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Literature Review

Titanium - ceramic restoration: How to improve the binding between titanium and ceramic

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ABSTRACT

Background: *Titanium alloys has been used as an alternative to nickel-chromium alloys for metal-ceramic restorations because of its good biocompatibility and mechanical properties. This indicated that it was possible to design coping according to standards established for metal-ceramics. However, titanium is chemically reacting strongly with gaseous elements which causes problems when ceramics are fused to titanium.* ***Purpose:*** *To provide information about improving the bonding between titanium and ceramic.* ***Review:*** *Titanium has two crystal modifications, the close-packed hexagonal (α) structure, up to 880° C, and above this temperature the body-centered cubic (β) structure. The principal problems is the extensive dissolution of oxygen resulting in thick, oxygen-rich titanium layers called α-case that harms the bonding of ceramic to titanium and the great mismatch in the coefficient of thermal expansion of conventional ultra-low fusing ceramic. Methods have been developed for fusing ceramic to titanium like processing methods, the used of ultra-low fusing titanium ceramic, bonding agent, and protocol for ceramic bonding to titanium.* ***Conclusion:*** *Titanium and titanium alloys, based on their physical and chemical properties suitable for titanium-ceramic restorations, but careful selection of processing methods, ceramic materials, laboratory skill and strict protocol for ceramic bonding to titanium are necessary to improve the bonding between titanium and ceramic.*

Key words: *Dental ceramic, titanium, bond strength*

ABSTRAK

Latar Belakang: *Logam campur titanium telah dipakai sebagai salah satu bahan alternatif untuk logam nikel-krom pada pembuatan restorasi keramik taut logam karena mempunyai biokompatibilitas dan sifat mekanik yang baik. Hal ini menunjukkan bahwa logam titanium dapat dipakai untuk pembuatan koping logam berdasarkan standar yang dipakai untuk pembuatan restorasi keramik taut logam. Meskipun, secara kimiawi logam titanium bereaksi dengan elemen-elemen gas yang menyebabkan masalah pada perlekatan keramik pada titanium.* ***Tujuan:*** *Memberikan informasi tentang cara meningkatkan kekuatan perlekatan antara keramik dengan titanium.* ***Tinjauan:*** *Titanium mempunyai 2 struktur kristal, struktur close-packed hexagonal (α) diatas 880°C dan struktur body-centered cubic (β) dibawah 883°C. Masalah utama adalah pelepasan gas oksigen yang menghasilkan lapisan titanium kaya oksigen yang tebal disebut α-case yang menghalangi perlekatan keramik pada titanium dan koefisien ekspansi panas dari bahan ultra-low fusing ceramic yang berbeda dengan titanium. Berbagai cara telah dikembangkan untuk mendapatkan perlekatan keramik pada titanium seperti teknik pembuatan, pemakaian bahan ultra-low fusing titanium ceramic, bahan bonding dan protokol untuk perlekatan bahan keramik pada titanium.* ***Kesimpulan:*** *Titanium dan logam campur titanium, berdasarkan sifat-sifat mekanik dan kimiawinya dapat dipakai untuk pembuatan restorasi keramik taut logam, tetapi pemilihan teknik pembuatan, bahan keramik, ketrampilan peteknik gigi dan mengikuti protokol untuk mendapatkan perlekatan keramik pada titanium dengan benar diperlukan untuk meningkatkan kekuatan perlekatan antara keramik dan titanium.*

Kata kunci: *Keramik kedokteran gigi, titanium, kekuatan perlekatan*

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INTRODUCTION

Metal-ceramic restorations have been increasingly used in esthetic crown and fixed prosthesis restorations since the 1960.[1] Rational selection of an alloy for metal-ceramic restorations should be based on physical properties, chemical properties, biocompatibility, laboratorium workability, and ceramic compatibility.[2] Selection of high quality materials and their appropriate manipulation are the most effective means to protect the patient from material-induced injury.[3] The fabrication of metal ceramic restoration is a technical sensitive procedure, including fabrication of metal coping, metal surface treatment for increasing bond strength which is considered the most important step for the success of ceramic fused-to-metal in the whole procedure, and application and firing of ceramic onto the metal to complete restoration.[4] In the early 1970, titanium has been used in cast dental prostheses because of excellent biocompatibility, light weight, high strength to weight ratio, low modulus of elasticity and excellent corrosion resistance.[5–7] Titanium is currently considered a key metal for successful implantology, published by Branemark et al. Recently, there have been increasing efforts to develop titanium technologies for other applications in prosthetic dentistry, including fusing to dental ceramics to commercially pure titanium (CP Ti).[8] According to the American Society for Testing and Materials (ASTM), CP Ti is available in four different grades (grade I to IV) and three titanium alloys. It is based on the incorporation of small amounts of oxygen, nitrogen, hydrogen, iron, and carbon during purification procedures where by each grade has different physical and mechanical properties.[9]

Titanium-ceramics has become a topic of interest for prosthetic applications as an alternative for patients sensitized to nickel-chrome or chrome-cobalt alloys.[10] A number of concepts have been presented, including metal frameworks (coping) produced by casting or milling and a number of materials and methods for veneering.[11] Based on research, the highly oxidative nature of titanium surface in high temperature has been thought as the potential problem of the weak bond between titanium and ceramic.[5] Thus, although titanium-ceramic systems are available today, there still seem to be unsolved problem related to the fusing of ceramics to titanium.

The purpose of this article is to provide information about improving the bonding between titanium and ceramic, because there are reasons to believe that titanium-ceramic restorations will become an important clinical concept.

Commercially pure titanium (CP Ti) and titanium alloys

The American Society for Testing and Materials recognizes four grades of CP Ti and three titanium alloys: Ti-6 Al-4 V, Ti-6 Al-4 V Extra low Interstitial (low components) and Ti-Al-Nb.[9] Clinically two forms of titanium have received the most interest, the CP Ti and an alloy of titanium is titanium-6% aluminium-4% vanadium (Ti-6Al-4V).[5] The titanium is used as an alternative to chrom-type alloys because of its high strength and rigidity, low density and light weight, ability to withstand high temperatures and resistance to corrosion, low cost and mechanical properties that resemble those of hard and extra-hard casting golds.[2,9,10] For fixed dental prostheses, titanium alloys can consider as viable option to more traditional noble and base metal alloys, but careful selection of processing methods and laboratory skill are necessary to ensure success.[9] "Commercially pure" disclaimed 100% purity and acknowledges that small amounts of oxygen (0.18 to 0.40% by weight) and iron (0.20 to 0.50% by weight) are combined with titanium.[2] The oxygen is in solution so that the metal is single phase. Elements such as oxygen, nitrogen and carbon have a greater solubility in the hexagonal closed-packed structure of the α-phase than in the cubic from of the β-phase. This elements form interstitial solid solution with titanium and help to stabilize the α-phase. Transition elements such as molybdenum, niobium and vanadium act as β stabilizers.[5]

Titanium can be alloyed with element such as aluminium, vanadium or niobium resulting in improved mechanical properties. Only a few titanium alloys are being used for the commercial production of fixed and removable dental prosthesis. A titanium alloy, Ti-6Al-4V, has been used for metal-ceramic restorations with special low thermal expansion ceramic (coefficient of expansion of 9×10^{-6}/°C) similar to that of titanium and baking technique, the bond strengths between titanium and ceramic have some what improved.[6] Aluminium and vanadium are added in only small quantities. The strength of the alloy is much increased over that of CP Ti, aluminium is an α stabilizer with vanadium acting as a β-stabiliser. When these materials are added to titanium, the temperature at which the α-β transition occurs is depressed such that both the α and β forms can exist at room temperature. Thus, Ti-6Al-4V has a two-phase structure of α and β grains.[5] The effects of interactions with atmospheric gases during melting, casting and other high-temperatures laboratory procedures are as destructive to titanium alloys as they are unalloyed titanium. The problems encountered in producing cast restorations from titanium alloys are not unlike those experienced with titanium of high or commercial purity.[2]

Physical and chemical properties

Pure titanium is a white, lustrous metal, which has the attraction of low density, good strength and an excellent corrosion resistance.[5] and present two major problems for metal ceramic restoration, a high melting point (1680^0 C) and high reactivity.[12] Titanium, in its metallic form at ambient temperature, with hexagonal, close-packed crystal lattice (α phase) at low temperature, which transform into a body-centered cubic form (β phase) above 880° C.[5,9,12] The tensile strength and elongation of pure titanium are about 250 MPa and 50%, respectively. However, seemingly slight variations in oxygen and iron content substantial and lasting effects on titanium's properties. Generally, as oxygen or iron content increases, strength increases and ductility decreases. Furthermore, the consequences of titanium-oxygen interaction seem vary according to melting and casting practices.[2,5] Titanium's elastic modulus of about 17 million psi (117 GPa) is higher than those of type III and type IV casting gold (–100 GPa), but lower than those of most chromium-type alloys (171 to 218 GPa). The Vickers Hardness Number (VHN) of cast CP Ti is 210. The strength and rigidity of titanium are comparable to those of other noble or high noble alloys commonly used in dentistry, and titanium ductility, when chemically pure, is similar to that of many dental alloys.[2]

Titanium alloy are a mixture of the α and β phase, where the α phase is relatively soft and ductile while the β phase is harder and stronger but also less ductile. The Ti-6 Al-4 V considerably higher tensile properties than pure titanium which makes it attractive for partial dentures. An important feature of these materials is the fatique resistance of titanium alloys, and the fatique limit is approximately 450 MPa.[5] Except for elastic modulus, the tensile properties of titanium alloys are similar to those of chromium type alloys.[2]

Good mechanical performance is corrosive-resistant in addition to having a neutral taste and a VHN of 180 to 250, and low thermal conductivity, less to experience sensitivity to hot and cold, and titanium will not react to surrounding materials.[13] The potential for corrosion of titanium in the biological environment has been studied and has confirmed its excellent corrosion resistance.[5] The metal can also be highly polished to help reduce tartar accumulation and the radiolucency of the titanium helps enable the dental team to view the underlying tooth structure for caries detection without removing the crown, the patient highly appreciates this, especially for more extensive restoration.[12] Titanium as a "biometal" because of its good biocompatibility and mechanical performance. This material is hypoallergenic (impervious to body fluids and is not recognized by the body as a foreign materials), making it very diserable for use in these with metal allergies.[1,8] Titanium as a coping material for metal-ceramic restorations has received attention in dentistry, with the idea that it could be as an affordale alternative for expensive precious metal alloys because it has a thermal expansion coefficient of 9×10^{-6} K^{-1}, low thermal conductivity, low density and biocomp atibility.[6,11,13,14]

Titanium-oxide (Ti-O) system or α-Ti (O)

Useful biological properties of titanium, especially biocompatibility, are based on the existence of Ti-O layers, which are naturally formed in oxygen-containing environments. In the hexagonal structure of titanium, each atom has one octahedral site which can be occupied by oxygen atoms. For example, one mole of oxygen atoms dissolves in titanium, forming a dilute solid solution, a large amount of energy is released. Thus, the Ti-O solid solution is thermodynamically very stable.[1,5] Even a low percentage of oxygen in the solid-solution phase makes it brittle, but not until the oxygen content reaches about 30% in the solution, the formation of the first oxide layer begin at elevated temperatures (> 700° C). Titanium has an exceptional ability to form several stoichiometric and non-stoichiometric oxides e.g., Ti-O, Ti_2O_3, Ti_3O_5 and Ti O_2. The non-stoichiometric titanium monoxide is one of the most interesting phases, because of its wide range of homogenity and several crystal modifications. Ti O_x is in "equilibrium" with the oxygen-rich bulk metal. Despite these formation conditions, the outer most oxide layer is always (the most oxygen-rich) titanium dioxide (Ti O_2).[1]

Titanium-ceramic system (Ti-Si-O system)

"Titanium ceramic" is used in the literature for a feldspathic ceramic used for veneering at titanium.[9] According to fusing temperature, ceramic can be classified into high fusing (1300° C) for denture tooth fabrication, medium fusing (1100–1300° C) for denture tooth fabrication, low fusing (850–1100° C) for crown and bridge construction and ultra low fusing (< 850° C) for crown and bridge construction. The high and medium fusing ceramics are similar in both composition and microstructure. In terms of actual use, denture teeth are made from the fusing materials, whereas the medium fusing most often are used to produce prefabricated pontics. The low fusing ceramic containing leucite (feldspar-based) became thermally compatible with metal-ceramic alloys. Ultra low fusing ceramic were designed to veneer a metal coping at even lower firing temperature.[4] As for metallic coping materials they are also classified into a) high noble (Au-Pt-Pd, Au-Pd-Ag, Au-Pd); b) noble (Pd-Au, Pd-Au-Ag, Pd-Ag, Pd-Cu, Pd-Co, Pd-Ga-Ag); and c) base metal (CP Ti, Ti-Al-V, Ni-Cr-Mo-Be, Ni-Cr-Mo, Co-Cr-Mo, Co-Cr-W).[15]

When Si O2-based dental ceramics are fused to titanium, the most important reaction occur among Ti, O and Si. When SiO_2-based dental ceramics and CP Ti are in contact at firing temperatures (720–750° C) for a given time, the dissociation of oxide layers by Ti (after dissolving its own native oxides) and the subsequent dissolution of the elements in Ti will occur (Ti-SiO_2 bond).[1] The Ti-ceramics system can be considered as a double-layer structure, comprising of at least titanium substrate and ceramic body, including bonding agent.[15] In contrast with most dental alloys for metal-ceramic restorations, titanium cannot be veneered with conventional feldspathic dental ceramic for several reasons. The use of adapted ceramics for veneering is therefore required. Titanium is known for its increasing oxidation at elevated temperatures and an increase of grain size and coarsening of microstructure nearby and passing through the β-transus at 880° C. This can cause ill-fitting copings. During the β titanium phase, the ceramic will form a white dioxide layer that is unsuitable for bonding, and its leads to impurity and brittleness.[13] Therefore, the firing temperature for fusing ceramic to titanium is restricted to a maximum of 800° C.[11] In addition to compatible thermal expansion coefficient of ceramics and metals, knowledge of the microstructures and compositions of the reaction zones is of great importance for optimizing the ceramic-fused-to-metal system and their processing. Several bonding agent have been used as interlayers in conventional metal-ceramic systems to improve the mechanical compatibility of the joint. Gold containing interlayers and ceramic interlayers have been applied to the titanium-ceramic system to increase bond strength.[1]

Processing methods of titanium coping

Several methods was incorporated to make the titanium coping fabricationare: casting, spark erosion and CAD/CAM. During the casting process, the high melting temperature of titanium has made the casting process difficult, rapid oxidation and the high affinity of molten titanium to investment materials has created reactive α-case layers (oxygen-rich surface layer) on the surface of the casting and results in inferior titanium-ceramic bonding.[14,16] Titanium melting is best done in specially designed furnaces with an argon atmosphere.[2,5] Titanium must be melted in a vacuum or under inert gas to prevent oxidation and the incorporation of oxygen that can lead to embrittlement of the cast metal. Contamination with even low concentration of atmospheric oxygen can lead to significant loss of ductility. The molten alloy also can react readily with refracting investment materials, requiring careful selection of compatible materials, removal of the surface-reacted layer of metal or both. Casting of titanium commonly are used to fabricate crowns, bridge copings and full partial denture frameworks. Several commercial machines for casting titanium are available, but their cost is considerably higher that for standard dental casting equipment. Materials with low reacting are used to prevent surface reaction with the molten metal, and materials with high setting expansion are used to compensate for the high casting shrinkage of titanium.[9]

To avoid formation of the α-case layer and to make coping fabrication process simpler and faster, computer aided design/computer aided machine (CAD/CAM) system have been used to mill coping from a prefabricated titanium block enables to control the uniformity of the alloy composition.[13,14,17] A wide variety of materials are available for use by CAD/CAM restorative systems, including ceramic, composite and titanium. The milling process using CAD/CAM technology enables the laboratory technician to fabricate an extremely well fitting crown,[13] excellent marginal accuracy to less 10 μm[18] and can create full anatomic crowns with automated computer-generated cut-backs, to ensure a uniform ideal thickness of the coping by reducing the full-anatomic virtual wax-up. Optical scanning is followed by CAD/CAM fabrication of crown coping. Once the coping has been verified to fit on die, it is ready for ceramic firing. Dental CAD/CAM system have advantages that cannot be matched with respect to the strength of materials and precision of the restorations. These materials are generally better in quality, strength and durability that those used to make dental restorations in the traditional casting process.[13,14]

Protocol for ceramic bonding to titanium

The more recent ceramic bonding success has been attributed to the strict protocol for ceramic bonding to titanium. The steps are as follows: Unidirectional grinding of the coping with a specialized bur (titanium cutters, cross cut burs) is use for roughening the surface with slow speed and low pressure (do not overheat the framework), diamonds and stones should not be used, and then decontamination of the coping by placing it in an ultrasonic bath of either alcohol for 30 minutes, this is a precautionary step because titanium copings and bridges are milled under a mixture of water and oil to keep the milling unit's burs cool. Because they do not undergo sintering, it is logical to conclude that a light coating of oil may remain on the coping, which could affect the reaction with ceramic under the firing sequences. After that, sandblaster machine is used for sandblasting the coping surface with aluminum oxide 120 μm to 150 μm grit, which is preformed to removed α oxidation layer prior to ceramic veneering. Then, steamcleaning and passivation able done. The coping must be allowed to interact with the open air for 5 to 10 minutes, but no more than 30 minutes, because at room temperature, titanium has a strong tendency to spontaneously form a very fine oxide layer. This layer prevents corrosion and therefore is responsible for the biocompatibility of the material. The coping is ready to be layered and the bonding agent is applied for surface wetting. Do not use of acid or etching agents. Spraying the bonding agent completely cover the marginal area in order to obtain excellent adhesion of the ceramic. After that, the opaque dentin is applied, then a second opaque dentin layer and the main build up occurs, followed by optional stain and glazing.

DISCUSSION

Bonding ceramic to dental alloys is accomplished during firing, a sintering process. Dental ceramic-metal bonding is frequently conducted at temperatures at which chemical reaction between dissimilar materials are to be expected. Ceramic-metal bonding is frequently conducted at temperatures at which chemical reactions between dissimilar materials are to be expected. Therefore, in addition to compatible thermal expansion coefficients of ceramics and metals, knowledge of the microstructure and compositions of the reaction zones is of great importance for optimizing the ceramics-fused-to-metal systems and their processing.[1] However, titanium is chemically an exceptional metal, reacting strongly with gaseous elements like oxygen, hydrogen, and nitrogen and also dissolving them extensively. This high reactivity causes problems related to the fusing of dental ceramics to titanium.[1,8] It should also be mentioned that CP Ti has a low thermal expansion coefficient that makes it a difficult substrat for ceramics to bond onto.[19]

Among the various titanium alloys, the Ti-6Al-4V system, or grade V, is the mostly used, because of its better physical and mechanical properties in comparison to CP Ti. Ti grade V shows greater bending strength (890 MPa against 340 MPa) and greater hardness (350 VHN against 210 VHN) than Ti grade II.[20] At temperature above 800° C, which are required for firing conventional ceramic (about 950° C), titanium oxides rapidly, producing a thick oxide layer (up to 1 mm) with a rather weak bond to the underlying titanium, resulting in inadequate metal-ceramic bond strength. Although low fusing ceramic are available for veneering CP Ti, the use of these ceramics is limited owing to the great mismatch in the coefficient of thermal expansion, since CP Ti has a much smaller thermal expansion coefficient (in units of 10^6 m/m° C, or ppm) than does conventional ceramics.[15,20] From the technical of ceramic over titanium requires a special protocol.[20] Several studies have been reported that the bond strength of grade II and V titanium substrate combined to low-fusing ceramics were significantly weaker than conventional noble-metal ceramic.[20,21]

Failure of the titanium-ceramic predominantly occurred at the titanium-oxide interface because only O, Ti and Al elements were found at the titanium surface and Ti-ceramic interface.[2] Although titanium has many stable oxides, it is distinct from other strong oxide-formers such as aluminum and magnesium by its having exceptionally great potential for dissolving large amounts of oxygen or nitrogen. This unique property is utilized, for example, in diffusion bonding or in the joining of metals to oxide or nitride ceramics. However, it is to be noted that too extensive dissolution of oxygen into β-titanium at high temperature (> 880° C) stabilizes the α-titanium. This later phase, having the hexagonal crystal structure, is formed on the top of β-titanium. Therefore, there is a relatively large difference in oxygen contents across the α/β-interface. During the cooling of the oxygen-contaminated surface of titanium, the β-titanium will transform into α-titanium, forming the so-called "α-case" (oxygen rich titanium layers), which detaches from the underlying α-titanium of low oxygen content. The solubility of oxygen in titanium is very great as compared with that of aluminum and magnesium. This Ti-O system produces the α-case, which impairs the mechanical compatibility of the titanium-ceramic joint. An additional problem is the formation of chemical reaction produces, especially oxides and silicides, generated during the firing, which can fracture under the influence of thermal stress.[1] An interfacial oxide layer, some 100–1000 nm (10–100 Ä) thick, forms during firing and the thicker this layer becomes, the weaker the bonding strength between the ceramics and the titanium. Fabricated titanium structures consisting mainly of β phase are stronger but less ductile than comparable structure with a dominant α phase. Thus, to obtain consistenly reproducible mechanical properties, the solidified metal's cooling rate and the time and temperature of subsequent heat treatment must be controlled.[9]

Methods have been developed for fusing dental ceramic to titanium for fixed partial prosthesis, but the choice of ceramic is limited by two critical factors: the ceramic fusion temperature must be below 800° C to avoid the α to β phase transition and the coefficient of thermal expansion of the ceramic must match that of the metal. The principal problem in the fusing of dental ceramic to titanium is the extensive dissolution of oxygen into the titanium lattice, resulting in thick, oxygen-rich titanium layers. A recent study showed that ceramic fired under inert atmosphere resulted in improved bonding. Furthermore, it is difficult to maintain consistency in titanium dental casting because of their inherently poor castability, and few laboratories are able to provide this service. Though titanium is economical, biocompatible and readily available, the technologies necessary for casting, machining and veneering this metal are relatively new and more expensive than those used for conventional dental metals. For these reasons, the use of titanium for dental casting has not become a prevalent laboratory and clinical practice.[9]

The low density of titanium (4.5 gcm^{-3}) lower than those of gold and palladium-silver alloys (18.3 and 10.7 gcm^{-3} and of the systems Ni-Cr and Co-Cr 8.0 and 9.0 gcm^{-3}) provides feather-light restorations.[20] The low density has also technical advantages during firing ceramic into a titanium coping.[11,13] Firing of appropriate ceramic masses is performed at nearly 800° C. Due to its specific combination of low density and high melting point, titanium exhibits a high sag resistance. This enables firing of even large span restoration without any thermally induced dimensional changes and with no need for joining processes after firing.[11] One study has been reported that the titanium alloys is a good alternative to gold alloys to metal-ceramic restorations emphasizing that it is biocompatible and is has a low density.[22]

Corrosion can be a serious problem, both in terms of degradation of the prosthesis and the release of potentially toxic or allergenic compounds.[5] The corrosion resistance and biocompatibility of titanium at room, oral, and body temperatures are attributed to the formation of a stable oxide film with a thickness of less then 1 mm (10^{-9} m). If the film is scratch or abraded, the involved area repassivates instaneously. At high temperatures, the oxide film is not protective because it thickness and becomes nonadherent. Numerous reports document the superior biocompatibility of titanium. The reaction of tissue that contacts titanium or its alloy, Ti-6Al-4V is extremely mild and direct bone ingrowth or osseointegration does occur.[2] One study has been reported that Ti-6Al-4V did not cause elevated interleukin-1 beta release from cells at non toxic levels. Interleukin-1 beta seems to play a central role in the inflammatory reaction.[23]

The casting of titanium alloy can cause many challenges for the dental technician because the material extremely light and does not flow well after reaching its high melting temperature. In addition, many concerns have been raised about the casting and firing procedure leading to the marginal accuracy and creation of a "reactive layer" that inhibited the bond between titanium-ceramic systems. This problem led to the fracture of ceramic from the titanium coping.[13] Micro and macroporosity remain consistent features of dental restorations cast from titanium. One study reports that the use of a double-sprue technique for titanium copings produces smoother cast surface and less internal porosity than a single-sprue design. Also remaining to be resolved definitively is the inordinate amount of difficulty experienced in making relatively thin casting. To make a suitable titanium coping for a ceramic-fused-to-metal restoration, the pattern is usually waxed to a thickness of about 0.6 mm. The resultant casting must be machined to desired thickness. When heated in air at temperatures in the vicinity at 750° C, titanium becomes embrittled through the absorption of oxygen, hydrogen and nitrogen. Such embrittlement may cause thin margins of restorations to fracture during burnishing. When heated at temperatures below 800° C for short periods, titanium of high purity forms a compact, adherent oxide scale. Moreover, at higher temperatures and extended periods of heat treatment, titanium form a porous and poorly adherent scale. During a few successive firing of a low fusing (750° C), low expansion (7.1×10^{-6}/° C on cooling) ceramic to titanium, the smooth adherent oxide produced on degassing at 750° C thickness and becomes flaky. An oxide of this type precludes attainment of reliable ceramic-to-metal bond. When melted and cast with the use of an argon arc-centrifugal casting machine, yield strength (0.2% offset), ultimate tensile strength, and elongation for grade 1 CP Ti are about 579 MPa, 701 MPa and 18%, respectively. Comparatively, castings made in an argon-tungsten arc vacuum pressure machine exhibit greater ductility (elongation = 31%), but yield strength and tensile strength drop to 285 MPa and 365 MPa, respectively.[2]

CAD/CAM titanium-ceramic restorations were developed with the potential for replacing expensive, high noble ceramic restorations, and the materials are not subjected to the high casting temperatures that can lead to problems, such as α-case layer formed as a result of the surface reaction with the molten metal are eliminated.[13,24] In terms of a restoration precision, because of the accuracy of the scanner, software and milling machine in a CAD/CAM system, the fit of the dental restorations is quite predictable.[14,25] Several studies have been reported that marginal accuracy of CAD/CAM system-fabricated titanium copings significantly better than casting technique.[18,25] The clinical performance of CAD/CAM titanium-ceramic restoration, a study has been reported that the CAD/CAM titanium-ceramic crowns were acceptable with no biologic complications and high cumulative survival rate for 3 years.[14] For fixed partial dentures (FPDs), a study has been reported that the CAD/CAM titanium-ceramic FPDs survived in the mouths of patients without major complication for 3 years, although the risk of ceramic fracture appeared to be relatively high.[25]

The quality of bonding between low-fusing ceramic to titanium has been extensively evaluated. A study by using a low fusing ceramic system, showed that the three-point flexure bond strength to degassed titanium was comparable to the strength of the ceramic to gold alloy.[26] Several researches have presented that such bonding was acceptable but variations could be occurred if different titanium-ceramic systems were used. It was found that there are several factors that enhance the titanium-ceramic bonding. These include alteration of the titanium surface using pre-oxidation treatment, airbone-particle abrasion, acid etching and application of a bonding agent prior to ceramic application.[27]

In the effect of surface texture on the titanium-ceramic system, a study has been reported that the morphology of the titanium surface influences the mechanical integrity of the joints. The joints of ceramic-fused-to sandblasted with pure Al_2O_3 particles were structurally better than those fired on the electropolished.[1] This study has been supported by another study that the bond strength of ceramic-titanium can be extremely improved by the application of sandblasting with silica-coated aluminum as well as the additional treatment of steam cleaning following sandblast regardless of the sand media.[28]

In the effects of interlayers on mechanical performance of the titanium-ceramic system, several studies have been carried out to minimize the formation of the non-adherent oxide layer involving an intermediate layer deposited on Ti prior to the application of ceramic.[26] The use of Au (gold),[6,29] Si_3N_4, chrome, SiO_2 and TiO_2 as intermediate layers has been investigated.[30] Several study showed that the titanium ceramic adhesion could be improved by coating cast titanium surface with Au.[29] This can be explained by the formation a Ti-Au intermetallic compound and surpressed the formation of a Ti-deficient intermediate layer, resulting in improved adherence between ceramic and titanium. The ceramic fused to-titanium without gold coating produced a Ti-deficient intermediate layer exposed of armorphous titania and highly oxygen-dissolved titanium on the titanium side, this layer was considered to be a cause of cohesive failure at the interface. The gold coated titanium did not have a Ti-deficient layer. Besides, there was fairly close contact between ceramic and titanium via the Ti_2Au and Ti_2Al phases under Ti-Au intermetallic compound layer. These result suggested that gold coating suppressed the formation of a Ti-deficient intermediate layer and contributed to the adhesion between ceramic and titanium.[6] A gold-containing bonding agent lowered the mechanical compatibility of the joint compared with that of the titanium-ceramic system without the agent. According to thermodynamic calculations, this can be explained by the formation of brittle Au-Ti intermetallic compounds during the firing procedure at given temperatures. When ceramic based bonding agents are used, there are always chemical reactions between titanium and oxygen as well as with metal elements of the ceramics. Since the brittleness of the titanium-oxygen solid solution is known, not to mention that of intermetallic compounds, it is difficult to understand how these agents can improve the bond strength. As to proper soft metallic interlayers, they can reduce thermal stress of the titanium-ceramic joint due to plastic deformation and have an important influence on the formation of reaction layers generated during fusing. Therefore, the interlayers should be selected so that the structures generated during the firing are not destroyed in intermetallic reactions or in oxygen reactions. An ideal interlayer should maintain its original properties as perfectly as possible. However, its reactions should still be minimal regarding titanium and the ceramics, so that the driving force allows for controlled fusing reactions. Reactivity is necessary for chemical bonding, whereas in titanium-ceramic systems, brittle reactions products may impair the mechanical compatibility of the joint.[1] Coating the titanium surface with SiO_2 has also been used because it was considered that SiO_2 is one of the main composition of the conventional dental ceramic powder (K_2O-Al_2O_3-$6SiO_2$ or Na_2O-Al_2O_3-$6SiO_2$). Silica on titanium surface would serve as an oxygen diffusion barrier while forming an oxide layer to which the ceramic would be more bondable.[2] Silica (SiO_2) coating was an effective intermediate layer to improve titanium-ceramic adhesion,[30] it could be suggested that the oxidation of the Ti-ceramic sysem; during the ceramic fusion, minute amounts of oxygen were able to penetrate the cracks and caused localized oxidation of the Ti-substrate. The SiO_2 coating prevented the diffusion of oxygen to the titanium surface and improved the mechanical and chemical bonding between titanium and ceramic and another study reported that when ceramic was fired in vacuum in the presence of the gold layer, the titanium-ceramic bonding was weakened in as-cast titanium and was not affected in machined titanium.[20]

Oxidation is one of the principal steps in the preparation of the coping for ceramic bonding and there is no single standard oxidizing technique for all alloys on the market. On the contrary, the type of atmosphere (vacuum or air) and the high temperature setting or duration differ among the numerous base metal-ceramic alloys.[4,31] According to one hypothesis, the oxide layer is permanently bonded to the coping on one side with the ceramic on the other side. The oxide layer itself is sandwiched between the coping and the opaque ceramic under this so-called sandwich theory and the possible presence of a thick oxide layer would weaken the bonding of metal to ceramic.[4] In the effect of oxidation on the bonding strength of Ti-ceramic, the pre-oxidation treatment of TiO_2 which was participate in the interfacial reaction was increased, and resulted in the thickening of reaction layer. Failure of the Ti-ceramic with pre-oxidation treatment predominantly occurred at the Ti-O interface, this suggested that the temperature of pre-oxidation had a great effect on the bond strength of Ti-ceramic. Pre-oxidation treatment did not increase the bonding strength of Ti-ceramic, it could be suggested that the titanium surface after oxidation treatment revealed the α-Ti(O) as the major phase and the rutile (mineral consisting of TiO_2) as a secondary phase. It revealed that a rutile layer was formed on the titanium surface after oxidation treatment. The rutile layer was more strongly bonded to the ceramic than titanium. The poor adhesion of the rutile with substrate was due to the thermal stress arising from large lattice mismatch and the large difference in coefficient of thermal expansion between titanium and rutile during cooling. Therefore, it is favourable to select slow cooling to improving the bond strength. The effect of cooling rate is due to the change of heat stress of Ti-ceramic interface.[30]

As a conclusion, the bond of ceramic over titanium is a sensitive technique influenced by the effects provoked mainly by the layer of surface oxide. Titanium and titanium alloys, based on their physical and chemical properties suitable for titanium-ceramic restorations, but careful selection of processing methods, ceramic materials, laboratory skill and strict protocol for ceramic bonding to titanium are necessary to improve the bonding between titanium and ceramic.

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