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Comparative Study of Bond Characteristics between Titanium/Titanium Alloy and Ceramic

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1. Introduction and statement of problem

Metals have been used in medicine and dentistry for many centuries. In 1565, it was reported that gold plate was used to repair cleft palate defects. Taggart developed dental casting process with gold alloys and their substitutes in 1907. Since then, gold restorations with cast technique have been popularly used in dentistry. [90, 137, 157]

Metal-ceramic restorations combine the aesthetic advantages of ceramics with the durability and marginal fit of cast substrates. [14] Therefore, metal-ceramic restorations have currently been popular in restorative dentistry. As dental ceramics advanced in the 1960s and as the price of gold increased in the 1970s, alternative alloys, such as palladium alloys and base metal alloys, were developed. [97, 157] Recently, titanium has also been increasingly used for the construction of metal-ceramic restorations.

In recent years, titanium has become a material of great attention in dentistry, because of its good biocompatibility and mechanical properties. The wrought forms of titanium have been used in the past decades, for example, orthodontic wire of beta titanium, orthodontic wire of Nitinol (Ni-Ti) with a shape-memory effect, and endosseous dental implants. [138]

Because it was difficult to cast in conventional methods, titanium and its alloys were impossible to be used for artificial crowns and partial prostheses. However, with the development of casting techniques and the preference for prosthetic superstructures of titanium endosseous implants, a growing tendency involves the use of titanium as an economical and biocompatible replacement for existing alloys for conventional restorations.

Now, titanium and its alloys are widely used in dental applications, because of the additional advantages of good local spot weldability, easy shaping, and finishing by mechanical and electrochemical processes. [83] To improve the strength of unalloyed titanium the TiAl6Nb7 alloy has been recently developed for biomedical use, particularly for orthopedics and dental applications.

Metal-ceramic restorations are commonly received, and several theories concerning the interfacial adherence of the metal-ceramic system have been introduced. However, there are also disadvantages such as occasional failures of the veneer. Moreover, the metallic coping can be distorted after the porcelain application.

Usually, to evaluate the thermal compatibility of the metal-ceramic system, the discrepancy of the thermal expansion coefficients is first considered. However, some dental alloys with the same thermal expansion coefficients showed different residual stresses in metal-ceramic interface after firing, which might be caused by the large difference in elastic modulus (non precious alloy; 180-220 GPa vs. precious alloy; 80-120 GPa [149]). [87, 88] Although the metal-ceramic interface is difficult to understand, metal-ceramic restorations must be exactly designed, and well-matched materials should be correctly handled.

Titanium is well known as a useful biometal, but titanium is also chemically an exceptional metal, having strong reactivity to non-metallic elements, such as oxygen, hydrogen, and nitrogen, at high temperatures. The high melting temperature and violent chemical reactivity at high temperature of titanium and its alloys result in difficulties with casting, and cause problems, when dental ceramics are fused to titanium. [1, 79] Thus, although commercial titanium-ceramic systems are available today, they still have unsolved problems related to the fusing of dental ceramics to titanium.

1.1 Purpose of this study

Today, titanium receives considerable amount of interests, as a ceramic fused metal. Although titanium-ceramic systems are used more and more in restorative dentistry, there are scarcely any studies about the bond behaviours of these systems, especially the effect of the thermal compatibility on the bond strength. With the use of titanium and its alloy, it becomes more important to assess their compatibilities with ceramics [161]. If more compatible titanium-ceramic systems are to be developed, it is necessary to better understand the bond characteristics of the titanium-ceramic system for conventional restorations.

The purposes of this study are to evaluate the bond strength in ceramic, developed for use with titanium, fused to cp titanium and TiAl6Nb7 alloy composites, and to employ the analytical model to determine the effective thermal contraction difference. This may help to comprehend the relationship between the effective thermal contraction difference and the bond strength, and the bond characteristics of the titanium-ceramic system. Finally, it may help to match properly titanium restorative castings to ceramics for metal-ceramic prosthetic treatment. The aim of this investigation is to provide data, concerning the thermal compatibility and the bond strength with cp titanium/TiAl6Nb7 alloy and ceramic.

2. Review of literature

2.1 Titanium

Titanium is the fourth-most-plentiful structural metal in the earth, following aluminum, iron, and magnesium. Naturally, it exists as rutile (TiO_2), or ilmenite ($FeTiO_3$), not in its elemental state. With extraction methods, for example, the Kroll process or the iodide process, a raw material can be produced. [83, 157]

2.1.1 Titanium development

Two hundred years ago, titanium was isolated and named for the first time. But the metal, which we know today, is not more than forty years old. Due to the high affinity of titanium for non-metallic elements, it is difficult to extract pure titanium from titanium ores or rutile (TiO_2), which is the most stable form of titanium oxides. Dr. Wilhelm Kroll devised useful metallurgical processes for the industrial production of titanium metal, and, nowadays, he is considered to be the “father” of the titanium industry [157].

Since 1950s, titanium and its alloys have been important metals for the aerospace industry, because they have attractive mechanical properties and excellent corrosion resistance [83]. In dentistry one of the first application was machined titanium dental implants. As a substitute to lost-wax cast technique, Andersson et al. [2] developed the Procera system (Nobelpharma) with titanium machining to fabricate unalloyed titanium crowns and fixed bridges.

2.1.2 Properties of titanium

Titanium belongs to the fourth group of the periodic table and is a comparatively strong and ductile transition metal. Titanium is relatively exceptional among metallic elements, since it exhibits various valences, ranging from two to four by the existence of numerous oxides. The high strength and low density of titanium are related to specific electronic states of titanium, which allow the formation of relatively strong bonds between titanium atoms. [79] Commercially pure titanium is available in four different grades (American Society of Testing and Material grades I to IV), based on the incorporation of small amounts of oxygen, nitrogen, hydrogen, iron, and carbon. The maximum impurity limits of grades I to IV pure titanium are listed up in Table 1.

The physical and mechanical properties of pure titanium and its alloys can be greatly influenced by the addition of small traces of other elements such as oxygen, iron, and nitrogen. Table 2, which presents the physical and mechanical properties of grade I to IV pure titanium and dental alloys, indicates that tiny additions to pure titanium significantly change the material properties. Table 2 also reveals that titanium's density, 4.5 g/cm^3, is significantly less than that of gold and Co-Cr alloy (19.3, 8.5, or 7.9 g/cm^3, respectively). This same table shows the elastic modulus of titanium and its alloys, which are comparable to gold, but only one-half that of Co-Cr alloy.

Table 1 Maximum impurity limits (wt %) of pure titanium [41]

Type	N_{Max}	Fe_{Max}	O_{Max}	C_{Max}	H_{Max}
ASTM grade I	0.03	0.20	0.18	0.10	0.015
ASTM grade II	0.03	0.30	0.25	0.10	0.015
ASTM grade III	0.05	0.30	0.35	0.10	0.015
ASTM grade IV	0.05	0.50	0.40	0.10	0.015

Theoretically, the attractive mechanical properties, including the lightweight, strength to weight ratio, high ductility, and low thermal conductivity, would permit design modifications in fixed and removable prostheses, resulting in more functional and comfortable use. [157]

Table 2 Selected physical and mechanical properties of cp titanium (grade I-VI), titanium alloys, and dental alloys compiled from different sources [53, 70, 90, 104, 105]

Material	Density (g/cm^3)	Elongation (%)	Tensile strength(MPa)	Yield strength (MPa)	Elastic modulus(GPa)
cp Ti(Grade I)	4.51	24	240	170(0.2%)	100
cp Ti(Grade II)	4.51	20	340	280(0.2%)	100
cp Ti(Grade III)	4.51	18	450	380(0.2%)	100
cp Ti(Grade IV)	4.51	15	550	480(0.2%)	100
TiAl6V4	4.43	10	900	890(0.1%)	113.8
TiAl6Nb7		10	900	800(0.2%)	100
Au alloys	18.3-19.3	10-18	840	~420(0.1%)	108.2(type IV)
Ni-Cr alloys	4.47-9.5	1.1-2.4		~450-760(0.1%)	
Co-Cr alloys	8.5	10	700		218.7
Enamel	3.0	0	70		12.2 50
Dentin	2.2	0	40		2.6 14
Bone	0.7(dry)	1	140		2.4 18(cortical)

2.1.2.1 Biocompatibility of titanium

Besides all the other properties of titanium, the excellent biocompatibility is the most practical aspect for the application in dentistry. This useful biological property of titanium is based on the existence of titanium oxide (TiO_2) layers, which are naturally formed in oxygen-containing environments. It is also possible to be produced with various artificial techniques, e.g., anodizing. [79]

When fresh titanium is exposed to the atmosphere by cutting acts, an oxide layer begins to form within nanoseconds (10^{-9}s). Only one second later, a surface oxide layer, some 2, to 5 nanometers (nm) in thickness, will be created. This oxide, mainly TiO_2, forms so readily, and is very adherent to the parent titanium. It also has good corrosion resistance and is quite impenetrable. Therefore, once this thin passivation film has been formed, further oxygen is prevented from reaching the metal beneath, and further oxide layer thickening is quickly stopped. [83]

Each titanium atom, in the hexagonal structure, has one octahedral site, and oxygen atoms can occupy this octahedral site. When one mole of oxygen atoms dissolves in titanium, a large amount of energy is released to form a dilute solid solution. [80] Thus, the Ti-O solid solution is thermodynamically very stable. Even though a small amount of oxygen in the solid-solution phase makes it brittle. However, until the oxygen content is up to about 30% in the solution, it does not begin to form the first oxide layer at elevated temperatures ($>$700°C), i.e., only with the fast enough diffusion of oxygen atoms. [77, 79]

This oxide film on titanium is stable over the wide range of pHs, potentials, and temperatures. Hence, titanium commonly resists mildly reducing, neutral, and highly oxidizing environments, including quite high temperatures. Only under highly reducing conditions, titanium oxide film breakdown and resultant corrosion may be found. But normally, it is impossible to find these phenomena in the mouth. [157]

2.1.3 Titanium alloys

Titanium can be alloyed with various elements to change its characteristics, primarily to improve the mechanical property, such as strength, high temperature performance, creep resistance, weldability, response to ageing heat treatments, and formability. [83] Unalloyed titanium shows low strength and poor wear resistance.

Pure titanium undergoes a transition from a hexagonal close packed structure (α phase) to a body centred cubic structure (β phase) at 883°C. It remains in this crystallographic structure until melting at 1672°C. [29] Alloying elements can be added to stabilize one or the other of these phases by either raising or lowering the transition temperatures. [138] Elements such as Al, Ga, and Sn, with the interstitial elements (C, O, and N) stabilize the α phase, resulting in alpha titanium alloy. On the other hand, elements such as V, Nb, Ta, and Mo, stabilize the β phase. [29] There are also titanium alloys, whose compositions in room temperature are a mixture of alpha-stabilizers and beta-stabilizers.

Alpha titanium alloy, generally used in aerospace industries, is weldable, more oxidation-resistant, and superior in high-temperature strength. But alpha titanium alloy is difficult to form or cold work at room temperature. In contrast, beta titanium alloy has weldability and a good formability at lower temperatures, which may be suitable for the dental applications. Alpha-beta titanium alloys are commonly strong, owing to the duplex phase structure. Alpha-beta titanium alloys are more formable than alpha alloys but somewhat more difficult to weld. [42] The most popular alloy of alpha-beta titanium is TiAl6V4.

Because of no interest in high performance at exceptionally high or low temperature, the applications in dentistry have been primarily confined to the cp Ti and the alloy Ti6Al4V. [83] However, vanadium (V) in TiAl6V4 is found as a problematic material due to its toxicity in recent years. To develop more biocompatible titanium alloys, investigations of new titanium alloys have been increased. Recently, the excellent biocompatibility of niobium (Nb) has been introduced and TiAl6Nb7 is considered as the substitute of cp Ti and TiAl6V4.

2.1.3.1 Aluminum

Aluminum, a typical alpha stabilizer, increases the alpha-beta transition temperature and maintains the improved mechanical properties over pure titanium. Other alpha stabilizers include oxygen, which forms interstitial solid solutions to titanium. [42]

2.1.3.2 Vanadium

Vanadium is a continuous solid-solution-type beta stabilizer, while copper and palladium are eutectoid-type beta stabilizers. [42] TiAl6V4 is the most commonly used titanium alloy especially in implant dentistry because of its lower elastic modulus. Dental implants require strength levels greater than that of bone and an elastic modulus close to that of bone. [157] The low elastic modulus (50 to 60% of those of the Co-Cr alloys) and high yield points of TiAl6V4 result in high springback suitable for the retentive forces required for the clasp of removable partial dentures or for orthodontic uses. [32, 106, 138] Although TiAl6V4 alloy is being widely used in dentistry, studies have shown that the release of aluminium and particularly vanadium ions from the alloy might cause some long-term problems, such as peripheral neuropathy, osteomalacia, and Alzheimer diseases. [93, 115, 154, 160]

2.1.3.3 Niobium

In early 1990s niobium was introduced to lower the thermal expansion coefficient of pure titanium and Ti-Nb alloys showed the thermal expansion coefficient similar to the high purity alumina ceramic over a large temperature range. [51] Niobium is regarded as a useful alloying element for titanium because of its corrosion resistance and recent studies have also reported the excellent short- and long-term biocompatibility of niobium. [112, 128] The heterogeneous TiAl6Nb7 alloy has an α-β structure, with enrichment of Al in the α-phase and Nb in the β-phase. [130]

Since cytotoxicity is an serious problem for biomaterials, TiAl6Nb7 alloy was developed by replacing vanadium in TiAl6V4 with the same atomic amount of niobium, which belongs to the same group Va in a periodic table. Niobium was reported to be much more biocompatible than vanadium, and the strength of TiAl6Nb7 alloy casting was slightly lower than that of TiAl6V4 alloy, however the ductility and corrosion resistance were better than TiAl6V4 alloy. Furthermore the TiAl6Nb7 alloy was easy to be polished and the finishing surface condition was better than cp titanium. [56] TiAl6Nb7 alloy castings shows better wear resistance than cp titanium castings, which can improve the quality of the dental prostheses in addition to the mechanical strength and the surface finishability. [64]

2.2 Titanium casting

In 1977 Waterstratt noticed the feasibility of the casting titanium alloy in dental appliances. Many studies have followed his work, in the direction of the development of casting machines, suitable investment materials and the precise technique of dental prostheses. [83]

Titanium’s high affinity for oxygen, especially at elevated temperatures (above 600°C), made the casting procedure very complicated and required special melting methods, investment material, and equipment to prevent metal contamination. In addition to reaction with environmental materials, the extremely low density of titanium, compared to conventional alloys, can cause casting difficulties, and a conventional broken-arm casting machine would not guarantee sufficient centrifugal forces for consistently complete castings. [33]

Problems of reactivity of molten titanium with oxygen have been solved by melting and casting in containment with very little oxygen. This is generally obtained by a combination of primarily vacuum and injection of an inactive gas such as argon. Recently, there are some titanium cast machines with vacuum and pressure equipments available on the market.

2.2.1 Titanium casting systems

Three types of Ti casting systems are currently available, that is: a pressure/vacuum casting system with separate melting and casting chambers (e.g. Castmatic, Dentaurum); a pressure/vacuum casting system with one chamber for melting and casting(e.g. Cyclarc, J Morita); and a vacuum/centrifuge casting system (e.g. Tycast, Jeneric/Penetron, and Titaniumer, Ohara). [55, 63,76]

Castibility of three different titanium-casting systems has been compared, and radiographic analyses indicated that the centrifugal casting method had the best castibility; the two pressure-differential casting systems showed similar results. [19] Because of initial accelerations of over twenty times that of gravity, the vacuum/centrifuge casting system (e.g. Ohara) generally created sharper and more detailed castings. And it scored better in the Whitlock wire mesh casting tests. In contrast, Castmatic was less susceptible to surface contamination. [60, 83]

2.2.2 Investment material for titanium

The suitable investment material and the definition of its optimal curing cycle have been founded one of the major difficulties in titanium casting. It is necessary for any investment to endure the initial molten titanium at nearly 1700°C without reacting with the surface of the titanium cast, and without significant sintering. Also, the investment material should have an ability to compensate for shrinkages of titanium cast as the metal returns to room temperature after casting procedure. [83]

Mori et al. investigated the influence of investment material on titanium casting and noted that the conventional investment materials reacted significantly with titanium and provided zero expansion for the compensation of metal shrinkage at recommended mold temperature (200°C). Al_2O_3-MgO-based investment material had the best compensation for Ti shrinkage and reacted little with titanium. [99] It also has been reported reasonable results with various combinations of quartz (SiO_2), cristobalite (SiO_2), and MgO powders in phosphate-bonded investments. [139] Others have examined face coatings of MgO and ZrO_2 and achieved some success in preventing surface contamination. [138]

2.2.3 “α-case” layer

At high temperatures (>882°C) the α-titanium can be stabilized by too-extensive dissolution of oxygen into β-titanium and is formed on the top of β-titanium. The oxygen contents (Δx_O in Fig.1) across the α/β-interface are quite different. As the oxygen rich-contained surface of titanium cooled, the β-titanium will transform into α-titanium with namely “α-case” layer. This layer can be removed from the underlying parent metal that is α-titanium with low oxygen content. [79] Besides the extensive dissolution of oxygen, the “α-case” layer of titanium castings is susceptible to possible interaction with the investment material. Molten and heated titanium reduces the oxide in investment material. The free oxygen diffuses from the surface into the inward of titanium castings. [138]

The “α-case” layer increases the microhardness proportional to the amount of absorbed oxygen and causes a three-times of surface hardness (600 KHN) versus the rest of the titanium casting (200KHN) after 200 micrometers interior from the surface.[139] Taira et al. [138] also examined four different titanium alloys and found U-type hardness distribution with cross-sectional microhardness measurements. Microhardness increased in the surface of titanium castings as a consequence of oxygen diffusion, titanium-investment reaction, [95, 96, 138, 139] and even thermocycling of the metals during porcelain application. [74, 75]

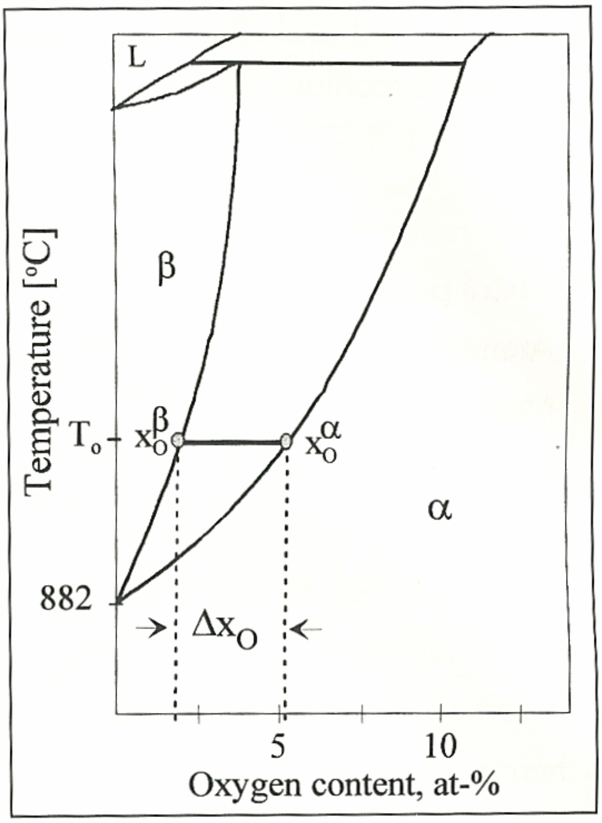

Fig.1 Chemical interaction of titanium with an oxide atmospheric oxygen and formation of the “α-case” layer below the titanium surface [79]

In particular, commercially pure titanium is subject to the “α-case” layer by oxygen, in contrast the hardening effect on other titanium alloys is little. Alloying could reduce the undesirable reaction by the subsequent two hypothetical mechanisms. First, alloying lowers the melting point of titanium. At the same time it may diminish the reaction level of titanium-investment. Second, the alloying with other metallic elements, which have higher affinity for oxygen, could decrease reactivity of titanium with oxygen. [138]

2.3 Titanium-ceramic bonding

2.3.1 Metal-ceramic system

In 1950s, Brecker [23] noted the application of prototype gold-ceramic systems. Since then metal-ceramic system has been increasingly available in prosthetic dentistry. In the beginning, high-gold alloys were applied, but other alloy systems have been used and quite popular over the past decade, primarily due to the cost factor. These include low-gold alloys, nonprecious alloys, and palladium-based alloys. More recently, titanium and titanium alloys have become available. [18] Today there is a strong tendency for single crowns to be fabricated in ceramic only without any metal copying; nevertheless a metal-ceramic technique still predominates in fixed prosthodontics. [15]

2.3.1.1 Theory of metal-ceramic bonding

There are so many literatures on the adherence of ceramic to metals. Metal-ceramic bonding is accomplished through the ceramic firing, a sintering process. [151] Bonding mechanisms have been classified into four categories: namely, chemical bonding, mechanical interlocking, van der Waals forces, and compressive forces. [27, 152, 160] The roles that each of these factors plays in the metal-ceramic bond have been controversial. However, chemical bonding has been described as the primary driving force for metal-ceramic bonding.

Chemical bond between metal and ceramic is achieved through the intermediate oxide layer at the metal-ceramic interface. The ceramic at the interface is partly saturated with metal oxide and stays in thermodynamic equilibrium with the metal oxide. The metal oxide is also saturated with metal, resulting in a thermodynamic equilibrium across the metal oxide-metal interface. Therefore, a continuous electronic structure is created from the metal through the oxide layer to the ceramic and the chemical bonding of the metal-ceramic system is available. [22, 108, 109] Observations of precious metal alloys have been found that the base metal elements accumulate on the outermost layer of the metal and form strongly adhering oxide layers, which are bound via their metal ions in the alloy lattice. During firing, these oxides enter into a bond with the silica network of the ceramic, which causes a bond to the silicon dioxide of the ceramic. Tin and indium oxides have been well recognized as major contributors to the chemical bonding in these systems. [159]

Mechanical interlocking is a bonding mechanism based on the interdigitation between metal and ceramic at the marginal surface of the contact. To this end, the metal surface is roughened with routing instruments [140] or sandblasting [49, 140] or both of them. Roughening can enhance the adhesion by enlarging the effective bonding surface [27, 44], improving wettability, and creating undercut areas. Sandblasting also cleans the surface through abrasion, improves wettability by changing surface energy, and alters the surface composition through localized fusion. [159] However, if roughness of a surface causes voids at the interface, bonding effect could be decreased. [111] The reported effects of surface roughness on metal ceramic bond strength are controversial, because the degree of surface roughness is either not defined or rarely used in dentistry. [47, 71, 84, 136]

Van der Waals forces refer to a bond by means of an electrostatic attraction between two atoms, which are too close that no chemical bond is effective. [160] This kind of bonding mechanism is accomplished by dipole formation [58, 124] and described as secondary bonding powers, because van der Waals forces have little direct influence on the bonding strength. However, they have important contribution to improve the wettability of a metal surface during firing the ceramic. [27, 124] The bond created by van der Waals forces is not dependent on the existence of an oxide layer. [159]

Compressive forces are derived from the difference of thermal expansion/contraction coefficients between metal and ceramic. The expansion behaviour of metal and ceramic should be optimally adjusted. Latent cracks or chipping can be found especially when the thermal expansion coefficients are not correctly synchronized with one another. A basic principle of metal-ceramic systems is that the thermal expansion of the metal should be slightly greater than that of the ceramic. The distinction of thermal contraction during the cooling process produces tension that lead to stabilize the bond. [159]

2.3.2 Titanium-ceramic system

In order to apply titanium’s distinct advantages for aesthetic restorations, the titanium-ceramic system becomes important. Because of titanium’s strong reactivity with oxygen, ceramic firing should take place below 800°C to prevent excess oxide formation. Furthermore, since little or no residual stress due to thermal mismatch should exist in the final titanium-ceramic system, the significant discrepancies of their thermal expansion coefficients should be modified to more closely match. [57]

In contrast to precious alloys that demand pre-oxidation for successful metal-ceramic adhesions [153], the highest bond strengths for a titanium-ceramic system are achieved by fusion in a high vacuum environment. [57] Moreover, while conventional metal-ceramic systems require high fusing temperatures to enhance needed reactions, the retardation of reactions under lower temperatures seems to be successful for the titanium-ceramic system. [57, 78, 157] During the last few years the low-fusing ceramics have been improved and their bond strength to titanium seems to be comparable to that of conventional metal-ceramic systems. However, surface and colour stability of low-fusing ceramics may be problematic in the long run. [15]

2.3.2.1 Titanium's reactions with non-metallic elements

Titanium has remarkably great potential for dissolving large amounts of oxygen or nitrogen, which is quite unique property compared with other strong oxide-formers: e.g., aluminium and magnesium. This property is very useful in diffusion bonding or in the joining of ceramics to meals. As SiO_2-based dental ceramics are fused to titanium, the most important reactions take place among titanium, oxygen, and silicon. [79]

Titanium is able to form several stoichiometric and non-stoichiometric oxides such as TiO, Ti_2O_3, Ti_3O_5, and TiO_2 and the layer structure of this oxides is very complicated. TiOx is in “equilibrium” with the oxygen-rich bulk metal. But the outermost oxide layer is always TiO_2 that is the most oxygen-rich. [79] In addition to the Ti-O system, the Ti-Si system includes one non-stoichiometric (Ti_5Si_3) and 4 stoichiometric ($TiSi_2$, TiSi, Ti_5Si_4, Ti_3Si) compounds.

Recently, Korhonen and Kivilahti [80] calculated the Ti-Si-O phase diagram at 750°C with the binary data measured by earlier studies. Fig. 2 displays the phase equilibrium at 750°C for the Ti-Si-O system founded on the results of thermodynamic calculations. The Ti-Si-O system contains several stoichiometric binary oxides and silicides. Except for the solid α-Ti [O, Si] solution, the other phases are regarded line compounds, and their polymorphic structures have been neglected. [79]

There is a difference between Ti-O system and Ti-Si system. The solid solution of titanium and oxygen is considered as the interstitial phase where oxygen atoms occupy the vacant octahedral sites, whereas silicon atoms reside in the same substitutional lattice as Ti atoms. [79]

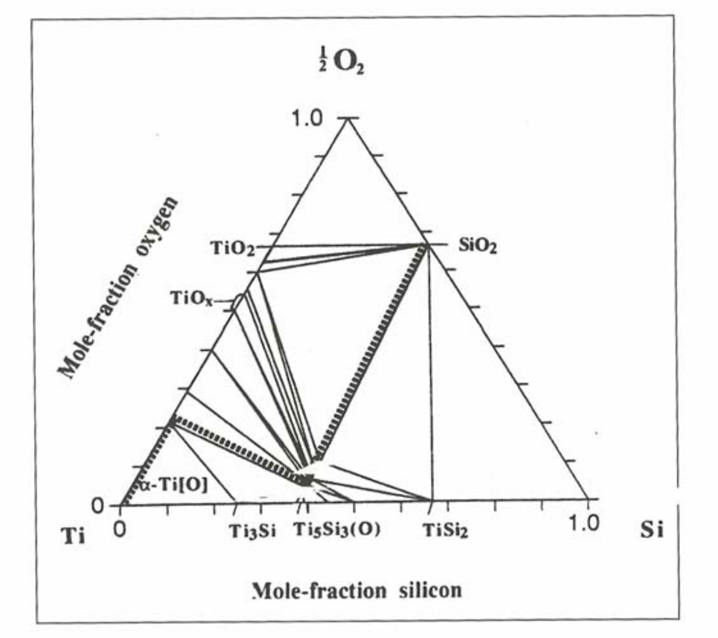

Fig. 2 Isothermal section of Ti-O-Si system at 750°C with predicted reaction path (dotted line) [79]

2.3.2.2 Interfacial chemistry of the titanium-ceramic system

Because a fusion of ceramic to metal is accomplished at the high temperatures to permit chemical reactions, it is important to understand the microstructures and compositions of the reaction zones for the purpose of optimising the metal-ceramic systems and their procedures. [79] When pure titanium is in contact with SiO_2-based dental ceramics at firing temperatures (720-750°C) for a given time, oxide layers will be dissociated by titanium following dissolving its own native oxides, and the subsequent dissolution of the elements in titanium will occur.

Generally chemical reactions are closely associated with thermodynamic temperature-composition diagrams of the system. Based on calculated phase diagrams, for instance Fig. 2, it is possible to predict displacement reactions. And the layer sequence of the titanium-ceramic bond can also be predicted by means of the mass action law and general principle of the diffusion theory. Fig. 2, in conjunction with the calculated activity values, shows that the diffusion path is:

$$SiO_2 \rightarrow Ti_5Si_3(O) \rightarrow \alpha\text{-}Ti[O] \rightarrow \alpha\text{-}Ti,$$

as was also observed experimentally, because silicon and oxygen atoms must follow a descending activity path (dotted line in Fig. 2) in a titanium-ceramic system. [79] It is found that the reaction layer consists of two adjacent layers, such as solid α-Ti[O] solution and an oxo-silicide [78], which means that the diffusion of oxygen and silicon takes place across the reaction zone [78, 110]. The solid solution part of the reaction zone is much thicker than the silicide layer, because the elements in the titanium silicides seem to have relatively low mobility. [79]

2.3.2.3 Affecting factors on the titanium-ceramic system

It is generally believed that **the surface texture** of metal influences the mechanical integrity of the metal-ceramic system. As a metal surface is roughened, a reduction in contact angle takes place [24], resulting in better adhesion. [100] Koenoenen and Kivilahti [78] reported that the ceramic adhesion on the sandblasted titanium surface was structurally better than that on the electropolished titanium surface. In same study, scanning electron microscopy images of the electropolished samples showed that the de-bonded areas were located at the titanium-ceramic interface, and they thought that the microscopic interlocking and stress vector distribution at the interface increased the mechanical bond strength of the sandblasted samples.

It was also noted that the morphology of the sandblasted surface could prevent the formation of continuous and planar reaction layers, which improved the bond strength. Among conventional dental alloys, the adhesion of metal oxides to bulk alloys has been found to be dependent on surface texture and rough surfaces of the alloys showed best results. [92] Effects of roughening, however, seem to depend on its method and extent. Carpenter and Goodkind [26] warned against excessive roughness, which may hinder complete wetting owing to stress concentration at the interface and steep re-entrant angles.

Coating agents have been used in conventional metal-ceramic systems to serve two purposes: promotion of adhesion and masking of the metal surface to prevent discoloration of opaque porcelain. [100] In the titanium-ceramic system, gold-containing materials and ceramic materials have been applied in order to improve bond strength. [38, 52]

Gilbert et al. [52] described that titanium particles in the bonding agent might play as scavengers, resulting in protecting the titanium surface from excessive oxidation. Proper coating agents can reduce residual stresses of the titanium-ceramic system as a result of plastic deformation. Moreover they have an important influence on the formation of reaction layers as ceramics are fused to titanium at firing temperatures. [79] However, the use of coating agents has been controversial. [38, 52]

2.3.2.4 Problems related to the titanium-ceramic system

It seems clear that the principal problem in the titanium-ceramic system is the extensive dissolution of oxygen into the titanium lattice, which causes oxygen-rich outermost layers, so-called the α-case layer. It is inhomogeneous, brittle, porous, and incompatible with ceramics. The α-case layer impairs the mechanical compatibility of the titanium-ceramic system. Therefore the α-case layer must be removed prior to the application of ceramics.

Another problem is oxides and silicides generated during the firing and these chemical reaction products can be broken under the influence of thermal stresses. Exposure of titanium to high temperature above 800°C will cause the formation of thick titanium oxide (TiO_2) layers. At approximately 1um in thickness, the oxide layer will spontaneously delaminate from the surface due to induced stresses caused by the volume differences between titanium and its oxide. [1, 73] In previous research it was found that the oxide formed on the titanium surface at ceramic firing temperatures is porous, nonadherent, and unsuitable for ceramic bonding. [38, 79, 81, 132, 157] Moreover, titanium changes its crystalline state at 883°C and the phase change is associated with volumetric and surface alterations that would affect the interface between titanium and ceramics. [69]

Adachi et al. studied the mechanisms of titanium oxidation and the adherence of titanium oxide to the bulk material. They evaluated the bonding of experimental low-fusing porcelain to titanium and TiAl6V4 alloy by an x-ray spectrometric technique, and found that the poor bond strength between ceramic and titanium was partially because of continual oxidation of titanium during the firings and formation of a nonadherent oxide layer. [1]

It was noted that an interfacial oxide layer can be some 100 to 1000nm thick after firing and the thicker this layer becomes, the weaker the bond between titanium and ceramic. [57] Kirmura et al. reported the oxidation effects of the interface reaction in titanium-ceramic system. They concluded that the conventional degassing procedure is not suitable in the titanium-ceramic system, and that ceramics should be fired below 800°C to minimize the metallic oxide formation on the titanium surface. [73]

To overcome problems related to the fusing of ceramics to titanium, investigators have suggested different vacuum conditions [57, 120], soft metallic interlayers [38], and/or low-fusing ceramics. [38, 78] To minimize the difference in thermal expansion between titanium and ceramic as well as to minimize high temperature oxidation, low temperature fusing ceramics with coefficients of thermal expansion which match that of titanium have been developed. [1, 94, 142]

Reactivity in the titanium-ceramic interface is essential for chemical bonding, whereas brittle reaction products may be harmful to the mechanical compatibility. This is a primary problem to be solved, when dental ceramic is fused to titanium. [79]

2.4 Thermal compatibility of the metal-ceramic system

2.4.1 Compatibility of the metal-ceramic system

Compatibility of the metal-ceramic system is dependent on the harmony of properties of both materials. Acceptable restorations require chemical-, thermal-, mechanical-, and esthetical compatibility between metal and ceramic. [14] Chemical compatibility through the oxide layer implies formation of a strong bond that resists stresses resulting from thermal and mechanical incompatibility without compromising esthetics. The oxide layer required for bonding is created during the degassing or oxidation firing. Oxidation firing time and temperature must be sufficient to create an adequate oxide layer for metal-ceramic bond.

The bond produced by chemical compatibility may be strong enough to overcome both transient and residual thermal stresses and mechanical forces encountered in clinical function. [14] Thermal and mechanical compatibility include a ceramic firing temperature that does not cause distortion of the metal substructure, in conjunction with the optimal combination of thermal expansion coefficients, α. [32] In clinical application compatibility of the metal-ceramic system must be capable of simulating a range of tooth shapes, shades, translucency, fluorescence, and surface finish. [14]

2.4.2 Thermal compatibility between metal and ceramic

Thermal compatibility problems have been evident. Occasionally, a well-fitting metal coping may not fit after ceramic application. When the passive fit of a metal substrate changes after ceramic firing, the thermal incompatibility may be the reason. This is a potential problem because the ceramic of tight-fitting metal-ceramic restorations can subsequently fail because of residual stress. [121]

Transient tensile stress may cause cracks during cooling, but if no cracks formed, the residual stress then becomes the principal variable, which can enhance or reduce the bond strength of a metal-ceramic system. [28]

Thermal stresses are caused by differences in thermal contraction and expansion of metal and ceramic during the firing cycle. To evaluate the signs and levels of magnitude of thermal stresses, we need to know the temperatures at which stresses are generated. A reasonable choice for the upper temperature is the glass transition temperature (T_g) of the ceramic, because above this temperature the stresses in the ceramics are virtually zero. [12]

The stresses which develop during cooling from the glass transition temperature of ceramics to room temperature are dependent not only upon the thermal contraction difference between metal and ceramics, but also upon the glass transition temperature of ceramics, the geometry of samples, and the elastic constants of the materials used. Furthermore, variables such as cooling rate and number of firing cycles naturally have their own effects. [6, 35] Delayed failure caused by residual stresses may also result from static fatigue, the presence of microcracks, or crack initiation and propagation due to the combination of residual tensile stress and the tensile component of stress due to an applied intra-oral load. [28]

In 1968 Tuccillo and Nielsen noted that controlled thermal stresses could strengthen ceramics because a compression stress at the metal-ceramic interface might be desirable in dental restorations [146]. Usually the thermal expansion coefficient of dental alloys (α_m) values range from 13.5 to 14.5 $\times 10^{-6}$/°C; that of dental ceramics (α_c) values range from 13.0 to 14.0 $\times 10^{-6}$/°C. [34] A slight mismatch between α_m and α_c with that of metal higher causes the ceramic to be in a beneficial state of residual compressive stress at room temperature.

A recent study discusses various factors that influence transient and residual stresses in dental metal-ceramic systems. These authors suggest that visco-elastic finite element analysis can be a valuable tool to aid in the understanding of stress development in dental restorations. [36]

2.4.3 Thermal compatibility between titanium and ceramic

Conventional ceramics are fused at the temperatures beyond 900°C and their coefficient of thermal expansion, adjusted to precious or non-precious dental alloys, differs significantly from that of titanium.

Togaya et al. [142] investigated the compatibility of ceramic to cast pure titanium and suggested that appropriate bond strength between ceramic and titanium was possible by reducing the thermal expansion coefficient of the ceramic to approximate that of titanium. They stated also that the use of a low-firing temperature cycle (800°C) was shown to prevent excessive oxidation of titanium.

Menis et al. attempted to bond a low-fusing ceramics to cast titanium at approximately 800°C. They found that the bond strength was comparable with that of ceramic fused to Ni-Cr alloy and separation of ceramics from the cast titanium occurred at the oxide-metal interface. [94]

The thermal expansion coefficient of the ceramic should be close to or slightly below that of titanium ($9.6 \times 10^{-6}/°C$). Therefore, low-fusing veneering ceramics with thermal expansion coefficient matching that of titanium have been developed. [1, 142] Recently, titanium alloy (TiAl6Nb7) that has relatively higher thermal expansion coefficient ($10.1 \pm 0.25 \times 10^{-6}/°C$) has been introduced for the fabrication of metal-ceramic restorations and partial prostheses.

2.5 Evaluation of the metal-ceramic bond

Metal-ceramic restorations have been popular over the years. Although bonding mechanisms are understood to a large extent, evaluation of the metal-ceramic bond has been illusive. Many investigations have attempted to predict and test compatibility between metal and ceramics. [14] For successful results, it is necessary to optimise compatibility of the metal-ceramic systems. Experimental variables are common and must be recorded. However, standardizing samples and testing methods should minimize these variables.

2.5.1 Predicting thermal compatibility

During the last 20 years, researchers have proposed a number of test methods that could be used to estimate the compatibility of metal-ceramic systems. Geometries of specimens that have been used include bimaterial strips [147], split metal-ceramic rings [16], simulated crowns [9], disks [5, 156], semicircular arch specimens with a gapped diametral segment [4], and ceramic-veneered spheres [156].

Attempts to predict thermal compatibility are commonly based on the bimetallic strip equations of Timoshenko [141] or derivations of his research. Timoshenko [141] proposed that thermally induced stresses in bi-material strips could be calculated using the formula σ max = K ($\Delta\alpha$ ΔT), where σ max is the maximum tensile or shear stress, $\Delta\alpha$ is the difference in thermal expansion coefficients of the two materials, and ΔT is the temperature range through which such stress would be generated. Nielsen and Tuccillo [102] reported that this stress equation could be applied to the metal-ceramic combinations used in dentistry.

Fairhurst et al. [46] suggested a compatibility index derived from the bimetallic strip equation and based on the thermal expansion coefficients of metal and ceramic with the glass transition temperature of ceramic. Other researchers have used thermal-shock testing to estimate the compatibility of metal-ceramic systems. [8] The compatibility index by Fairhurst et al. [46] correlated well with the thermal shock-resistance by Anusavice et al. [9]. A resistance to transient thermal stresses can be measured with the thermal-shock resistance that may recognize grossly incompatible systems. But, the thermal-shock resistance will not correlate with clinical situation because it does not simulate applied mechanical stress. [14]

Rekhoson [116, 117, 118] and Hsueh [59] included the relaxation of the stress in the ceramic when they confirmed that the compatibility of the metal-ceramic system depended upon the thickness ratio of two materials. As the thickness ratio is changed, the relative stiffness varies, which results in the alteration of the transient thermal stress, together with stress relaxation.

Bertolotti and Fukui [16] confirmed that a decreasing stress relaxation is more suitable than a glass transition temperature with an unexpected change from viscous to elastic state. They incorporated this glass transition range and stress relaxation in calculations of interfacial stress in metal-ceramic systems. Bertolotti [17] acquired predictable agreement between calculated and measured stress values.

2.5.2 Testing compatibility

To measure the compatibility of metal ceramic systems some kinds of methods have been investigated, such as (1) measuring distortion of specimens after ceramic firing, (2) various bond strength tests, (3) ceramic adherence tests, and (4) measuring residual stresses. However, agreements between predicted and measured results are rare. [14]

Investigations have directly examined the adhesion of metal-ceramic combinations to determine the resistance to mechanical stress. [3, 84, 129] Bond strength tests measure resistance to applied stress and residual stress alike. Several geometries have been used to evaluate bond strengths, including testing in tension, shear, and three- and four-point bending. [3]

Bond strength tests have been used to examine the effects of the α mismatch. Although Rowe and Asgar [125] found no relationship between α mismatch and bond strength, Coffey et al. [28] did. Vickers hardness indentations have also been used to study interface toughness of metal-ceramic systems. [143] The microcracks ran through the interface of poorly bonded systems, whereas in strongly bonded systems cracks propagated through ceramics. Several researchers actually measured residual stress present at the metal-ceramic interface. Values determined in ceramic at the metal-ceramic interface were compressive stresses of –11,000 and –9,000 psi (–76 and –60 MPa) by Haller et al. [54] with x-ray diffraction and –4,500 to –9,000 psi (–30 to –60 MPa) by Tsutsumi et al. [145] using dissection. These values were lower than measured metal-ceramic strengths. [10]

Several groups have used finite element analysis to study the compatibility of metal ceramic systems and the effect of stress. [7, 13, 37, 48] However, the models lacked the refinement to calculate stress of metal ceramic systems clinically. The models were two-dimensional or axiosymmetric and assumed constant physical and thermal properties of materials. [14] Bertolotti [17] has confirmed the calculated stress values of a model system with laboratory measurements and established suitable agreement for bimaterial strips.

2.5.3 ADA acceptance

The American Dental Association’s Council on Dental Materials, Instruments, and Equipment has recommended that compatibility can be evaluated by matching of thermal expansion data in combination with two of three other tests: thermal shock test, bond characterization using a three-point loading or flexure test, and multiple firings without cracking. [31] These predictors possess a measure of practical success, but agreement on their use is limited. Researchers are still examining the various laboratory tests used to assess the compatibility of materials. [14]

2.5.4 ISO standard

A metal-ceramic bond strength test should be quantitative, reproducible, and easy to perform. In comparison to other tests such as shear tests, simple flexure tests, torsion tests, and pull through tests, the three-point flexure bond test has prevailed as a widely used method, and is contained in the draft proposal for the German standard DIN 13927.

The three-point flexure bond test has the following advantages: simple and reproducible manufacturing of specimens, quantitative determination of the bond strength, testing of all possible metal-ceramic combinations, and use of a commercially available testing machine. The stress distribution in three-point bending specimens has been analysed with finite element methods, and hence this method is well defined. [39, 85, 86, 127]

3. Materials and Methods

In this study the effective thermal contraction difference was measured to compare the thermal compatibility of commercial pure titanium grade 2 and TiAl6Nb7 with titanium ceramic, and bond strength was evaluated with Schwickerath crack initiation test according to ISO 9693.

3.1 Materials

TiAl6Nb7 (Girotan L®; Girrbach Dental GmbH, Germany) and cpTitanium grade 2 (Girotan R/Grade II®; Girrbach Dental GmbH, Germany) were selected. Then titanium ceramic (Initial Ti®; GC, Japan) was fused to each metal specimen. The alloy compositions and the concentrations of interstitial impurities are listed up in Table 3. Titanium ceramic (Initial Ti®; GC, Japan) was developed for the application on titanium and its alloys. As Table 4 describes, titanium ceramic has relatively low thermal expansion coefficient that is lower than that of cp titanium and TiAl6Nb7 alloy.

Table 3 Chemical Requirements of TiAl6Nb7 (ASTM Standard F 1295) and cp Titanium grade 2 (ASTM Standard F 67) [25]

Element (%)	TiAl6Nb7	cp Ti grade 2
Aluminum	5.50 to 6.50	-
Niobium	6.50 to 7.50	-
Tantalum	0.50 max	-
Iron	0.25 max	0.30 max
Oxygen	0.20 max	0.25 max
Carbon	0.08 max	0.10 max
Nitrogen	0.05 max	0.03 max
Hydrogen	0.009 max	0.015 max
Titanium	Balance	Balance

Fig. 3 TiAl6Nb7 alloy (Girotan L®; Girrbach Dental GmbH, Germany)

Fig. 4 Titanim ceramic (Initial Ti®; GC, Japan)

Table 4 Properties of titanium ceramic [50]

Property	Value
Dentin firing (°C)	780
Thermal expansion coefficient ($10^{-6}\times K^{-1}$)	8.5-8.7
Glass transition temperature (°C)	580
Solubility ($\mu g/cm^2$)	11
Density (g/cm^2)	2.45
Flexural strength (Mpa)	70
Grain size (D 50%)	22.2

3.2 Specimen fabrication

3.2.1 Tuebinger Gabel test (Measurement of the effective thermal contraction difference)

3.2.1.1 Preparation of titanium Gabel

Split samples with two branches 25 × 3 × 0.7 mm in size were made of autopolymerizing acrylic resin (Palavit®G; Heraeus Kulzer GmbH & Co. KG, Germany). Split size between two branches was 1 × 25 × 0.7 mm, and complete specimen length was 30 mm. Ten samples of each group were invested with a titanium casting investment (Girovest TC®; Girrbach Dental GmbH, Germany) and cast with the American Society for Testing and Materials (ASTM) grade 2 commercially pure titanium (Girotan R/Grade II®; Girrbach Dental GmbH, Germany) and TiAl6Nb7 alloy (Girotan L®; Girrbach Dental GmbH, Germany) using a pressure casting unit (SymbioCast®; Girrbach Dental GmbH, Germany) in argon atmosphere. SymbioCast® system, one chamber, arc-melting, vacuum-pressure casting machine, has a shortened transfer distance from crucible to mold, and optimized cycles of vacuum and argon pressure.

Cast titanium strips were sandblasted with 110μm aluminum oxide powder (Al_2O_3) and ground in sequence of 600 grit, 800 grit, and 1200 grit SiC paper on a horizontal grinder (TG 200®; Buehler-Wirtz GmbH, Germany) to ensure complete removal of the α-case layer. When a thickness of 0.5 mm achieved, titanium strips were cleaned in ethanol. The final dimensions of titanium strips were 30 mm × 7 mm × 0.5 mm with middle open split 25 mm × 1 mm × 0.5 mm in size. Fig 5 shows the form and the final size of the titanium split sample. Thickness was controlled with a digital calliper.

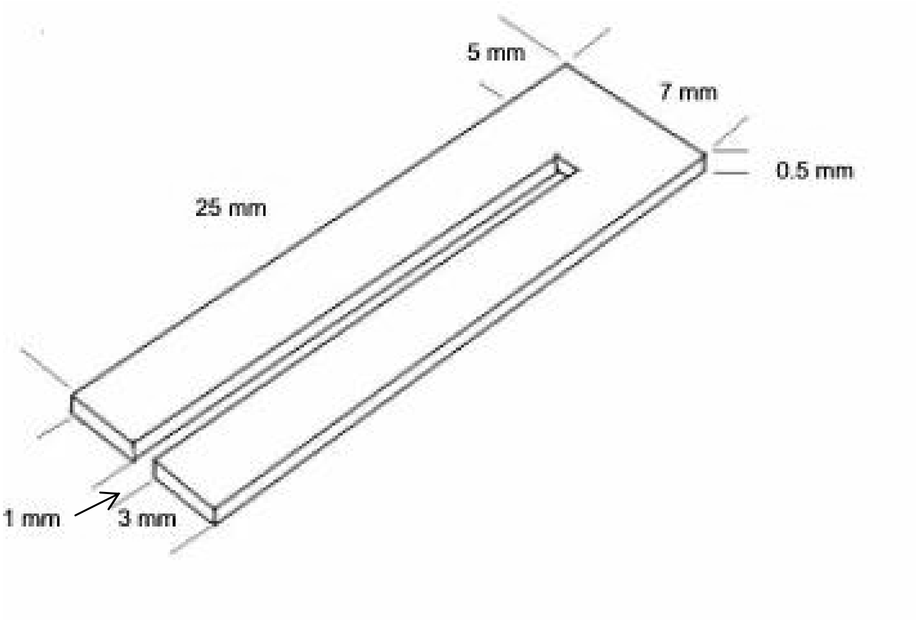

Fig. 5 Form and dimensions of titanium Gabel

Fig. 6 Titanium casting unit (SymbioCast®; Girrbach Dental GmbH, Germany)

3.2.1.2 Ceramic application

Prior to the application of ceramic to titanium strips, the surfaces to be veneered with ceramic were sandblasted with 125μm aluminum oxide (Al_2O_3) at a pressure of 2 bar and after passivation (five minutes) cleaned under steam according to the manufacturer's instruction.

For each titanium strip, titanium ceramic (Initial Ti®; GC, Japan) was applied on the opposite side of each branch and fired in a furnace (Focus 2007®; Girrbach Dental GmbH, Germany). First the titanium strips were coated with a thin layer of bonder ceramic, and opaque and dentin ceramic were added sequentially.

The firing schedules followed the recommendations given by the manufacturers. Table 5 presents the ceramic firing schedules of titanium ceramic. After 2nd opaque firing a thickness of opaque ceramic was 0.2 mm, and then dentin ceramic was added and fired to form a total ceramic thickness of (1.1 ± 0.1) mm after 2nd dentin firing. Fig. 7 shows the change of ceramic fused titanium Gabel after firing.

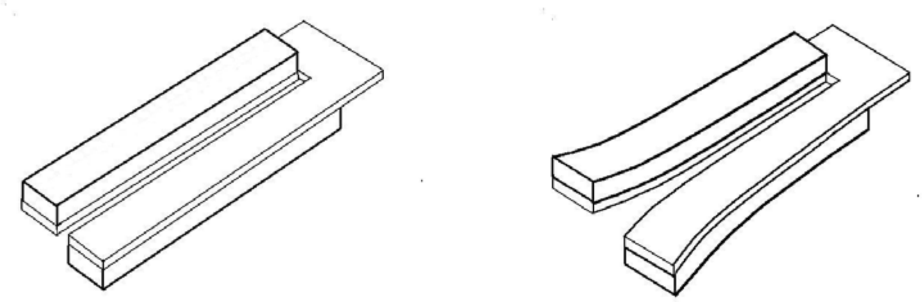

Fig. 7 Change of ceramic fused titanium Gabel after firing. (left-before firibg, right-after firing)

Table 5 Firing introductions of titanium ceramic (Initial Ti®; GC, Japan) [50]

	Preheating temperature	Drying time	Raise of temperature	vacuum	Final temperature	Holding time	Appearance
Bonder firing	450°C	4min	55°C/min	Yes	810°C	1min	Shining
1st opaque firing	450°C	4min	55°C/min	Yes	810°C	1min	Shining
2nd opaque firing	450°C	4min	55°C/min	Yes	810°C	1min	Slightly shining
1st dentin firing	400°C	6min	45°C/min	Yes	780°C	1min	Slightly shining
2nd dentin firing	400°C	6min	45°C/min	Yes	775°C	1min	Slightly shining

3.2.2 Schwickerath crack initiation test (ISO 9693)

3.2.2.1 Preparation of titanium strips

Titanium strips were prepared with the same materials and the same procedures of the Tuebinger Gabel test. The only differences were the dimension and geometry of resin samples and titanium strips. The final size of titanium strips was (25 ± 1) mm × (3 ± 0.1) mm × (0.5 ± 0.05) mm according to ISO 9693. [65]

3.2.2.2 Ceramic application

Prior to the bonder application, the surfaces were treated by sandblasting with 125μm Al_2O_3 at a pressure of 2 bar, and after passivation during 5 minutes cleaned with steam cleaner. According to the manufacturer’s instructions, bonder and opaque ceramic were applied in sequence over a length of (8 ± 0.1) mm in the middle of each titanium strips. After second opaque firing, dentin ceramic was build up and fired in a rectangular shape until a total ceramic dimension of (8 ± 0.1) × 3 × (1.1 ± 0.1) mm was achieved. [65]

The final shape of the ceramic veneer was accomplished by trimming, and, if necessary, ceramic was removed from the side of the titanium strips. Finally, each specimen was submitted to a glaze firing in accordance with the manufacturer’s instructions. Fig. 8 presents the configuration and the size of the specimen that finally prepared.

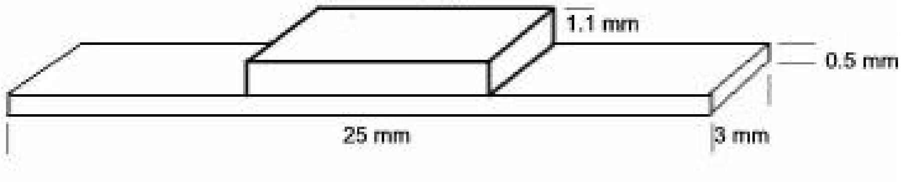

Fig. 8 The configuration of test specimen according to ISO 9693

3.3 Test procedure

3.3.1 Tuebinger Gabel test (Measurement of the effective thermal contraction difference)

Before ceramic application, the distance between two tips of titanium Gabel branches was measured from the front. The expanded distance of each specimen was measured twice: after second opaque firing and after second dentin firing.

After cooling a photo of thirty magnifications was taken with camera (CoolSNAP-Pro MEDIA CYBERNETICS®, The Imaging Expert™) in a stereo-microscope (WILD PHOTOMAKROSKOP M400, WILD HEERBUGG, Swiss) and the distance between two branches was measured with the aid of digital computerized and calibrated pictures and related soft ware (Image-Pro® PLUS ver. 4.5, Media Cybermetrics Inc.).

Based on these data the effective thermal contraction difference between titanium and ceramic was calculated according to the bi-metal theory with respect to the sample geometry as well as to the elastic modulus of the materials used.

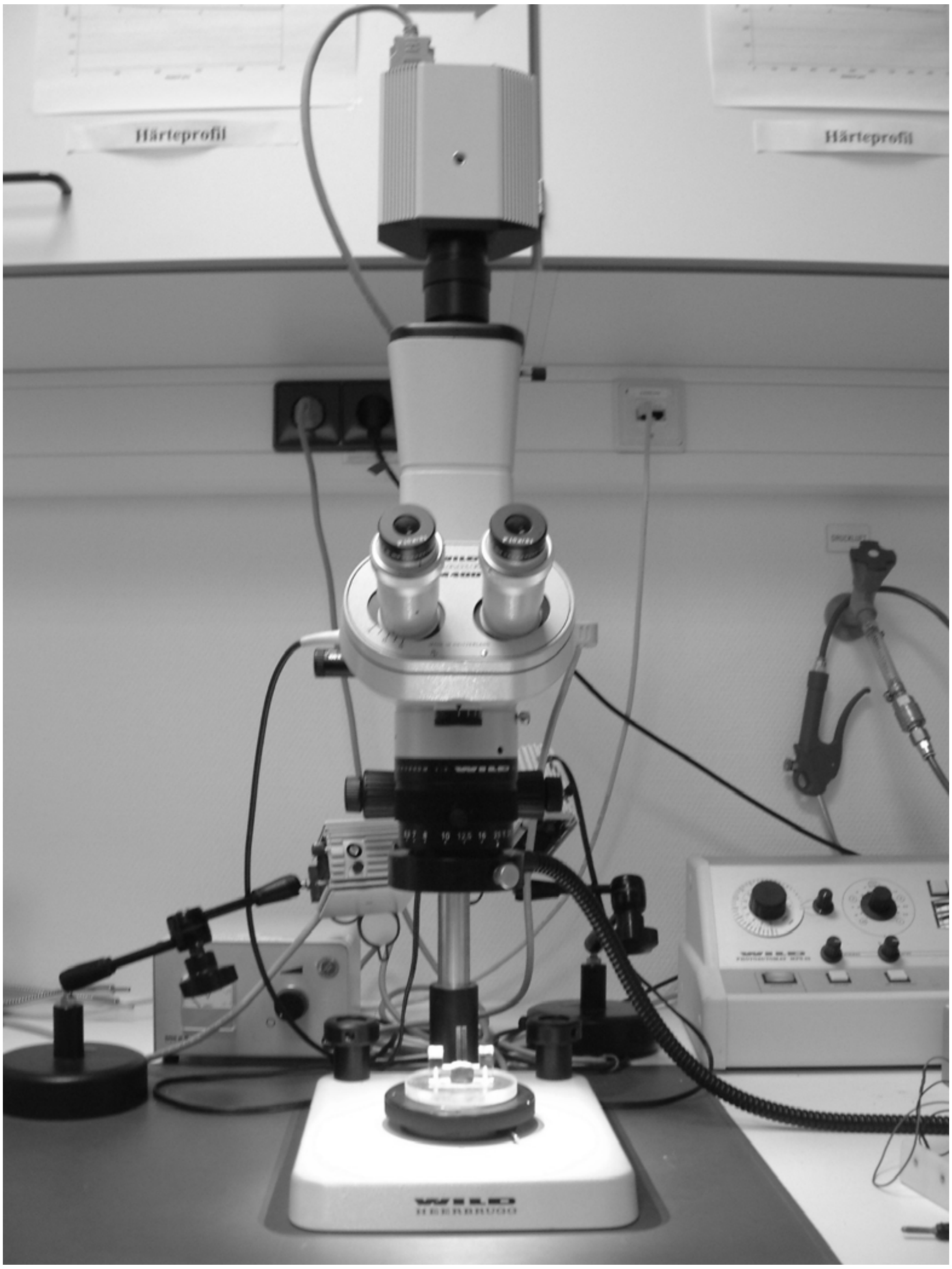

Fig. 9 Stereo-microscope (WILD PHOTOMAKROSKOP M400, WILD HEERBUGG, Swiss) with camera (CoolSNAP-Pro MEDIA CYBERNETICS®, The Imaging Expert™)

3.3.1.1 Effective thermal contraction difference

Common convention associates compressive stresses in ceramic with a positive thermal expansion/contraction mismatch ($\alpha_m > \alpha_c$) and tensile stresses in the ceramic with a negative thermal expansion/contraction mismatch ($\alpha_m < \alpha_c$). [36] With a positive value of residual stresses, the state of ceramic is under the compression, as regarded to be desirable for the success of the metal-ceramic systems. However, too high positive difference in the thermal expansion coefficients of metal and ceramic, especially in long span bridges, can induce to deform the metal substrate and result in the loss of passive fit, and it may cause the ceramic fracture in the mouth.

Residual stresses of metal-ceramic system depend upon the difference of thermal expansion/contraction coefficients and can be influenced by E-modulus and thickness of metal and ceramic. Residual stresses can be estimated by the formula:

$$\text{Residual stress } (\delta) = k \times (\alpha_m - \alpha_c) \times (T_g - RT).$$

k: coefficient

α_m: thermal expansion coefficient of metal

α_c: thermal expansion coefficient of ceramic

T_g: glass transition temperature of ceramic

RT: room temperature

Thermal induced stress between T_e and RT can be formulated with the thermal contraction coefficient instead of the thermal expansion coefficient,

$$\text{Residual stress } (\delta) = k \times (\beta_m - \beta_c) \times (T_e - RT).$$

k: coefficient

β_m: thermal contraction coefficient of metal

β_c: thermal contraction coefficient of ceramic

T_e: glass solidification temperature of ceramic

RT: room temperature

Value of $(\beta_m - \beta_c) \times (T_e - RT)$ is introduced as the effective thermal contraction difference ($\Delta\gamma$):

$$\Delta\gamma = (\beta_m - \beta_c) \times (T_e - RT).$$

Because glass solidification temperature (T_e) is not constant, value of the effective thermal contraction difference ($\Delta\gamma$) is dependant upon the temperature control.

Based on the bi-metal theory [68], deformed distance (ΔY) of free end in two-layered sample can be calculated with the following equation:

$$\Delta Y = \frac{(\beta_m - \beta_c) \Delta T\, l^2}{2\, H\, [\, 2/3 + (m^2 n - 1)^2/6mn(m+1)^2]} \qquad . [150]$$

h: metal thickness
d: ceramic thickness
H: h + d
m : h / d
l: ceramic veneered length
E_m: Elastic modulus of metal
E_c: Elastic modulus of ceramic
n: E_m / E_c
β_m: thermal contraction coefficient of metal
β_c: thermal contraction coefficient of ceramic
ΔT: $T_e - RT$
T_e: glass solidification temperature of ceramic
RT: room temperature

Deformation of two branches in the Gabel shape specimens is:

$$V = 2\,\Delta Y.$$

Therefore, the effective thermal contraction difference ($\Delta\gamma$) can be calculated as

$$\Delta\gamma = \frac{H\,V}{l^2\left[\,2/3 + (m^2 n - 1)^2/6mn(m+1)^2\right]}\;.$$

This formula indicates that neither the proportion of elastic modulus nor that of veneered thickness has comparable influences on the results. Without the knowledge of the glass solidification temperature (T_e) that is not constant, the effective contraction difference can be quantitatively calculated with the distance of the expanded tip, measured experimentally by the Tuebinger Gabel test.

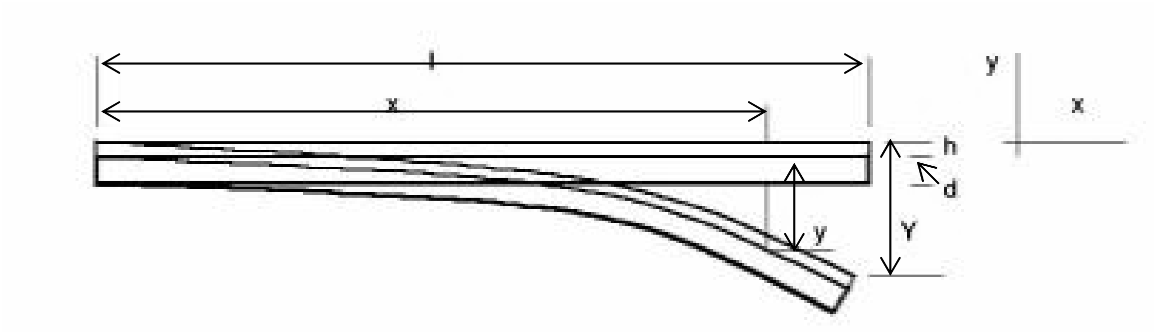

Fig 10 Deformation of ceramic veneered metal plate after ceramic firing

3.3.2 Schwickerath crack initiation test (Three point bending test)

The test of the bond strength was performed with a three-point flexural device on a universal testing machine (Zwick / Z010, Zwick GmbH Co., Ulm, Germany). The specimens were placed with the ceramic facing down in the bending apparatus with rounded supporting rods 20mm apart. The specimens were loaded in the center with a rounded bending piston; radius 1mm. Fig 11 shows the schematic of test conditions.

Force was applied at a constant rate of (1.5 ± 0.5) mm/min and recorded until a disruption of the load-deflection curve occurred that indicated bond failure. The fracture force F (in newtons) was measured for specimen’s failure by a debonding crack occurring at one end of the ceramic layer. The loads that resulted in bond failure were recorded digitally with computer using software (Zwick testeXpert ver. 8.0, Zwick GmbH Co., Ulm, Germany).

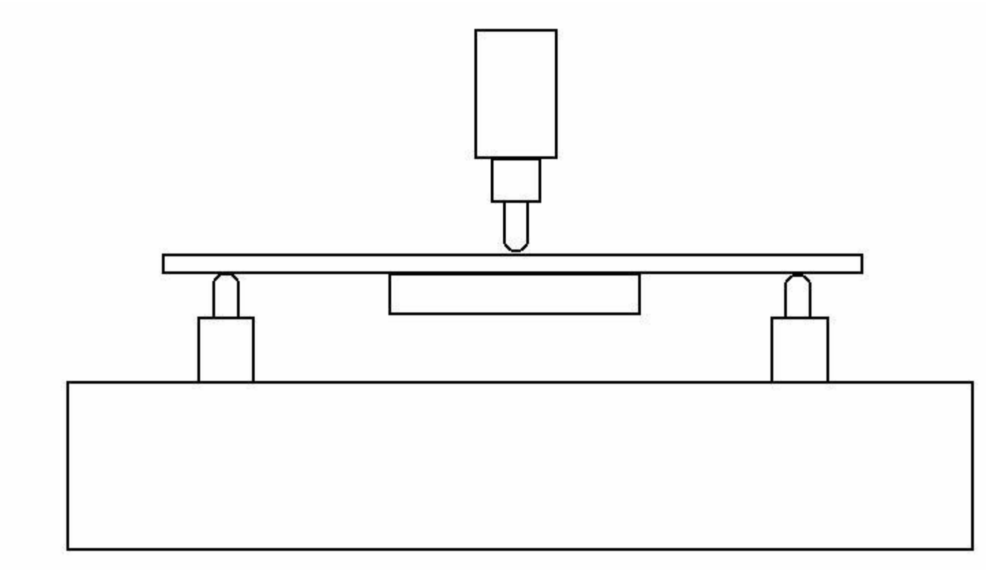

Fig. 11 Schematic illustration of the three-point bending test

Fig. 12 Universal testing machine (Zwick / Z010, Zwick GmbH Co., Ulm, Germany)

The fracture force F was multiplied with a coefficient k that can be read from Fig. 13. The coefficient k is a function of the thickness of the metal substrate and the value of Young’s modulus of the used metallic material. To read the value k for a certain thickness, the curve for the proper value of Young’s modulus is first selected, then the value k can be read from the picked curve for the thickness.

The debonding/crack-initiation strength τ is calculated using the equation:

$$\tau = k \times F$$

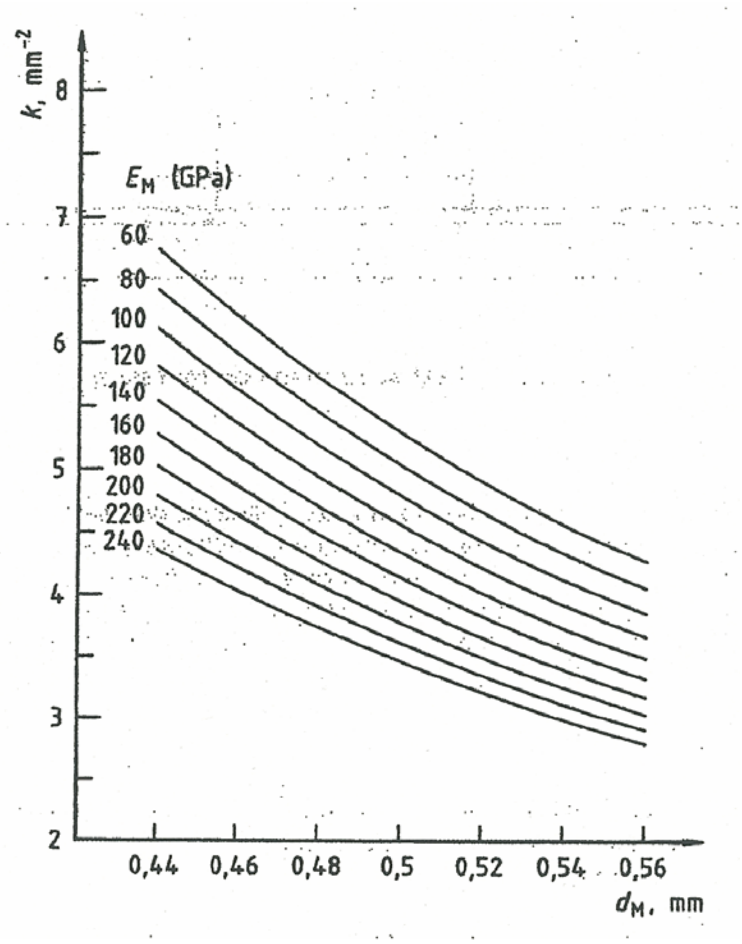

Fig. 13 Diagram to determine the coefficient k as a function of metal substrate thickness dm and Young's modulus E_M of the metallic material [65]

3.4 Statistical analysis of data

For each test ten specimens (n=10) of cp Ti and TiAl6Nb7 were tested. T-test was used to evaluate statistical significance of the data. A level of significance of 0.05 was chosen (p=0.05).

4. Results

4.1 Comparison of the effective thermal contraction difference

Ten specimens (n=10) of each group were measured before ceramic application, after 2nd opaque firing, and 2nd dentin firing. Photomicrographs of thirty magnifications of specimen are shown in Fig 14 and Fig. 15. The effective thermal contraction difference between titanium and opaque ceramic was calculated. To simulate the clinical situation, the effective thermal contraction difference between titanium and complete ceramic layer (opaque and dentin) was also calculated. The following tables show the means and standard deviations of each group.

Table 6 The effective thermal contraction difference between cp Ti and titanium ceramic

Cp Titanium	Mean	S.D.
Opaque	1.29×10^{-3}	0.43×10^{-3}
Opaque and Dentin	2.37×10^{-3}	0.88×10^{-3}

Table 7 The effective thermal contraction difference between Tial6Nb7 and titanium ceramic

TiAl6Nb7	Mean	S.D.
Opaque	0.39×10^{-3}	0.18×10^{-3}
Opaque and Dentin	0.89×10^{-3}	0.25×10^{-3}

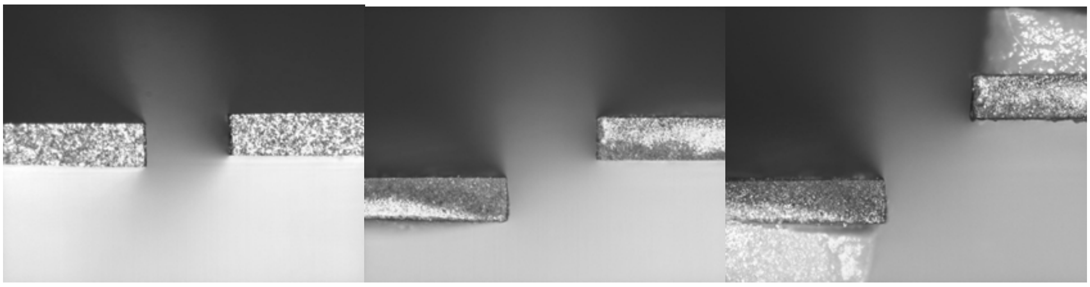

Fig.14 Magnified photomicrographs of cp titanium-ceramic specimen. (left: before ceramic application, middle: after second opaque ceramic firing, right: after dentin ceramic firing)

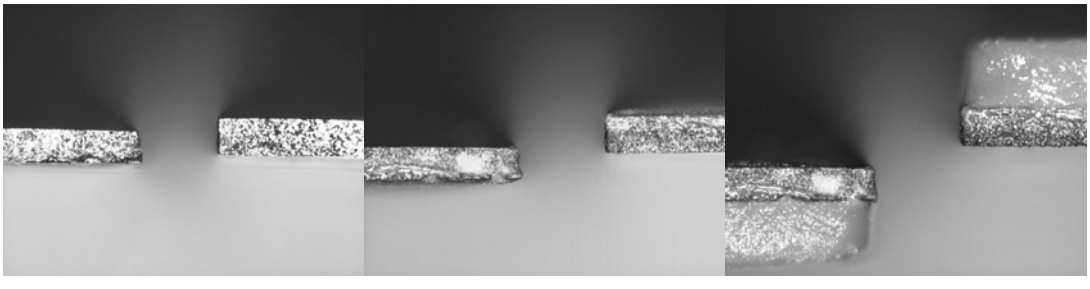

Fig.15 Magnified photomicrographs of TiAl6Nb7-ceramic specimen. (left: before ceramic application, middle: after second opaque ceramic firing, right: after dentin ceramic firing)

4.2 Comparison of three point bending strength

The bond strength of the titanium-ceramic system was determined by the Schwickerath crack initiation test according to ISO 9693 and the mean values of two groups are presented in Table 8. Ten specimens (n=10) of each group were tested.

Table 8 Bond strength between titanium and titanium ceramic

	Fracture force (N)		Debonding/crack-initiation strength (MPa)	
	Mean	S.D.	Mean	S.D.
cp Titanium	7.3	0.9	41.0	5.9
TiAl6Nb7	9.0	2.8	41.6	12.6

4.3 Statistical analysis

T-test was performed to determine the statistical significance of the effective thermal contraction difference between two titanium groups. The bond strengths of cp titanium- and TiAl6Nb7-ceramic system were also compared by t-test.

T-test found a significant difference of the effective thermal contraction differences between two titanium groups at the 95% confidence level ($p<0.05$). However, the bond strength of ceramic fused to cp titanium was similar to that of TiAl6Nb7 alloy respectively, and t-test showed no significant difference between means of bond strength ($p>0.05$). The sample number of two titanium groups in each test was ten (n=10).

4.4 Diagrams

The following diagrams show the comparison of the effective thermal contraction difference and that of the bond strength.

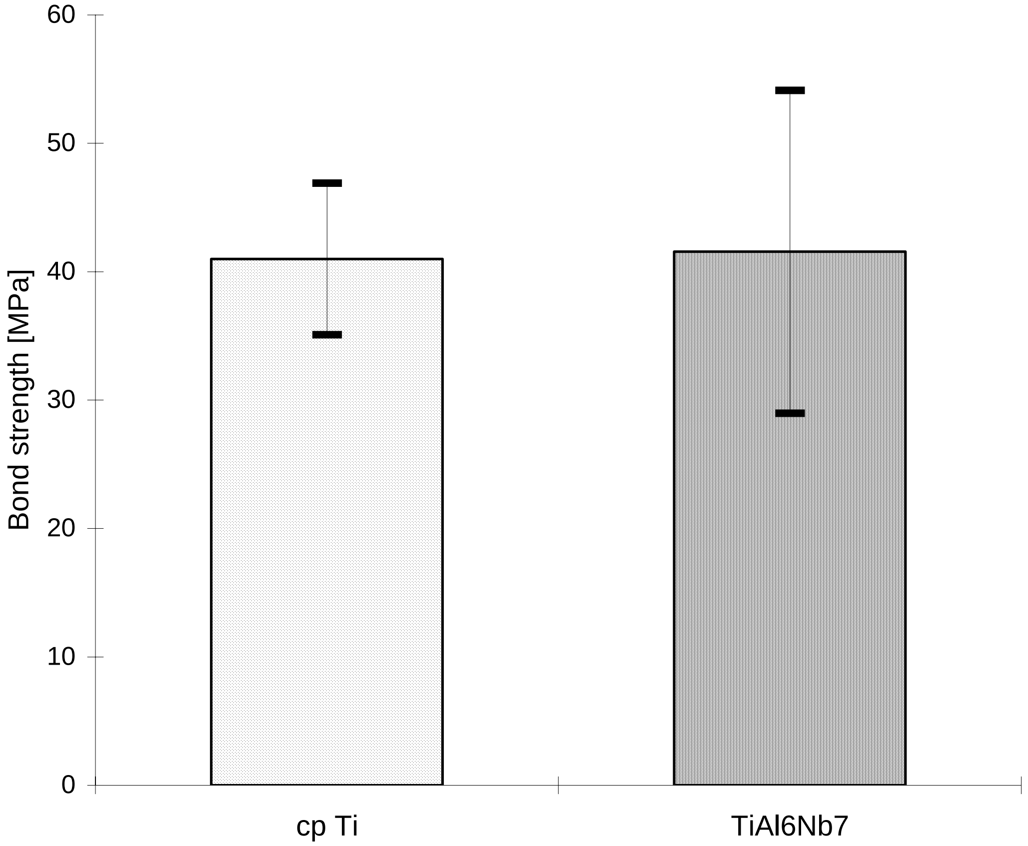

Fig. 16 The bond strength of cpTi- and TiAl6Nb7-ceramic

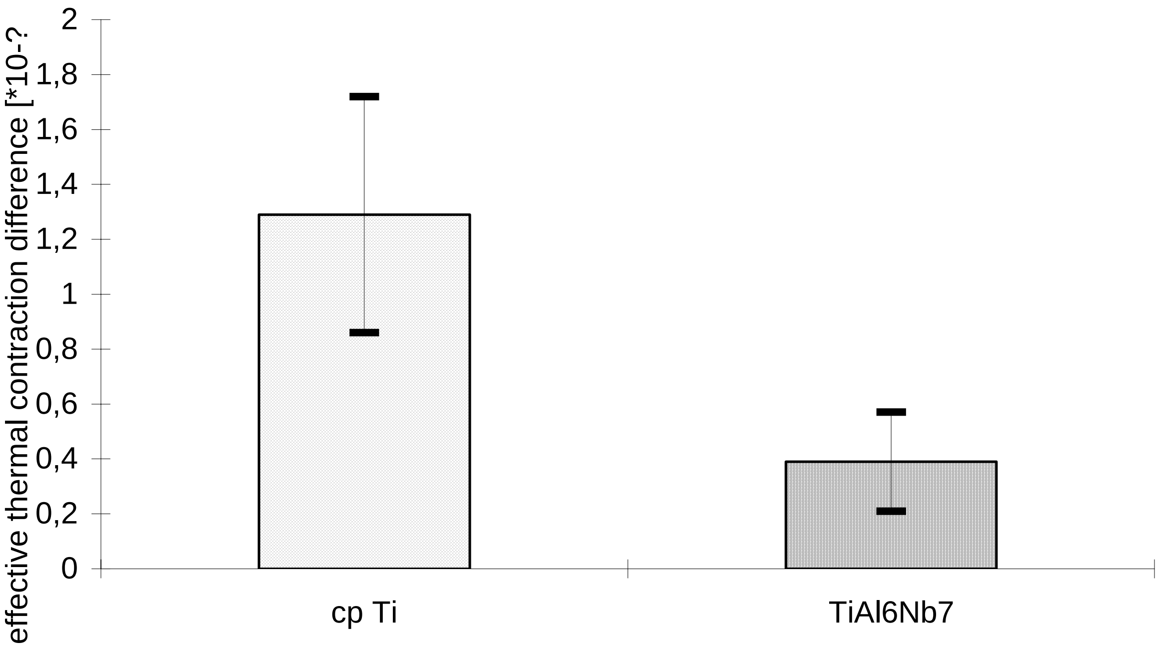

Fig. 17 The effective thermal contraction difference of cpTi- and TiAl6Nb7-Opaque ceramic

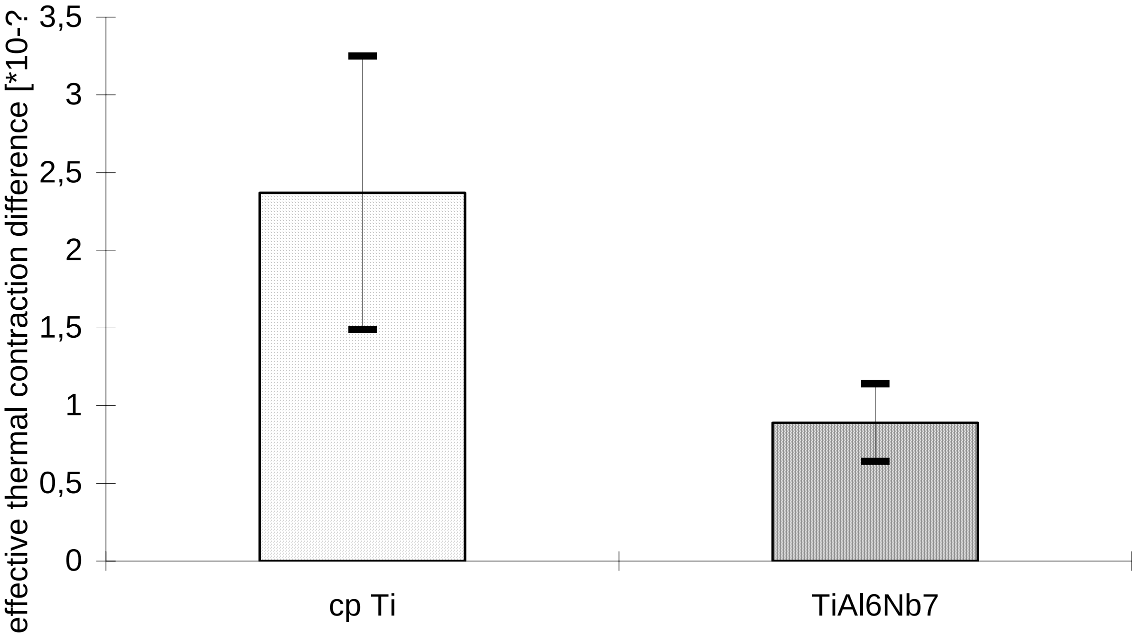

Fig. 18 The effective thermal contraction difference of cpTi- and TiAl6Nb7-Opaque&Dentin ceramic

5. Discussion

This study investigated the bond characteristics of titanium-ceramic systems, such as the thermal compatibility and the bond strength, using the Tuebinger Gabel Test and three point bending test (ISO9693).

The justification for the selection of the two titanium metals investigated in this study is as follows. Cp Ti is FDA-approved, and ASTM has standards for their usage. TiAl6Nb7 was selected because of the possible compatibility in thermal expansion coefficient with titanium ceramic, higher strength, and the biocompatible property.

5.1 Measurement of the effective thermal contraction difference

A slightly lower coefficient of thermal expansion of ceramic compared with that of metal is considered beneficial, because it may place the ceramic under compression after firing. To determine the thermal compatibility, it is necessary to consider not only the thermal expansion/contraction coefficient, but also elastic modulus of metal and ceramic, specimen geometry, glass-transition or solidification temperature and cooling late of ceramic.

The bimetal thermostat equation of Timoshenko [141] has been used to calculate residual stresses in metal-ceramic systems beginning with the study of Tuccillo and Nielsen [148]. The modified equation of Timoshenko provide a convenient means to estimate residual stresses due to thermal contraction difference in metal-ceramic systems. The theoretical development of the Tuebinger Gabel test was based on the equation presented by Timoshenko [141] for calculating the deflection of a bimetallic strip, and the effective thermal contraction difference seems to be reasonable to determine the thermal compatibility of the metal-ceramic systems.

The particular shape of split samples and the ceramic application, veneered on the different side of each branch, make the final effects clearer. The amount of distortion can be recorded and calculated by the bi-metal theory. Although all of the specimens had identical dimensions, the results of comparison of the effective thermal contraction difference indicate that the amount of deflection in TiAl6Nb7-titanium ceramic system is smaller than that in cp titanium-titanium ceramic system.

As a result of the Tuebinger Gabel test, cp titanium- and TiAl6Nb7 alloy-ceramic pairs showed positive values of the effective thermal contraction difference, which reflected the expansion of cp titanium and TiAl6Nb7 alloy exceeding that of the ceramic, resulting in compressive residual stress states in ceramic. On the contrary, if negative values of the effective thermal contraction difference occur, than this indicates a tensile state. Cp titanium-ceramic pair exhibited larger positive values, however cp titanium-ceramic pair showed more discrepancy of the thermal expansion coefficients ($\Delta\alpha$) than that of TiAl6Nb7 alloy-ceramic system.

Although cp titanium-ceramic pair had ideal and smaller discrepancy of the thermal expansion coefficients, the effective thermal contraction difference of ceramic fused to cp titanium was greater than that of ceramic fused to TiAl6Nb7 alloy, which means that the thermal compatibility of metal-ceramic system seems to be influenced not only by the discrepancy of the thermal expansion coefficients but also by another factors.

A possible explanation of these findings is that the discrepancy of the thermal expansion coefficients between the ceramic and the titanium was appreciably altered after firings. This study simulated the clinical situation of repeated applications of ceramics and the thickness ration of materials was clinically realistic. The coefficient of thermal expansion of ceramics is primarily dependant on its content of alkaline oxide such as those of potassium and sodium. [82] However, it was demonstrated that the coefficient of thermal expansion of ceramics changed from one and five firings. [46, 122]

The increase in the coefficient of thermal expansion for ceramic with repeated firing has been attributed to the formation of leucite crystals. [131] Repeated firing of ceramic would theoretically induce the mismatch of thermal compatibility in metal ceramic combinations and subsequently decrease the bond strength. [107] Dorsch [43] reported a large increase in thermal expansion coefficients of certain body porcelains and a slight decrease in the expansion coefficients for some opaque ceramics with an increasing number of firings. However, Stannard et al. [134] found no significant reduction of the bond strength of opaque ceramic bonded to compatible metal alloy after different firing cycles.

In addition, it seems that the elastic modulus of ceramic and titanium can affect on the residual stresses after ceramic firings, which might result in lower effective contraction difference of TiAl6Nb7 alloy-ceramic specimens than that of cp titanium-ceramic specimens. Table 9 presents the thermal expansion coefficients of materials used in this study. Reliable values of the thermal expansion coefficients are required to achieve a positive thermal mismatch between titanium and ceramic. The tolerable difference in coefficient of thermal expansion between these two materials is approximately 0.5×10^{-6} °C. [33] Despite the more positive value of the difference in thermal expansion coefficients of cp titanium/ceramic system, the amount of distortion in TiAl6Nb7 alloy-ceramic system was smaller than that in cp titanium-ceramic system after firings.

It should be emphasized that the thermal expansion data were obtained with a controlled heating rate; however actual thermal expansion/contraction coefficient differentials in specimens simulated clinical situation may have differed significantly from thermal expansion data.

Table 9 The thermal expansion coefficients of materials used (given by the company)

Material	Thermal expansion coefficient($\times 10^{-6}$/K)
Cp Ti (giroTan R)	9.6 ± 0.25
TiAl6Nb7 (giroTan L)	10.1 ± 0.25
Opaque ceramic (Titanium Ceramic)	8.9
Dentin ceramic (Titanium Ceramic)	8.6

When the ceramic cooled in firing procedure, the stress starts to be produced at the temperature of glass solidification (T_e) that seems to be higher than glass transition temperature (T_g) and dependant upon the cooling condition. The thermal expansion coefficient is recorded normally with the heating rate of 3-5°C/min, but cooling rate is really higher in the fabrication of metal-ceramic restorations. Solidification effect causes to create the relaxation when repeated firing. It should be noted that the contraction behaviour is not identical with the expansion behaviour. [126] However, the residual stress is generally estimated with the expansion behaviour, not with the contraction behaviour.

Low et al. [89] investigated thermal expansion coefficients of titanium casting, and founded that the coefficient of thermal expansion, calculated from the heating cycle, was higher values than the coefficient of thermal contraction, calculated from the cooling cycle. They also recommended the coefficient values from the cooling cycle. They concluded that the discrepancy of the coefficients between thermal expansion (heating condition) and thermal contraction (cooling condition) was insignificant when the heating (cooling) rate was reduced to 1 °C/min. However, the heating or cooling rate in dental labour is relatively high, for example, heating rate of 55°C/min for opaque firing and that of 45°C/min for dentin firing in this study, which might cause the inertia effect or temperature gradient within a furnace or specimen. [89] The thermal expansion/contraction coefficient should be measured at the same high heating and cooling rates common in dental laboratories.

Thermal compatibility is a complex issue; therefore, it seems unlikely that thermal expansion differences alone will be sufficient to predict a susceptibility of metal-ceramic systems to failures in clinical situations. [36] The compatibility index, introduced by Fairhurst et al. [46] was based primarily on an integration of expansion/contraction difference between metal and ceramic. Fairhurst et al. [45] also reported that the thermal expansion coefficient of opaque does not always match the thermal expansion coefficient of specific ceramic system. Yilmaz and Dincer [161] obtained the same results.

In the past, radius of curvature measurements of bimaterial strips or gap changes of split-metal rings have been used to calculate stress values based on the bimetal thermostat equation of Timoshenko [141]. Currently there are no international standards to define the maximum difference in thermal contraction coefficients that can exist between a metal and veneered ceramic without transient failures of ceramic during cooling or delayed failure in ceramic due to high residual tensile stresses. [36]

Residual stress gradients depend not only upon differences in thermal expansion coefficients of metal and ceramics but also on reaction products generated during the fusing of dental ceramics to a metal alloy. [79]

A difference in thermal expansion coefficients of the porcelain and metal has been recognized as a major parameter in predicting compatibility. However, the effective thermal contraction difference can be suggested as a useful and reasonable method to compare the thermal compatibility of metal-ceramic systems in the absence of exact values of the thermal contraction coefficients and glass solidification temperature of ceramics that are clinically used.

5.2 Schwickerath crack initiation test(ISO 9693)

Many of metal-ceramic bond tests have been performed until now. These different tests may be classified as actual shear tests, flexure tests, torsion tests, and the so-called pull-through tests. [85]

The three-point bending test has been suggested as a possibility for the examination of the bond characteristic, especially dependent upon the metal surface treatment or metal surface conditioning, in metal-ceramic system [67]. It was considered that the fracture strength, which derived from the residual stresses created in the metal-ceramic interface, depends upon the elastic modulus of alloys. It was also possible to compare the bend shear strength in different metal-ceramic systems.

This test was recommended in DIN 13927 for the examination of the metal-ceramic bond and succeeded in ISO 9693. [39, 66] For the purpose of the assessment of results, the numerical method of finite element analysis, in which the influence of elastic modulus and thickness of metal plate could be considered, has been used [127] and also in this study.

The success of the metal-ceramic restoration depends upon the successful adherence between the metal substrate and ceramics. Many investigations proved that the metal-ceramic bond between dental alloys and ceramics has excellent strength for the clinical use. (Table 10)

The titanium-ceramic system has also been examined. Table 11 illustrates that three-point bending strength between titanium and ceramic was lower than that of other dental alloys, however Persson and Bergman reported that two titanium low-fusing ceramic systems showed even higher shear strength values than a high-gold ceramic system. Table 11 also shows that some combination had enough bond strength for ISO requirement whose minimal acceptable bond strength is 25MPa. [65] The results of this study indicated that the bond strengths of ceramic fused to cp titanium and TiAl6Nb7 alloy were found to be within the acceptable standard levels.

Adachi et al. proposed that the low bond strength between ceramic and titanium was attributable to inconsistent oxide adherence to the metal and suggested that the nonadherent titanium oxide was formed during the firing of ceramics. [1] Therefore the vacuum firing system has been developed for the fusing of ceramics on the titanium.

Table 10 Literature overview of three-point bending strength between dental alloy and ceramics [133]

Author	Alloy	Ceramic	Mean
Schwarz [127]	MT 600	Vita	57.3 MPa
	Verinor	Vita	54.7 MPa
Dörfler [40]	5 Au-Pt-In Alloy	Vita VMK 68	64.0 MPa
Lenz [85]	Herador H	Vita VMK 68	31.1 MPa
Rinke [123]	Degudent U	Vita Omega	47.2 MPa
Walther [155]	Dentitan	Vita Omega	46.1 MPa
	Remanium CS	Vita Omega	35.0 MPa
	Remanium CD	Vita Omega	34.7 MPa
	Remanium 2000	Vita Omega	38.7 MPa
Traub [144]	Remanium 2000	Vita	63.0 MPa
	Remanium 2000	Ducera	42.0 MPa
	Remanium 2000	De Trey	53.0 MPa
Kappert [67]	Dentitan	Vita VMK 68	47.7 Mpa
	Elite	Vita VMK 68	35.1 MPa
	Wiron 88	Vita VMK 68	43.8 Mpa
Schwarz [127]	Wiron 88	Vita	45.2 Mpa
	Wirobond	Vita	54.5 MPa
	Dentitan	Luxor	41.0 MPa
	Ivotect U	Luxor	44.8 MPa
		Vita	47.8 MPa
		Biodent	39.3 Mpa

Table 11 Literature overview of three-point bending strength between titanium and ceramics [133]

Name	Metal	Ceramic	Mean
Traub [144]	Ti-cast Ti-cast Ti-cast	VitaTitan Duceratin TiBond	28.0 Mpa 34.0 MPa 36.0 Mpa
Blume [20]	Ti-cast Ti-cast Ti-cast Ti-cast	VitaTitan VitaTitan TiBond Duceratin	35.0 Mpa 29.0 MPa without Pasteopque 41.0 MPa 51.0 MPa
Sommer [132]	Ti-cast Ti-cast	VitaTitan Duceratin	25.0 MPa 32.0 MPa without Bonder
Böning [21]	Ti-cast Ti-machined	Duceratin Duceratin	35.4 MPa 36.0 MPa
Pröbster [113]	Ti-cast Ti-cast Ti-cast	VitaTitan Duceratin TiBond	21.4 MPa 32.0 MPa 34.0 MPa
Arlom [11]	Ti-cast	VitaTitan	33.2 MPa
Nergiz [101]	Ti-cast Ti-cast Ti-cast Ti-machined Ti-machined Ti-machined Ti-ma/sparkero Ti-ma/sparkero Ti-ma/sparkero	VitaTitan TiBond Duceratin VitaTitan TiBond Duceratin VitaTitan TiBond Duceratin	27.8 MPa 31.1 MPa 30.5 MPa 32.6 MPa 35.7 MPa 39.1 MPa 30.2 MPa 33.6 MPa 40.3 MPa
Rinke [123]	Ti-cast Ti-machined	Duceratin Duceratin	32.6 MPa 33.0 MPa
Rammelsberg et al. [114]	Ti-cast Ti-cast Ti-cast Ti-cast Ti-cast Ti-cast	VitaTitan VitaTitan TiBond TiBond Duceratin Duceratin	24.0 MPa without Rocatec 22.0 MPa with Rocatec 22.0 MPa without Rocatec 24.0 MPa with Rocatec 11.0 MPa without Rocatec 32.0 MPa with Rocatec

5.3 Overview and Outlook

The key factors in the adhesion of ceramic to titanium include the control of high temperature titanium oxidation and adjustment for the titanium's low thermal expansion coefficient. [52] A large thermal incompatibility between two materials caused residual tangential compressive stresses in ceramic, which may cause failure. [46]

As the results of this study, the effective thermal contraction difference of TiAl6Nb7 alloy-ceramic system was considerably lower than that of cp titanium-ceramic system. However, the difference of bond strength between cp titanium-ceramic system and TiAl6Nb7 alloy-ceramic system was insignificant.

It seems that the difference in the thermal expansion coefficients between cp titanium and TiAl6Nb7 is small, which might have no influence on the bond strength. But the value of elastic modulus of TiAl6Nb7 alloy (100,000 MPa) is relatively higher than that of cp titanium (80,000 MPa), which might affect on the results of the Tuebinger Gabel test.

Generally, the mismatch of the coefficients of thermal expansion between metal and ceramic significantly affected the flexural bond strength of metal ceramic systems [28], which contradicts the results of this study. Moreover, the results of present study indicated that metal-ceramic bimaterial strips are sensitive indicators of stress development caused by a thermal contraction mismatch. However, the deflection of two branches generated by the thermal induced stresses does not necessarily correlate with the discrepancy of the thermal extension coefficients between metal and ceramic.

Because of different thermal contraction and stress relaxation behaviors of metal and ceramic in bimaterial strips, it is difficult to identify one or two factors that could reliably be used to predict thermal compatibility. [36] When clinical situation was simulated, it would be more difficult to estimate the thermal expansion/contraction coefficient of the whole ceramic as a mixture of opaque and dentin ceramic. Without the exact values of the thermal contraction coefficient and the glass solidification temperature of ceramic, the effective thermal contraction difference could be estimated experimentally by the Tuebinger Gabel test. Therefore, the Tuebinger Gabel test can be a useful method to determine the thermal compatibility of metal-ceramic systems.

In this study, very low value of standard deviation of the results indicates that the Tuebinger Gabel test is reproducible, quantifiable, manageable, and very delicate method. Furthermore, it could be useful in such cases like: test of new developed ceramic and alloy, test of multiple firing, optimisation of ceramic firing cycle, etc.

Although it is difficult to identify simple factors that would clearly define thermal compatibility, the results of this study encouraging and the Tuebinger Gabel test can provide a convenient and inexpensive means to calculate stresses in multi layered Gabel-shaped beams due to differential contraction between adjacent layers, and valuable information toward comprehension of thermal incompatibility in restorations.

5.4 Comparison with clinical study

It is known that thermal coefficient of expansion, thermal conductivity, and the nature and strength of the bond are all factors that influence the ability of the ceramic to resist fracture during clinical use of the restorations. [31] The success of a metal-ceramic restoration is highly dependant upon the state of residual stress that exists under intraoral conditions. In recent years, several clinical follow-up studies with titanium-ceramic restorations have been published. However, the results of these studies are contradictory.

Ida et al. [62] reported the clinical application of titanium for fixed and removable partial dentures. They revealed that the marginal fit of titanium crowns were intermediate between a group of high noble alloy (Au-Pd-Ag) and Ni-Cr alloy crowns. [61]

Short- and medium-term clinical results for titanium ceramic restorations indicate that there are relative higher failure rates, such as 15% after 18 months [119], and 15% with single crowns, and 41% with fixed partial dentures after 30 months [69], compared with the results of conventional metal-ceramic restorations: 2.2% [72], 2.4% [30], and 2.7% [135] for observation periods from 7 to 10 years. Nilson et al. [103] noted two ceramic fractures and marked color and surface changes after 26-30 months with Procera restorations veneered with ceramics, and this change was still more pronounces after 60 to 78 months. [15]

Recently, Bergman et al. [15] reported an intraindividual clinical comparison of two metal-ceramic systems: Procera crown veneered with low-fusing ceramic and gold alloy veneered with a medium-fusing ceramic. They concluded that the metal-ceramic bond strength between titanium and the low-fusing ceramic compared well with that of the precious alloy and the medium-fusing ceramic.

Thomas et al. [68] examined eighty-four cast titanium restorations with 125 ceramic veneers in 32 patients. After a time interval of 30 months, a Kaplan-Meier survival analysis was performed, giving a survival probability of 0.85 for single crowns and 0.59 for fixed partial denture. They thought that discrepancies between the thermal expansion coefficients of titanium and ceramic might cause fractures, as cracks were observed with larger fixed partial dentures during ceramic firing or the day after, and the lower rigidity of titanium compared to conventional alloys for ceramics might be another reason for failures since chipping and cracking mainly occurred with fixed partial dentures.

The results of the present study indicate that titanium ceramic restorations may be clinically tested. However, additional documentations of the long-term clinical data are necessary to prove the effectiveness of titanium ceramic restorations.

6. Conclusions

Titanium-ceramic bonding is an unsolved problem because of relatively low thermal expansion/contraction coefficient of titanium, and excessive and nonadherent titanium oxide scale formation during ceramic firing.

The purpose of this study was to investigate the bond characteristics between ceramic fused to cp titanium and TiAl6Nb7 alloy, using three-point bending test according to ISO 9693 and additionally Tuebinger Gabel test to determine the effective thermal contraction difference.

Tuebinger Gabel test was developed to determine the effective thermal contraction difference in titanium- and TiAl6Nb7 alloy-ceramic systems. It can also be useful in estimating the thermal compatibility between precious or nonprecious dental alloys and veneered ceramics.

1. The results of Tuebinger Gabel test showed that ceramic fused to TiAl6Nb7 alloy had smaller values of the effective thermal contraction difference than that of ceramic fused to cp titanium.

2. Although the discrepancy of the thermal expansion coefficients between cp titanium and ceramic was smaller, TiAl6Nb7 alloy-ceramic system had lower value of the effective thermal contraction difference.

3. The value of elastic modulus might also be a critical factor affecting the thermal compatibility of titanium-ceramic systems.

4. The results of three-point bending test showed that the bond strength values of cp titanium-ceramic and TiAl6Nb7 alloy-ceramic pairs were within the acceptable standard levels.

5. Even though cp titanium-ceramic system had higher value of the effective thermal contraction difference, the results of three-point bending test showed no significant difference in bond strength.

6. The Tuebinger Gabel test used in the present study is delicate and reproducible test that is easy to perform, and applicable to all currently known material combinations, especially the metal-ceramic system in dentistry.

7. Summary

In contemporary dentistry titanium and its alloys are very widely used, and for the superstructure of titanium implant it is necessary to develop conventional prosthodontics with titanium. Because of its attractive properties titanium dental implant is popular in recent days and titanium has been used to fabricate prosthetic restorations using machining, or casting process.

Although single crowns or short span bridges are preferred to be made of ceramic materials without metal substrates, metal-ceramic restorations are generally accepted to match the marginal adaptation of metal frame and esthetic advantage of ceramics. Titanium has exceptional reactivity at elevated temperatures, which may cause problems in titanium casting and ceramic application on titanium. Because of high temperature reactivity and relatively low coefficient of thermal expansion/contraction of titanium, low fusing ceramics with adjusted coefficient of thermal expansion/contraction have been developed. Nowadays the use of titanium-ceramic restorations is increased, but there are some problems to be solved. To improve the strength of unalloyed titanium, the TiAl6Nb7 alloy was introduced, and TiAl6Nb7 alloy has higher coefficient of thermal expansion compared with cp titanium.

Due to the different thermal expansion coefficients and elastic properties of titanium/titanium alloy and veneered ceramic, the resulting stress influences the metal–ceramic compatibility. Tuebinger Gabel test was developed to estimate the thermal compatibility between metal and veneered ceramic experimentally. The aim of this study was to calculate the effective thermal contraction difference and to measure the bond strength of cp titanium/TiAl6Nb7 alloy-ceramic composites.

Split samples of cp titanium grade 2 and TiAl6Nb7 alloy with two branches were cast using a pressure unit. After grinding to 1200 SiC and cleaning in ethanol, titanium ceramic that has been developed for the use with titanium was fused on the opposite side of each branch according to the manufacturer. After cooling, the expanded distance between tips of two branches was measured microscopically at the front of the branches. Based on these data the effective thermal contraction difference between cp titanium/TiAl6Nb7 alloy and ceramic was calculated. The Schwickerath crack initiation test was performed to measure bond strength according to ISO 9693. Number of each group was ten and results were analyzed using t-test.

The bond strength of ceramic to cp titanium was 41.0 ± 5.9 MPa, which was similar to that of ceramic to TiAl6Nb7 alloy with 41.6 ± 12.6 MPa. However, the effective thermal contraction differences varied considerably: cp TI-Opaque $(1.29 \pm 0.43) \times 10^{-3}$, TiAl6Nb7-Opaque $(0.39 \pm 0.18) \times 10^{-3}$, cp Ti-Opaque&Dentin $(2.37 \pm 0.88) \times 10^{-3}$, TiAl6Nb7-Opaque&Dentin $(0.89 \pm 0.25) \times 10^{-3}$.

In contrast to the results of the three-point bending test, which revealed no statistically significant difference, the calculated effective contraction difference values were susceptible to the material combination and to the processing conditions. Thus, Tuebinger Gabel test to estimate the thermal compatibility gives additional information on the metal-ceramic compatibility and is found to be a simple and reproducible method.

8. Appendix

8.1 Tuebinger Gabel test

8.1.1 Dimensions of specimens

Table 10 Length of ceramic veneered cp titanium branch

Nr.	Gl1[mm]	Gl2[mm]	Gl3[mm]	Gr1[mm]	Gr2[mm]	Gr3[mm]	Mean	S.D.
1	23.24	23.14	23.08	23.32	23.30	23.18	23.21	0.04
2	23.19	23.38	23.12	22.83	23.07	22.93	23.09	0.18
3	23.53	23.62	23.55	23.52	23.77	23.52	23.59	0.01
4	23.68	23.96	23.86	23.14	23.25	23.22	23.52	0.33
5	23.82	23.73	23.46	24.11	24.10	23.88	23.85	0.04
6	23.66	23.84	23.52	23.65	23.60	23.59	23.64	0.05
7	23.68	23.81	23.53	23.80	23.81	23.83	23.74	0.11
8	23.60	23.59	23.56	23.49	23.49	23.48	23.54	0.08
9	23.78	23.78	23.40	23.76	23.72	23.52	23.66	0.18
10	23.45	23.60	23.55	23.54	23.84	23.84	23.64	0.28

Table 11 Length of ceramic veneered TiAl6Nb7 alloy branch

Nr.	Gl1[mm]	Gl2[mm]	Gl3[mm]	Gr1[mm]	Gr2[mm]	Gr3[mm]	Mean	S.D.
1	23.84	23.84	23.75	24.06	23.91	23.81	23.87	0.02
2	23.79	23.74	23.57	23.57	23.75	23.74	23.69	0.04
3	23.92	23.90	23.86	24.10	24.45	24.41	24.11	0.35
4	23.12	23.10	22.99	23.65	23.52	23.53	23.32	0.29
5	24.38	24.38	24.22	24.11	24.07	24.06	24.20	0.23
6	23.76	23.69	23.67	23.98	24.02	23.96	23.85	0.14
7	24.39	24.29	24.10	23.77	23.74	23.33	23.94	0.75
8	23.42	23.42	23.18	23.05	22.83	22.68	23.10	0.52
9	23.08	23.08	22.98	23.90	23.86	23.80	23.45	0.51
10	24.39	24.38	24.29	23.86	23.97	23.92	24.14	0.33

Table 12 Thickness of cp titanium Gabel branch (before ceramic application)

Nr.	Gl1[mm]	Gl2[mm]	Gl3[mm]	Gr1[mm]	Gr2[mm]	Gr3[mm]	Mean	S.D.
1	0.52	0.48	0.42	0.52	0.49	0.41	0.47	0.05
2	0.55	0.52	0.43	0.54	0.54	0.46	0.51	0.05
3	0.53	0.54	0.44	0.56	0.53	0.41	0.50	0.06
4	0.50	0.50	0.42	0.50	0.51	0.45	0.48	0.04
5	0.62	0.58	0.50	0.58	0.58	0.52	0.56	0.04
6	0.40	0.43	0.37	0.44	0.43	0.35	0.40	0.04
7	0.58	0.55	0.54	0.53	0.53	0.55	0.55	0.02
8	0.53	0.52	0.47	0.57	0.58	0.52	0.53	0.04
9	0.57	0.50	0.38	0.51	0.51	0.33	0.47	0.09
10	0.63	0.63	0.59	0.66	0.63	0.50	0.61	0.06

Table 13 Thickness of opaque ceramic veneered cp titanium Gabel branch (after second opaque ceramic firing)

Nr.	Gl1[mm]	Gl2[mm]	Gl3[mm]	Gr1[mm]	Gr2[mm]	Gr3[mm]	Mean	S.D.
1	0.64	0.64	0.56	0.69	0.70	0.64	0.65	0.05
2	0.67	0.69	0.65	0.75	0.72	0.71	0.70	0.04
3	0.65	0.68	0.63	0.69	0.74	0.56	0.66	0.06
4	0.76	0.66	0.73	0.65	0.72	0.66	0.70	0.05
5	0.75	0.78	0.68	0.70	0.77	0.70	0.73	0.04
6	0.56	0.59	0.54	0.56	0.58	0.50	0.56	0.03
7	0.69	0.64	0.69	0.65	0.70	0.73	0.68	0.03
8	0.67	0.65	0.62	0.74	0.71	0.69	0.68	0.04
9	0.62	0.59	0.51	0.60	0.60	0.50	0.57	0.05
10	0.75	0.76	0.68	0.74	0.77	0.69	0.73	0.04

Table 14 Thickness of opaque & dentin ceramic veneered cp titanium Gabel branch (after second dentin firing)

Nr.	Gl1[mm]	Gl2[mm]	Gl3[mm]	Gr1[mm]	Gr2[mm]	Gr3[mm]	Mean	S.D.
1	1.40	1.36	1.24	1.55	1.56	1.54	1.44	0,12
2	1.41	1.37	1.36	1.58	1.57	1.58	1.48	0,12
3	1.53	1.48	1.57	1.59	1.62	1.63	1.57	0,11
4	1.37	1.26	1.28	1.34	1.27	1.27	1.30	0,11
5	1.42	1.46	1.30	1.44	1.33	1.43	1.40	0,11
6	1.34	1.30	1.41	1.31	1.34	1.20	1.32	0,11
7	1.52	1.42	1.50	1.52	1.49	1.53	1.50	0,11
8	1.41	1.37	1.37	1.35	1.31	1.35	1.36	0,11
9	1.26	1.20	1.19	1.24	1.21	1.22	1.22	0,12
10	1.46	1.45	1.43	1.36	1.32	1.31	1.39	0,12

Table 15 Thickness of Tial6Nb7 alloy Gabel branch (before ceramic application)

Nr.	Gl1[mm]	Gl2[mm]	Gl3[mm]	Gr1[mm]	Gr2[mm]	Gr3[mm]	Mean	S.D.
1	0,53	0,53	0,46	0,53	0,53	0,44	0,50	0,05
2	0,52	0,46	0,40	0,52	0,52	0,42	0,47	0,05
3	0,54	0,51	0,38	0,57	0,56	0,38	0,49	0,06
4	0,43	0,44	0,44	0,46	0,50	0,39	0,44	0,05
5	0,52	0,49	0,40	0,47	0,51	0,40	0,47	0,05
6	0,49	0,50	0,41	0,49	0,51	0,43	0,47	0,05
7	0,59	0,56	0,42	0,57	0,52	0,41	0,51	0,06
8	0,49	0,50	0,36	0,51	0,51	0,40	0,46	0,06
9	0,48	0,48	0,35	0,44	0,48	0,46	0,45	0,06
10	0,51	0,53	0,41	0,46	0,46	0,45	0,47	0,06

Table 16 Thickness of opaque ceramic veneered TiAl6Nb7 alloy Gabel branch (after second opaque ceramic firing)

Nr.	Gl1[mm]	Gl2[mm]	Gl3[mm]	Gr1[mm]	Gr2[mm]	Gr3[mm]	Mean	S.D.
1	0,65	0,70	0,64	0,71	0,68	0,59	0,66	0,04
2	0,70	0,68	0,56	0,69	0,69	0,62	0,66	0,06
3	0,74	0,63	0,56	0,74	0,73	0,65	0,68	0,07
4	0,68	0,63	0,58	0,67	0,63	0,54	0,62	0,05
5	0,70	0,70	0,63	0,69	0,74	0,70	0,69	0,04
6	0,72	0,74	0,61	0,74	0,75	0,63	0,70	0,06
7	0,70	0,70	0,62	0,74	0,73	0,62	0,69	0,05
8	0,65	0,71	0,64	0,71	0,69	0,61	0,67	0,04
9	0,65	0,65	0,59	0,59	0,67	0,71	0,64	0,05
10	0,67	0,66	0,61	0,70	0,68	0,66	0,66	0,03

Table 17 Thickness of opaque & dentin ceramic veneered TiAl6Nb7 alloy Gabel branch (after second dentin firing)

Nr.	Gl1[mm]	Gl2[mm]	Gl3[mm]	Gr1[mm]	Gr2[mm]	Gr3[mm]	Mean	S.D.
1	1,41	1,38	1,32	1,35	1,25	1,29	1,33	0,06
2	1,42	1,41	1,43	1,47	1,44	1,30	1,41	0,06
3	1,41	1,41	1,31	1,32	1,39	1,26	1,35	0,06
4	1,30	1,30	1,21	1,37	1,35	1,35	1,31	0,06
5	1,33	1,34	1,29	1,27	1,18	1,15	1,26	0,08
6	1,28	1,20	1,13	1,42	1,36	1,26	1,28	0,11
7	1,36	1,27	1,24	1,32	1,30	1,21	1,28	0,05
8	1,35	1,40	1,18	1,32	1,24	1,17	1,28	0,09
9	1,39	1,27	1,20	1,29	1,28	1,32	1,29	0,06
10	1,35	1,23	1,21	1,34	1,28	1,24	1,28	0,06

8.1.2 Distance between tips of two branches

Table 18 Cp Ti - before ceramic application

Nr.	Gll-Grl	Gll-Grm	Gll-Grr	Glm-Grl	Glm-Grm	Glm-Grr	Glr-Grl	Glr-Grm	Glr-Grr	Mean	S.D.	V
1	0,542	0,542	0,528	0,560	0,554	0,541	0,535	0,541	0,535	0,542	0,010	0,000
2	0,348	0,348	0,367	0,342	0,348	0,360	0,322	0,329	0,348	0,346	0,014	0,000
3	0,470	0,458	0,451	0,470	0,458	0,458	0,477	0,483	0,464	0,465	0,010	0,000
4	0,406	0,419	0,425	0,400	0,413	0,413	0,380	0,400	0,419	0,408	0,014	0,000
5	0,387	0,393	0,393	0,387	0,393	0,374	0,387	0,393	0,374	0,387	0,008	0,000
6	0,309	0,322	0,309	0,316	0,335	0,329	0,335	0,335	0,329	0,324	0,011	0,000
7	0,535	0,516	0,503	0,535	0,516	0,503	0,548	0,522	0,509	0,521	0,016	0,000
8	0,393	0,406	0,393	0,393	0,412	0,406	0,393	0,393	0,393	0,398	0,008	0,000
9	0,084	0,097	0,097	0,090	0,097	0,103	0,090	0,097	0,103	0,095	0,006	0,000
10	0,496	0,490	0,490	0,464	0,471	0,464	0,483	0,458	0,471	0,476	0,014	0,000

Table 19 Cp Ti - after second opaque ceramic firing

Nr.	Gll-Grl	Gll-Grm	Gll-Grr	Glm-Grl	Glm-Grm	Glm-Grr	Glr-Grl	Glr-Grm	Glr-Grr	Mean	S.D.	V
1	-0,789	-0,780	-0,780	-0,789	-0,780	-0,780	-0,810	-0,793	-0,800	-0,789	0,011	1,331
2	-0,410	-0,393	-0,400	-0,410	-0,393	-0,400	-0,413	-0,410	-0,413	-0,405	0,008	0,751
3	-0,683	-0,677	-0,683	-0,683	-0,677	-0,683	-0,690	-0,696	-0,696	-0,685	0,007	1,150
4	-0,683	-0,661	-0,658	-0,683	-0,661	-0,658	-0,683	-0,661	-0,658	-0,667	0,012	1,075
5	-0,213	-0,213	-0,220	-0,213	-0,213	-0,220	-0,213	-0,213	-0,220	-0,215	0,003	0,602
6	-0,935	-0,928	-0,941	-0,915	-0,914	-0,925	-0,915	-0,914	-0,925	-0,924	0,010	1,248
7	0,219	0,219	0,200	0,219	0,219	0,200	0,219	0,219	0,200	0,213	0,009	0,308
8	-0,090	-0,090	-0,097	-0,084	-0,084	-0,097	-0,084	-0,084	-0,097	-0,090	0,006	0,488
9	-0,335	-0,322	-0,322	-0,335	-0,322	-0,322	-0,348	-0,342	-0,342	-0,332	0,010	0,427
10	-0,135	-0,129	-0,135	-0,135	-0,129	-0,135	-0,135	-0,129	-0,135	-0,133	0,003	0,609

Table 20 Cp Ti - after second dentin ceramic firing

Nr.	Gll-Grl	Gll-Grm	Gll-Grr	Glm-Grl	Glm-Grm	Glm-Grr	Glr-Grl	Glr-Grm	Glr-Grr	Mean	S.D.	V
1	-1,541	-1,541	-1,534	-1,547	-1,547	-1,547	-1,547	-1,547	-1,547	-1,544	0,005	2,086
2	-1,025	-1,038	-1,057	-1,025	-1,038	-1,057	-1,019	-1,038	-1,038	-1,037	0,013	1,383
3	-1,322	-1,328	-1,328	-1,334	-1,334	-1,354	-1,334	-1,334	-1,354	-1,336	0,011	1,801
4	-1,438	-1,457	-1,463	-1,457	-1,450	-1,473	-1,425	-1,431	-1,438	-1,448	0,016	1,856
5	-0,741	-0,754	-0,767	-0,735	-0,748	-0,764	-0,735	-0,748	-0,764	-0,751	0,012	1,138
6	-1,547	-1,570	-1,570	-1,547	-1,570	-1,570	-1,550	-1,560	-1,547	-1,559	0,011	1,883
7	-0,264	-0,251	-0,245	-0,277	-0,271	-0,258	-0,277	-0,271	-0,258	-0,264	0,011	0,785
8	-0,484	-0,509	-0,522	-0,484	-0,509	-0,522	-0,484	-0,509	-0,522	-0,505	0,017	0,903
9	-0,915	-0,896	-0,928	-0,915	-0,896	-0,928	-0,938	-0,902	-0,928	-0,916	0,015	1,011
10	-0,567	-0,561	-0,554	-0,567	-0,561	-0,554	-0,571	-0,564	-0,564	-0,563	0,006	1,039

Table 21 TiAl6Nb7 – before ceramic application

Nr.	Gll-Grl	Gll-Grm	Gll-Grr	Glm-Grl	Glm-Grm	Glm-Grr	Glr-Grl	Glr-Grm	Glr-Grr	Mean	S.D.	V
1	0,342	0,355	0,374	0,303	0,316	0,329	0,271	0,290	0,297	0,320	0,0332	0,000
2	0,290	0,316	0,297	0,290	0,316	0,297	0,290	0,300	0,300	0,300	0,0102	0,000
3	0,258	0,271	0,271	0,245	0,246	0,264	0,219	0,239	0,239	0,250	0,0173	0,000
4	0,348	0,368	0,361	0,361	0,368	0,374	0,351	0,368	0,374	0,364	0,0093	0,000
5	0,322	0,329	0,329	0,316	0,322	0,322	0,297	0,303	0,297	0,315	0,0129	0,000
6	0,277	0,284	0,277	0,264	0,284	0,251	0,264	0,284	0,251	0,271	0,0136	0,000
7	0,400	0,413	0,400	0,413	0,425	0,400	0,413	0,425	0,406	0,411	0,0099	0,000
8	0,367	0,387	0,380	0,377	0,377	0,380	0,387	0,377	0,374	0,378	0,0062	0,000
9	0,303	0,326	0,303	0,303	0,319	0,303	0,303	0,319	0,303	0,309	0,0094	0,000
10	0,277	0,271	0,264	0,264	0,264	0,251	0,264	0,264	0,251	0,263	0,0083	0,000

Table 22 TiAl6Nb7 - after second opaque ceramic firing

Nr.	Gll-Grl	Gll-Grm	Gll-Grr	Glm-Grl	Glm-Grm	Glm-Grr	Glr-Grl	Glr-Grm	Glr-Grr	Mean	S.D.	V
1	0,064	0,064	0,071	0,064	0,064	0,071	0,064	0,064	0,071	0,066	0,0035	0,254
2	0,168	0,161	0,174	0,168	0,161	0,174	0,155	0,149	0,168	0,164	0,0085	0,136
3	-0,058	-0,052	-0,058	-0,058	-0,052	-0,058	-0,058	-0,052	-0,058	-0,056	0,0030	0,306
4	0,100	0,103	0,100	0,129	0,116	0,122	0,129	0,116	0,122	0,115	0,0116	0,249
5	-0,129	-0,110	-0,110	-0,129	-0,110	-0,110	-0,142	-0,122	-0,142	-0,123	0,0136	0,438
6	-0,052	-0,052	-0,077	-0,039	-0,045	-0,064	-0,032	-0,032	-0,052	-0,049	0,0147	0,320
7	0,342	0,361	0,374	0,342	0,367	0,361	0,322	0,348	0,342	0,351	0,0161	0,060
8	0,187	0,193	0,200	0,200	0,206	0,200	0,200	0,206	0,200	0,199	0,0059	0,179
9	-0,187	-0,180	-0,193	-0,187	-0,180	-0,193	-0,187	-0,180	-0,193	-0,187	0,0056	0,496
10	-0,027	-0,032	-0,033	-0,027	-0,032	-0,033	-0,027	-0,032	-0,033	-0,031	0,0028	0,294

Table 23 TiAl6Nb7 - after second dentin ceramic firing

Nr.	Gll-Grl	Gll-Grm	Gll-Grr	Glm-Grl	Glm-Grm	Glm-Grr	Glr-Grl	Glr-Grm	Glr-Grr	Mean	S.D.	V
1	-0,271	-0,258	-0,251	-0,271	-0,258	-0,251	-0,271	-0,258	-0,251	-0,260	0,0088	0,580
2	-0,161	-0,161	-0,168	-0,142	-0,148	-0,155	-0,155	-0,161	-0,161	-0,157	0,0079	0,457
3	-0,309	-0,290	-0,297	-0,309	-0,290	-0,297	-0,322	-0,303	-0,309	-0,303	0,0105	0,553
4	-0,193	-0,193	-0,174	-0,193	-0,193	-0,174	-0,193	-0,193	-0,174	-0,187	0,0095	0,551
5	-0,413	-0,406	-0,419	-0,413	-0,406	-0,419	-0,419	-0,425	-0,438	-0,418	0,0099	0,733
6	-0,335	-0,335	-0,355	-0,335	-0,335	-0,355	-0,329	-0,335	-0,348	-0,340	0,0097	0,611
7	0,174	0,187	0,174	0,142	0,155	0,148	0,135	0,142	0,135	0,155	0,0191	0,256
8	-0,090	-0,077	-0,077	-0,058	-0,052	-0,052	-0,058	-0,052	-0,052	-0,052	0,0144	0,430
9	-0,541	-0,535	-0,541	-0,541	-0,535	-0,541	-0,541	-0,535	-0,541	-0,539	0,0030	0,848
10	-0,335	-0,335	-0,348	-0,335	-0,335	-0,348	-0,312	-0,348	-0,355	-0,339	0,0127	0,602

8.1.3 Effective thermal contraction difference

Table 24 Cp Ti - opaque ceramic

Nr.	h [mm]	D [mm]	l [mm]	V [mm]	$\Delta\gamma$ [10^{-3}]
1	0.47	0.18	23.21	1.33	1.879
2	0.51	0.19	23.09	0.75	1.178
3	0.50	0.16	23.59	1.15	1.848
4	0.48	0.22	23.52	1.08	1.396
5	0.56	0.17	23.85	0.60	1.09
6	0.40	0.16	23.64	1.25	1.42
7	0.55	0.13	23.74	0.31	0.66
8	0.53	0.15	23.54	0.49	0.90
9	0.47	0.10	23.66	0.43	0.85
10	0.61	0.12	23.64	0.61	1.67
				Mean	1.29
				S.D.	0.43

Table 25 Cp Ti - opaque & dentin ceramic

Nr.	h [mm]	D [mm]	l [mm]	V [mm]	$\Delta\gamma$ [10^{-3}]
1	0.47	0.97	23.21	2.09	3.75
2	0.51	0.97	23.09	1.38	2.57
3	0.50	1.07	23.59	1.80	3.43
4	0.48	0.82	23.52	1.86	2.91
5	0.56	0.84	23.85	1.14	1.87
6	0.40	0.92	23.64	1.88	3.03
7	0.55	0.95	23.74	0.79	1.39
8	0.53	0.83	23.54	0.90	1.48
9	0.47	0.75	23.66	1.01	1.47
10	0.61	0.78	23.64	1.04	1.76
				Mean	2.37
				S.D.	0.88

Table 26 TiAl6Nb7 alloy - opaque ceramic

Nr.	h [mm]	d [mm]	l [mm]	V [mm]	$\Delta\gamma$ [10^{-3}]
1	0.50	0.16	23.87	0.25	0.45
2	0.47	0.19	23.69	0.14	0.20
3	0.49	0.19	24.11	0.31	0.47
4	0.44	0.18	23.32	0.25	0.35
5	0.47	0.22	24.20	0.44	0.57
6	0.47	0.23	23.85	0.32	0.42
7	0.51	0.18	23.94	0.06	0.10
8	0.46	0.21	23.10	0.18	0.26
9	0.45	0.19	23.45	0.50	0.70
10	0.47	0.19	24.14	0.29	0.42
				Mean	0.39
				S.D.	0.18

Table 27 TiAl6Nb7 alloy - opaque & dentin ceramic

Nr.	h [mm]	d [mm]	l [mm]	V [mm]	$\Delta\gamma$ [10^{-3}]
1	0.50	0.83	23.87	0.58	0.96
2	0.47	0.94	23.69	0.46	0.81
3	0.49	0.86	24.11	0.55	0.96
4	0.44	0.87	23.32	0.55	0.87
5	0.47	0.79	24.20	0.73	1.21
6	0.47	0.81	23.85	0.61	0.92
7	0.51	0.77	23.94	0.26	0.40
8	0.46	0.82	23.10	0.43	0.61
9	0.45	0.84	23.45	0.85	1.22
10	0.47	0.81	24.14	0.60	0.92
				Mean	0.89
				S.D.	0.25

8.2 Schwickerath crack initiation test

8.2.1 Dimensions of specimens

Table 28 Thickness of cp titanium plate

Nr.	d1 [mm]	d2 [mm]	d3 [mm]	Mean	S.D.
1	0.45	0.46	0.48	0.46	0.02
2	0.52	0.48	0.45	0.48	0.04
3	0.47	0.50	0.43	0.47	0.04
4	0.45	0.49	0.44	0.46	0.03
5	0.48	0.51	0.48	0.49	0.02
6	0.49	0.54	0.49	0.51	0.03
7	0.46	0.50	0.49	0.48	0.02
8	0.47	0.52	0.45	0.48	0.04
9	0.44	0.46	0.44	0.45	0.01
10	0.47	0.48	0.44	0.46	0.02

Table 29 Thickness of TiAl6Nb7 alloy plate

Nr.	d1 [mm]	d2 [mm]	d3 [mm]	Mean	S.D.
1	0.54	0.50	0.50	0.51	0.02
2	0.52	0.53	0.49	0.51	0.02
3	0.46	0.54	0.50	0.50	0.04
4	0.48	0.53	0.50	0.50	0.03
5	0.53	0.55	0.50	0.53	0.03
6	0.47	0.43	0.45	0.45	0.02
7	0.51	0.55	0.53	0.53	0.02
8	0.52	0.53	0.53	0.53	0.01
9	0.54	0.56	0.53	0.54	0.02
10	0.48	0.55	0.50	0.51	0.04

8.2.2 Tested values of cp titanium/TiAl6Nb7 alloy-ceramic bond strength

Table 30 Three point bending strength of cp titanium-ceramic

Nr.	d[mm]	k	Fmax [N]	t [Mpa]
1	0.46	5.94	5.83	34.63
2	0.48	5.48	7.92	43.40
3	0.47	5.68	6.44	36.58
4	0.46	5.94	6.27	37.24
5	0.49	5.28	7.02	37.07
6	0.51	4.88	8.13	39.67
7	0.48	5.48	7.21	39.51
8	0.48	5.48	7.17	39.29
9	0.45	6.19	8.43	52.18
10	0.46	5.94	8.47	50.31
		Mean	7.29	40.99
		S.D.	0.93	5.91

Table 31 Three point bending strength of TiAl6Nb7 alloy-ceramic

Nr.	d[mm]	k	Fmax [N]	t [Mpa]
1	0.51	4.64	14.50	67.28
2	0.51	4.64	7.84	36.38
3	0.50	4.84	11.69	56.58
4	0.50	4.84	7.72	37.36
5	0.53	4.32	7.51	32.44
6	0.45	5.89	4.81	28.33
7	0.53	4.32	10.19	44.02
8	0.53	4.32	8.86	38.28
9	0.54	4.19	6.68	27.99
10	0.51	4.64	10.10	46.86
		Mean	8.99	41.55
		S.D.	2.75	12.56

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11. Curriculum Vitae

Name:	Lee, Ho-Rim
Nationality:	Rep. Korea
Status:	Married to Tho, Hyun-Jeong, 1 Child: Si-Woo
Gentle:	Male
07.05.1971	Born in Yeosu, Rep Korea Father: Lee, Young Sil Mother: Kim, Young Ja
03.1978-02.1984	Seo-elementary school
03.1984-02.1987	Jonggo-middle school(=Gymnasium)
03.1987-02.1990	Yeosu-high school(=Gymnasium)
03.1991-02.1993	Study of Premedical course of dentistry at Kyunghee-University in Seoul
03.1993-02.1998	Study of Dentistry at Kyunghee-University in Seoul
01.1998	National Examination for Dentists
03.1998	Acceptance of Dentistry License
04.1998-04.2001	Public Health Doctor (Dental) at Okcheon-Health Center in Chungcheongbuk-do, Rep. Korea (Compulsory Military Service)
06.2000-12.2000	Continuing Dental Education Programs in Dental College, Kyunghee-University in the field of "Contemporary Fixed Prosthodontic Course"
Since 09.2001	Scientific staff member at the Department of Medical Materials & Technology, Eberhard-Karls-University, Tuebingen
Since 09.2001	Participant of ‘Qualified Post Graduate Specialist of Prosthetics of the German Society for Prosthetics & Dental materials (PS-GSPDM)’ at the department of Prosthodontics and Center of Implantology, Eberhard-Karls-University, Tuebingen