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Review Article

The dental applications of titanium and its alloys: A review

Rodrigues S[1], Shenoy V[2], Shetty T[3], Jain N[4]

[1]Associate Professor, [2,3]Professor, [4]Assistant Professor, Department of Prosthodontics, Manipal College of Dental Sciences, India

Abstract

The advances made in dental materials science suggest that intriguing changes will continue to occur in the practice of dentistry. Titanium is one dental material that promises to play an important role in the materials of the future and is a potentially important metal for medical and dental applications, currently being at the heart of most dental implantology. Being biocompatible it is also a suitable replacement for existing alloys in fixed and removable prostheses. Its future use in Prosthodontics would increase based on advanced research and clinical trials. Although the reports on the prosthodontic application of titanium have been increasing, its use in clinical dentistry for conventional removable partial denture is rather limited. This article will present the applications of titanium and reviews the literature on its status in Prosthodontics, especially Removable Prosthodontics by conducting an electronic search of Pub Med and reviewing English language peer reviewed articles from the years 1996-2008 coupled with additional references from citations within the articles. The articles were accessed by using the keyword “titanium, titanium alloys, pressure casting, removable partial denture framework”.

Key words: Titanium, Titanium alloy

Introduction

Titanium is a fascinating material being the focus of attention of dental researchers and clinicians. It has been referred to as, “the wonder metal”, for two different reasons[1]. One was because it had many unique and wonderful properties. The other being one just had to wonder what role titanium would play in the materials of the future.

The controversy surrounding the biocompatibility of cobalt and nickel containing alloys as potential allergenics and the biological risks of metal ions released in the mouth during corrosion suggests the merits of another base metal alloy as an alternative[2]. Although none of the materials used in dentistry are totally inert, the evolution of titanium as an economical and nontoxic biocompatible replacement for existing alloys for fixed and removable prosthesis has rekindled interest in this wonder metal.

Until recently, the use of titanium for casting and its prosthodontic application was limited, probably because of technical difficulties in the casting procedure. Advances in research, development of new materials and devices for titanium casting has resulted in clinical and laboratory success with titanium based alloys. Its further use in Prosthodontics would increase based on research and trials to compare its effectiveness to other existing and commonly used metals. The purpose of this article is to describe the properties of Titanium and to review its status in Prosthodontics. A literature search of Pub med was performed and English language peer reviewed articles published from 1998- 2008 that addressed the question of the properties of Titanium and its application in Prosthodontics were included. The Medline search was supplemented with a hand search to identify relevant peer reviewed articles published in dental journals.

Titanium: A historical perspective

Although first identified by Gregor in 1791 as Mechanite and rechristened as Titanium by Klaproth after the Titans of the Greek mythology it was Dr. Wilhelm Kroll who invented useful metallurgical processes for the commercial production of titanium and is considered to be the father of titanium industry[3,4].

Correspondence
Dr. Shobha Rodrigues, Associate Professor, Department of Prosthodontics, Manipal College of Dental Sciences, India
E-mail: ereldiaz@yahoo.com

General properties

A comprehensive review of the properties of titanium is essential to understand its working and applicability. Concepts have been organized to understand its applications despite deterrents to its use. Titanium has physical and mechanical properties, which have led its increased use in dental prosthesis despite casting difficulties due to high melting point (1700^{0}C), low density, high affinity to gases, and its reactivity with most components of most investment materials resulting in surface contamination, the removal of which is difficult, and complicating[5,6,7]. Although manufacturers do not recommend electrolytic polishing, this procedure may minimize residual irregularities not reached by conventional polishing, thereby optimizing the polishing process and providing a smoother surface[8]. Titanium has low thermal conductivity (22 W/m2)[9] and is considered more physiological material than gold since its thermal conductivity is the closest one to the enamel's proper value. This feature also allows for excellent localized electric arc spot welding, though when cutting heat will not be dissipated quickly[1]. Another important feature of titanium its is ability to form a very stable oxide layer which contributes to corrosion resistance, osseointegration and permits close apposition to physiological fluids, proteins and hard tissues to the metal surface[10].

Studies on the in vitro corrosion of titanium found that the titanium ion release increased in the presence of fluoride ions; hence chemical agents primarily fluoridated solutions must be avoided even though no corrosion effects were observed clinically[11,12,13]. Similar studies on the corrosion resistance revealed that corrosion resistance was inversely proportional to surface roughness and pH of the solution[12,14,15]. Spectrophotometry studies further revealed that all titanium alloys were covered mainly with rutile type oxide after corrosion tests[16].

Studies done by Ikeda and Igarashi demonstrated that titanium plates anodized by being discharged in various concentrations of NaCl, Na F and KI solutions acquired antibacterial activity, which were found to be cell compatible suggesting greater clinical success of implants, due to reduced colonization of oral bacteria thus reducing one of the causes of peri-implantitis[17,18].

Titanium casting machines

The casting of titanium dental appliances was noted in the early 1970 with the work of Water Stratt[1]of the US National Institute of Standards and Technology. This was followed by numerous studies in Japan, Europe and USA towards the precision casting of dental prostheses, and the development of casting machines and suitable investment materials. Titanium casting machines are classified into 3 types[19].

1) Inert gas arc- melting /gas pressure casting machines that consist of 2 chambers:
   - an upper chamber (melting chamber) for arc melting under an inert atmosphere (Argon gas) and
   - Lower chamber (mold Chamber) with a muffle in which the molten metal is forced under Gravitational acceleration and inert gas pressure. e.g. Castamatic, Dentaurum.
2) Inert gas melting /centrifugal casting machines with vertical or horizontal centrifugal casting e.g. Cyclarc, J Morita
3) High frequency induction melting/ gas pressure casting machines.e.g. Tycast, Jeneric/Penetron and Titaniumer, Ohara

Regardless of these new developments and the advance in the equipment used, porosity associated with titanium casting remains a problem resulting in inferior restorations[19-22]. Porosity is mainly on account of the gas entrapment due to vast temperature difference in molten Ti and that of the investment material causing rapid solidification, reducing the chances of gas to escape, and eventually trapping these bubbles in the metal casting and metal shrinkage upon solidification[21,23]. These differences are more than 1100^{0}C for magnesia based investment alloys and 1600^{0}C for silica based investment materials[23]. Radiographic digital imaging study analyses have confirmed that among the different casting systems, the centrifugal casting systems showed better results than other pressure differential casting systems and Ti castings made under an argon pressure of 50 mm Hg are significantly more porous than are castings made under a pressure of 400 mm of Hg. The non vented molds of a highly permeable refractory material yield the soundest castings[20,21]. The turbulent flow of molten titanium is responsible for gas incorporation and increasing albeit smaller casting defects in centrifugal systems. On the other hand the laminar flow of molten metal produces fewer but larger defects in the gas pressure/ vacuum systems[5, 24-26].

In some situations, larger sized pores are more beneficial than the smaller sized pores because they can be easily detected by the laboratory radiographic units and can be eliminated by laser welding[27]. However in the case of extremely large pores, welding repair is questionable due to the high energy required resulting in a possible alteration of the mechanical properties[28].

Cast titanium removable partial denture

Titanium is a relative new material for removable partial denture (RPD) frameworks. Because of its unique mechanical and chemical properties, Titanium is an ideal biomaterial and a suitable alternative for patients sensitive and allergic to other metals. The combination of high strength and low weight makes Titanium and its alloys some of the highest strength/weight ratio materials, second only to fiber glass and other highly reinforced polymers[1]. On account of its low elastic modulus Titanium requires more bulk to prevent permanent deformation during function therefore clasps have to be wider than usually seen with Co-Cr or stainless Steel Another benefit of the low elastic modulus is that titanium can engage deeper retentive undercuts on teeth without applying lateral forces to the abutment teeth during insertion and removal of the appliance.

On the other hand, due to its inherent large flexibility, cast bilateral long span RPD made in titanium are contraindicated. These appliances are better made of stiffer Co- Cr alloys[1]. One of the most common problems that necessitate replacement of RPD's is fracture of metal framework. Within the framework, clasp assemblies are cited as fracture sites[29]. Internal porosity is reported as a potential factor in the fracture mechanism because it reduces bulk of the metal and causes stress concentration. Even with special casting methods, titanium is prone to porosity, especially with complicated structures. Therefore castings should be examined with non destructive methods, for example with radiographs. Removable partial denture frameworks that were 0.70mm thick had better castability than did 0.35 mm thick RPD frameworks. The same study also showed that Ti commonly failed to cast perfect mesh specimens, although the same problem was not seen in Co-Cr alloys[30]. Baltag.I. et al[22] investigated the influence of sprue design on internal porosity of circumferential clasps of cast titanium removable partial dentures and concluded that curved sprue design produced significantly less porosity than conventional straight design.

Blackman et al[31] investigated the dimensional changes during casting of titanium for RPD frameworks. The authors concluded that dimensional changes in both horizontal and the vertical planes occurred, with mean cross arch shrinkage of 2.6% horizontally and expansion of 1.8% vertically. Shrinkage in the premolar region was less than that in the molar region. They concluded that methods for best controlling factors influencing dimensional changes need to be fully investigated.

Pekka K Vallittu et al[32] studied the deflection fatigue of cobalt chromium, titanium and gold alloy cast denture clasp. The results of the study suggested that significant differences exist in the fatigue resistance of removable denture clasps made from different commercial cast metals, which may cause loss of retention of the removable partial denture and clasp failures. They concluded that from a clinical standpoint activation of cobalt chromium and gold alloy clasps lengthens their fatigue life, but decreases their retention. They suggested that activation of titanium clasps to be avoided as they had lower fatigue resistance.

Vander Brink et al[33]. compared various RPD clasp materials and fabrication procedures including Nickel Titanium alloys (Ni-Ti). The alloy was found to be unacceptable for an RPD clasp even when a 0.8 mm diameter was used. One outcome of the study was the need to compare materials in a curved clasp configuration rather than in straight specimens.

Bridgeman et al[34] investigated the retentiveness of titanium and cobalt chromium removable denture clasps over a 3 year period of simulated clinical use, and concluded that the flexibility and long term retentive resiliency of the clasps made Ti and its alloys suitable for Removable partial dentures especially for situations involving deep undercuts. They also suggested that though casting defects contribute to material degradation and loss of retention in a small percentage of the titanium and titanium alloy clasps, the risk of fracture was actually greater for the Cobalt Chromium clasps than for the pure titanium or titanium alloy clasps.

Dong Suk Kim et. al[35] compared the clasp retention of Cast Ti-Ni alloys with conventional removable partial denture clasps and found that though the end point retention for all the clasps were similar, there was less change in the retentive force of the cast Ti-Ni alloys after repeated cyclic sequences of simulated placement and removal, finding them a very desirable option for RPD fabrication.

Titanium in crowns and bridges

A study on the marginal fit of Titanium crowns was found to be intermediate between a group of high noble alloy (Au-Pd-Ag) and Ni-Cr alloy crowns[36]. In 1989, Andersson et.al[37] introduced a new system of titanium crowns that used a copy milling spark erosion technique to fabricate titanium copings and veneered them with composite resin. In this technique the external contour of the titanium crown or coping can be shaped out of a solid piece of titanium by a milling machine, while the internal contour of the titanium crown is spark eroded with a carbon electrode. Single titanium crowns can be fabricated with this method, and multiple unit fixed prostheses can be made by laser welding individual units together. The advantages of this system includes low cost, standardized fabrication and biocompatibility[38.] A study on the fit of 20 cast titanium copings divided into two equal groups with 45 and 90 degree shoulders revealed the surface of marginal discrepancy was greatest with the 90-degree configuration[39]. Casting shrinkage occurred particularly along the horizontal axis in the plane of the shoulder.

The overall fit of the spark eroded titanium crowns on the basis of the size and character of the cement film at three selected sites from inside the finish line was found to be less than cast gold alloys[40].

Porcelain bonded to titanium

If titanium's distinct advantage is to be used, for aesthetic crowns and bridges, the ability to apply porcelain veneer becomes important. Fusion of porcelain on titanium is not without difficulties. The characteristic high temperature oxidation of titanium is the main obstacle to strong titanium bonding[5, 41-44] Kirmura et al[45] reported the oxidation effects of the porcelain titanium interface reaction. They concluded that the thickness of TiO_2 on commercially pure titanium surface increased with the increase in oxidation temperature. Titanium surface hardness also increased substantially after oxidation at and above 900^{0}C. Lower titanium bond strength was attributed to a thick TiO_2 on the metal surfaces when titanium was oxidized at higher temperatures[46]. Menis et. al[47] attempted to bond low fusing porcelain to cast titanium at approximately 800^{0}C. Although the bond strength was nominally comparable with the bond strength of porcelain bonded to Ni-Cr alloy, separation of porcelain from the cast titanium occurred at the oxide-metal interface.

Togaya et al[48]. investigated the compatibility of porcelain from the cast titanium and suggested that appropriate bond strength between porcelain and titanium was possible by reducing the thermal expansion coefficient of the porcelain to approximate that of titanium.

Adachi et al[49] evaluated the bonding of low fusing porcelain to titanium and Ti-6Al-4V alloy by an x-ray spectrometric technique. Oxide adherent strength values were measured at 750^{0}C and1000^{0}C via simulated porcelain firings and actual porcelain application. The porcelain delaminated completely from the metal substrate in the constant flexural test, leaving less than 1% of the surface covered with porcelain. The oxide adherence of the specimen oxidized at 750^{0}C was good; however was too thin to be visualized in the scanning electron microscope. Little or no residual stress due to thermal mismatch should exist in the final titanium / porcelain bond interface. The significant discrepancies already noted in their thermal coefficients of expansion will have to be more closely matched. An interfacial oxide layer some 100 to 1000 microns thick, forms during firing and the thicker this layer becomes, the weaker the bonding between the porcelain and the titanium.

An enhanced titanium ceramic bond was reported when porcelain was fired on cast titanium in a reduced argon atmosphere[50]. An argon atmosphere limited the titanium oxidation during porcelain firing and therefore improved ceramic bonding[51].

Changing titanium surface to control its high temperature oxidation has been examined. Published studies showed that titanium surface nitridation[52] or a thin Chromium coating is an effective method of limiting titanium oxidation at high temperature[53]. Regardless of the interfacial variables, conventional noble ceramic bonding was superior to titanium bonding[51].

Currently at least one system Procera (Noble Biocare, Gothenburg, Sweden) has had success in fabricating single unit crowns and multiple unit bridges from commercially pure wrought titanium. A compatible low fusing porcelain, Ti-Ceram has been developed for veneering these restorations. The advantage of the Procera system over cast Ti is that it overcomes the hardened surface layer that is encountered with Ti castings, therefore providing adequate porcelain titanium bonding[1, 54, 55].

Boeing et al[56] in an invitro study indicated that Procera crowns had a good marginal fit, if a feather edge or chamfer preparation is used. Marginal gaps range from 270 to 750 microns with shoulder preparation because of the construction of the duplication milling machine. Their results also showed that the Ti ceramic bond passed the Deutsche Industrie Norm test but failed the International Standards Organization test.

Pang et al[57] studied the bond strength of palladium copper (Ney) to VMK68 (Vident), cast Ti to Duceratin (Degussa) and machined milled Titanium to Procera. The bond strength of palladium-copper to VMK68 porcelain was greater than that of the two Ti porcelain combinations. There was no significant difference in the bond strength of porcelain bonded or cast to machined Ti. The multiple firing schedules did not significantly affect the bond strength between low fusing porcelain and grade2 Titanium.

Nilson et al[58] conducted a year clinical study on 44 Procera ceramic crowns and indicated that two crowns had ceramic fracture, ratings for surface and color had changed markedly from the excellent to the acceptable level and anatomic form had a small shift from the excellent to the acceptable level.

Further studies on clinical trial of Procera crowns veneered with resin composites were performed by Bergman et al[59]. Ten (5.2%) of 192 titanium crowns had fractures of the resin composite veneer, but 99.5%of the crowns were rated excellent or satisfactory. There was a decrease from 83.4% to 70.1% in anatomic form and marginal integrity after 1 year of follow up. 96.8% of the crowns showed excellent or satisfactory clinical properties for their surfaces or colors. The authors summarized that the initial marginal integrity was satisfactory and remained so throughout the 2-year follow up period.

Titanium as a dental implant material

Ossoeintegration has had a dramatic influence on Prosthodontic practice. The best long term results obtaining effective osseointegration have been produced with commercially pure titanium (CPT). Another material, Ti6Al4V which produces similar in vitro tissue reactions as CPT has not produced as much clinical success, probably though not conclusively due to leak of aluminum ions that compete with calcium during early stage of calcification[2].

While titanium is the material of choice mainly on account of its biocompatibility, its low modulus of elasticity, its machinability into strong hollow tubes, and its potential to be plasma sprayed or heat sintered in powder form to create porous implant surface makes it a preferred metal[1]. Modulus of Titanium is much closer to that of bone than either stainless steel or Cobalt chromium, although it is still five times that of cortical bone[60]. This property leads to a more even distribution of stress at the critical bone-implant interface, because bone and implant will flex in a more similar fashion. Another classical way to further make a device less stiff is to reduce cross sectional area or to make it porous. Titanium lends itself well to both these methods. It can be machined to hollow and perforated designs and the implant surface can be porous coated either by a plasma jet spraying it with powder or by heat sintering Titanium or Titanium alloy beads. Although there is some controversies regarding optimal pore size, in general, openings of 100 micrometers or larger appear to permit bone in growth and calcified bone ground substance may invade pores in 1-10 micron size[2]. However if pores become too large or too numerous, there is a danger of weakening the coating to the point of mechanical instability. Also porosity increases the exposed titanium surface area. So even though the corrosion type reactions per unit area are minimal, the significant increase in surface area will increase the amount of reaction products[61]. Success of dental implants would not only depend on the material selection alone but also on the continual improvements in the device design and clinical implantation techniques.

Titanium Joining

Tungsten inert gas (Tig), laser beam welding and brazing by infrared radiation heating techniques have been used to join titanium metal in a protective environment. Because of the low thermal conductivity of Titanium, and greater rate of laser beam absorption makes it easier to laser weld titanium[62]. Short span multiple bridges and bridges with pier abutments may be simple to fabricate, since individual case units can be welded together rather than being brazed. Since the bulk of the titanium framework is unaffected by local heating, room temperature assembly of appliances using accurate casts can eliminate many factors where distortion might be otherwise introduced.

Yamagishi et al[63] examined the mechanical properties of Nd:YAG laser welds of titanium plates (1mm thick) and found that there is a significant relationship between three point bending strength and the irradiation atmosphere, irradiation intensity and the combination of atmosphere and intensity. Laser welding is effective when performed in an argon atmosphere. Results vary with various intensities of radiation.

Sjogren[27] evaluated the tensile strength of welded titanium rods and concluded that the penetration of laser energy could be up to 0.9mm, leaving the central portion of the rods unwelded. The welded specimens showed different defects such as gas pores and cracks at the fractured surfaces. The size and distribution of such defects seemed to be dependent on the laser variables used.

Berg et al[64] evaluated the mechanical properties of laser welded cast and wrought titanium base and compared them to those of a brazed type IV cast gold alloy. No significant difference in tensile strength was demonstrated between cast and wrought titanium. When the ductility of the Ti specimen was reduced the welded titanium was found to be as strong as brazed gold, suggesting that experimentally restorations made up of cast and wrought titanium would satisfy clinical requirements. Wang and Welsch[65] compared three joining methods for pure Ti and Ti6AlV alloys, using laser, tungsten inert gas and infrared radiation and concluded that tungsten inert gas method demonstrates overall better results in terms of tensile strength and ductility, was also easy to operate, and economically feasible. In this study lack of complete joining was found among all the laser welded samples, corroborating with similar results by Sjogren.

Summary

Selection of materials is based on a reconciliation of their biocompatibility, optimum physical and mechanical properties and where indicated their superior esthetic qualities. A fundamental knowledge of the properties as well as the limitations of dental materials is crucial, so that the dentist can manipulate these materials to the best benefit of the patient

Titanium and its alloys are known to have lightweight, high strength to weight ratio, low modulus of elasticity and excellent corrosion resistance. In addition it is biocompatible and can be shaped and finished finding its way into dental applications like implants and restorative castings. Although more research is needed in areas such as development of optimal casting investments, porcelain veneering systems and controlled biological responses its future use in dentistry appears very bright.

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