co, Cr, Cu, Fe, Mn, and Pd. Results from our tests of mechanical properties of these cast experimental alloys (Table 1) showed that the bulk hardness values are higher, but the elongation values are lower compared to cast dental base metals and cast gold alloys [4]. Overall, the cast titanium metals are well within acceptable ranges for dental prosthetic requirements.

In addition to studying experimental alloys, we also focused attention on some commercial titanium alloys. A successful metal used in many industrial applications is an α+β alloy, Ti-6Al-4V. It has high strength and retains formability. Considering the strength obtained, Okuno [5] suggested that this alloy could be used for fabricating partial denture frameworks and even complete cast denture bases. Another commercial alloy that was actually indicated for dental casting is Ti-6Al-7Nb, originally developed in Switzerland for surgical implants. β-titanium alloys have recently been favored for biomedical uses because the modulus of elasticity is lower than that of the α or α+β alloys and is similar to hard tissue. An important commercial β-titanium
alloy is Timet 21 SRx (Timet Metals Corp.), which was created by removing Al from Timet 21S, also an alloy developed for surgical implants. Other such alloys are Ti-12Mo-6Cr-1Fe (Howmedica Pfizer Hospital Products, Inc.) and Ti-13Nb-13Zr (Smith and Nephew Richards, Inc.). Compared to Ti-6Al-4V, these $\beta$-titanium alloys are more biocompatible and showed better mechanical properties and corrosion resistance [6,7]. Thus, we studied not only the properties of a group of experimental alloys, but we also tested several of these commercial alloys (see Casting performance; Fig. 1).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>TS (MPa)</th>
<th>YS (MPa)</th>
<th>E (%)</th>
<th>ME (GPa)</th>
<th>H (VHN)</th>
</tr>
</thead>
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<tr>
<td>Ti 9%Co</td>
<td>938/88</td>
<td>-</td>
<td>0.8/0.1</td>
<td>116/11</td>
<td>403/22</td>
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<tr>
<td>Ti 20%Cr</td>
<td>907/37</td>
<td>864/12</td>
<td>2.8/1.8</td>
<td>105/11</td>
<td>320/26</td>
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<tr>
<td>Ti 0.5%Cu</td>
<td>452/29</td>
<td>573/19</td>
<td>3.3/1.3</td>
<td>133/18</td>
<td>200/10</td>
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<tr>
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<td>-</td>
<td>678/47</td>
<td>0.8/0.0</td>
<td>122/9</td>
<td>200/10</td>
</tr>
<tr>
<td>Ti 10%Fe</td>
<td>700/102</td>
<td>-</td>
<td>0.7/0.2</td>
<td>108/15</td>
<td>388/37</td>
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<tr>
<td>Ti 5%Mn</td>
<td>755/13</td>
<td>2.000.0</td>
<td>10100</td>
<td>01011</td>
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<tr>
<td>10%Mn</td>
<td>-</td>
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<td>-</td>
<td>0</td>
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<tr>
<td>Ti 20%Pd</td>
<td>549/44</td>
<td>293/19</td>
<td>2.9/0.3</td>
<td>64/10</td>
<td>240/12</td>
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</tbody>
</table>

**Casting performance**

The castability of several metals was tested using an experimental gas pressure casting machine and a high-speed centrifugal casting unit (Ticast Super R, Selec, Japan). CP titanium, a gold alloy, and a Ni-Cr alloy were cast into a mesh pattern and a perforated disc pattern (the gold and Ni-Cr alloys were cast in a conventional “broken-arm” centrifugal casting machine). Castability indices were determined as the amount of metal filling the patterns. In the high-speed centrifugal casting machine, the castability of titanium was similar to that of the conventional dental casting alloys. The values for titanium cast in the gas pressure unit were significantly lower (p<0.05) than those found for the centrifugal casting machine; radiographs taken of the castings made in the gas pressure unit showed much larger pores. The castings made in the centrifugal casting machine had fewer pores; the soundness of these castings was attributed to the high casting force (the force exerted on the molten titanium in the mesh pattern is estimated to be 98.6 N for the centrifugal unit vs. 1.5 N for the gas pressure unit) [8]. Casting performance can also be judged by determining the mechanical properties of the castings. Some commercial alloys other than CP titanium were cast in the centrifugal casting machine and their properties tested (tensile strength, yield strength, elongation and modulus of elasticity) (Fig. 1). All of the alloys showed significantly lower elongation than CP titanium, but there were no significant differences among the alloys. The tensile strength and yield strength of the alloys were significantly higher (p<0.05) than CP titanium, and no appreciable porosity was seen in radiographs of the cast alloys. We thus found that satisfactory castings can be made from these alloys under optimal casting conditions.
Machinability

Before a cast dental prosthesis can be delivered to the patient, the metal must be machined to remove structures attached to it, such as runners, sprues and risers, fins, or any unused melted metal. In some instances, failed metal crown restorations must be removed intraorally by cutting. These machining procedures are performed with burs (rod-shaped bits) coated or cemented with abrasives (diamond chips or particles of silicon carbide, diamond, and alumina) or with abrasive wheels or discs. Tungsten-carbide burs and steel burs are also used to remove small imperfections. These various tools are attached to equipment known as handpieces that are either electric motor-driven or air turbine-driven. The machinability of a metal is of utmost importance; poor machinability means that a dental prosthetic appliance will not fit correctly and may not be esthetically acceptable.

Titanium and its alloys are generally not considered to be metals that can be machined well. Again, the inherent properties of titanium such as high chemical reactivity, relatively low thermal conductivity, and high strength at high temperature [9] cause it to be difficult to cut and grind. We performed several studies on the machinability of both commercial and experimental alloys. In one of the studies, the machinability of CP titanium and two alloys, Ti-6Al-4V and DT2F (Daido Special Steel, Japan; a free-cutting titanium alloy reported to be grade two CP titanium with small amounts of sulfur and rare-earth elements) [10] were tested and compared to a dental gold alloy and a Co-Cr alloy. An SiC wheel was used to grind, and comparison was made based on the amount of metal removed (mm³) for one minute at four different circumferential speeds (500, 750, 1000, 1250 m/min). Ti-6Al-4V was the easiest to grind for speeds of 750-1000 m/min; its grinding efficiency was about three times better than for CP...
titanium. DT2F was slightly better compared to CP titanium. We also investigated the
machinability of CP titanium and Ti-6Al-4V castings with and without the hard surface layer
known as the α-case. Two types of tools were used (steel burs and SiC points) under two
machining conditions. Conventionally cast Co-Cr and dental casting gold alloys served as
controls. With the steel burs, there was a great difference in machinability between CP Ti with
and without the α-case. It was also found that CP titanium and Ti-6Al-4V seemed to be much
easier to cut or grind using either of the instruments compared to the Co-Cr alloy.

In addition to studying commercial alloys, we tested the machinability of some of our
experimental alloys. We believed that to develop an easily machinable alloy, it was necessary
to produce an alloy with precipitation of intermetallic compounds along the grain boundaries or
with a brittle phase in the structure while retaining enough ductility for dental use. Our
experimental cast Ti-Cu alloy (<5%) had satisfactory tensile strength, yield strength, and
elongation. Because the eutectoid (α Ti/Ti2Cu) was included in the microstructure, the ductility
was reduced, which we hoped would improve the machinability. Results showed that the
machinability increased using an SiC wheel with an increase in the Cu concentration (especially
the 5% and 10% alloys) compared to CP titanium. The alloys with 2% Cu showed results
similar to CP Ti. It thus seems that the inclusion of the eutectoid made the metal easier to grind.

Wear resistance

Titanium wears easily. Dental practitioners have found severe wear of CP titanium teeth,
particularly when the same grades of CP titanium were used for both upper and lower teeth [11].
It is obvious that good wear resistance is necessary to maintain long-term restored occlusion.
Our group studied the wear resistance of several titanium alloys and a dental casting gold alloy
using a custom-made two-body testing apparatus that simulated chewing function [12]. Metal
teeth were fabricated from Timetal SRx, Ti-13Zr-13Nb (13), Ti-15V-3Cr-3Sn-3Al (15-3), Ti-
6Al-4V (6-4), and Ti-6Al-7Nb (6-7), plus the gold alloy. A 5-kg load was repeatedly applied to
the upper tooth for 60 cycles/min under continuous water spray. The same metal was used for
the opposing tooth. Wear was evaluated as the sum of the volume loss after 50,000 cycles for one
set of teeth. The gold alloy showed the best wear resistance (Fig. 2). Of the titanium teeth, the
two β titanium metals had the worst wear resistance. There was no correlation between the metal
hardness and the amount of wear. The greater amount of wear of the β titanium metals seemed
to be due to their higher ductility. Because of the poor wear resistance of some of the cast
titanium alloys, we continued testing using Ti-Cu alloy with the hope that precipitated Ti2Cu in
the matrix would improve the wear resistance. A more recent study using 3 and 5% Cu alloys
showed that the mean volume loss (mm³) was less than that for CP Ti (1.89 mm³ for CP Ti vs.
1.27 mm³ for 5% Cu).
Electrochemical behavior

The degree of corrosion resistance of a metal in the oral environment is important to the longevity of the cast appliance. To test this property, seven binary titanium alloys were examined (up to 30% Co, Cr, Cu, Fe, Mn, and Pd, and up to 45% Ag) for rest potential changes over 70 hours and potentiodynamic anodic polarization in 0.9% NaCl solution [13]. Except for some of the Ti-Ag alloys, the rest potentials of all the alloys quickly increased to potentials above 0.175 V within 10 hours. They showed almost the same potential profiles with time as for CP titanium, which indicates that passivation behavior of all alloys was similar to pure titanium. However, the rest potential profiles of the 30-45% Ag alloy were clearly different from the other alloys: the potentials were unstable during the entire time period and were less noble. Microstructural examination of the alloy surfaces after testing showed pitting corrosion around the precipitated Ti2Ag in the α matrix structure.

The potentiodynamic anodic polarization curves for all the experimental alloys, except for the high Ag-content alloys, were similar to that of pure titanium: passive regions appeared from about 0.1V to above 1.2 V, and the passive current densities of the alloys were similar. When the Ag content exceeded 20%, changes in the anodic polarization curve occurred. In the 20% Ag alloy, a current density peak appeared at 0.25 V. As the potential increased, the current density peak decreased and became passive. The current density of the 30% Ag alloy increased at the same potential as the 20% alloy, with breakdown of the passive state at relatively low anodic potentials. The current density for 45% alloy increased more rapidly from the early stage of scanning.

Because the α-case (brittle surface layer) routinely forms on cast titanium metals (CP and alloys), the effect of this layer on corrosion resistance must also be characterized. We studied the effect of the α-case on the corrosion resistance of Ti-6Al-4V, Ti-6Al-7Nb, and Ti-13Nb-13Zr and compared it with the corrosion behavior of CP titanium. Castings underwent three surface alterations: A) cast surface after sandblasting; B) polished surface after removal of the surface reaction structure; and C) sandblasted surface after removal of the surface structure. The rest
potential was measured and potentiodynamic polarization performed. After 16 hours, the rest potential stabilized for all metal surface conditions. Differences in anodic polarization behavior were observed among the surfaces for all the metals. It seems that the $\alpha$-case has a limited effect on the electrochemical behavior of the metals tested. Sandblasting had a prominent effect on the anodic polarization behavior of titanium and titanium alloys.

**Biocompatibility**

Titanium’s worth as a biomaterial primarily lies in its lack of toxicity to the human body. Without this attractive feature, researchers might not have gone to the lengths they have to make this a workable dental material. One danger of alloying other elements with pure titanium is that the biocompatibility might be compromised. We tested experimental alloys containing Cu, Cr, Mn, and Pd, and two industrial alloys, Ti-6Al-4V and Timetal 21SRx, for biocompatibility [14]; two types of specimens were used for each metal (slightly polished specimens with the $\alpha$-case intact and specimens with the $\alpha$-case removed). Both types of specimens were given a final polishing with SiC paper. The specimens were immersed in biological medium (Balb/C3T3 mouse fibroblasts) for 72 hours. Information about cellular mitochondrial function (measured by succinic dehydrogenase activity) was collected. The results indicated that none of the metals, except for Ti-6Al-4V and the experimental 10% Cu alloy, are cytotoxic. The presence or absence of the $\alpha$-case does not appear to matter, with the exception of the 10% Cu alloy.

**Quality of casting**

A major problem facing dental lab technicians is the same as that in industry: due to the reactivity of molten titanium with the oxides in the mold material, a hardened surface layer (150-200 $\mu$m thick) forms, known as the $\alpha$-case. Industrial manufacturers of titanium products completely remove the $\alpha$-case but dental practitioners cannot because the precise fit of cast prosthetic appliances may be compromised. Researchers have studied the nature of the oxides in the mold ingredients and binder materials and refractories for titanium casting have been developed. In the titanium industry where large structures are cast, using stable oxide binder/mold combinations is not feasible because of the cost. However, these methods may prove to be more helpful in dentistry due to the limited size of the cast appliances.

One approach to reducing the $\alpha$-case is to face-coat a pattern with a stable oxide before investing it with the mold material. We studied the microstructure and mechanical properties of titanium cast in molds coated with Y$_2$O$_3$ (a slurry with methyl-cellulose)[15]. The hardness profiles near the surfaces of the specimens were particularly interesting. We made specimens cast in both a magnesia-based investment (Selevest CB, Selec Co., Japan) and a silica-phosphate bonded investment (T21, Whip Mix Corp., USA). No matter the investment, the surface hardness of the Y$_2$O$_3$-coated specimens was considerably reduced compared to the uncoated specimens (Fig. 3). The yield strength and elongation values showed no significant differences among the specimens. Only the tensile strength for specimens cast in the uncoated magnesia-based investment was significantly lower than that of the other types of specimens.
While we expected increased ductility for specimens cast in Y$_2$O$_3$-coated patterns, we found instead that the means of elongation were higher for specimens without yttria coating, regardless of the investment material. SEM examination of the surfaces fractured during tensile testing indicated that there was brittle fracture on the coated specimens. At higher magnification, the surfaces showed particles along the grain boundaries that we thought were contaminated yttria particles, which apparently contributed to brittle intragranular fracture. Thus, it seems that improvement is required in the face-coating technique in order to produce castings with satisfactory ductility.

Veneering with dental porcelain

Patients desire esthetically pleasing dental restorations, so appliances such as crowns must be veneered with dental porcelain to make them look like natural teeth. The technology of veneering by firing porcelain or bonding a dental resin (polymer) on metal crowns, fixed partial dentures, and other prostheses is well established for conventional dental casting alloys. As with other aspects of titanium casting, the technology of veneering porcelain on titanium had to be modified due to the properties of titanium, such as the high reactivity of titanium with oxygen at temperatures above 800 °C, its lower linear coefficient of thermal expansion compared to conventional alloys, and the titanium phase transformation at 882 °C. We fired dental porcelain on some of our experimental alloys with Ag, Cr, Cu, Fe, Mn, and Pd [16,17]. A porcelain specifically made for titanium veneering (Titan, Noritake, Japan) was applied to the cast titanium to create bilayered beam specimens, which were debonded in three-point flexure testing. Results were compared to the results from the controls (veneered CP titanium and gold alloy bonded with an appropriate porcelain). The bond strengths for all the experimental alloys were not significantly different (p>0.05) from those of the two control alloys, indicating that the experimental alloys have enough bond strength for clinical use. The mean bond strengths were higher than the minimum value specified in ISO standard 9693 [18]. These results were encouraging but further study is needed to improve upon these findings.

CONCLUSION

Successful adaptation of titanium to dentistry has already begun to take place through
research performed in the last 20 years. As seen in the variety of topics summarized above, there are many aspects of titanium casting to be studied and improved. Work in these areas will continue in our laboratory and others in order to make titanium a truly feasible material for dental practitioners.

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