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The fatigue resistance of commercially pure titanium(grade II), titanium alloy (Ti6Al7Nb) and conventional cobalt-chromium cast clasps

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To my families in Thailand and in Germany

Contents

I Introduction	1
II Review of Literature	
II.1. Titanium	3
II.1.1. History	3
II.1.2. Biological, chemical and physical characteristics	3
II.2. Titanium and removable partial denture	7
II.2.1. Clasp function and its properties	7
II.2.2. Casting technology for titanium in dentistry	9
II.2.3. Surface processing methods	11
II.2.4. Laser welding and removable partial denture cast clasp	15
III.3. Aim of study	17
III. Materials and Methods	
III.1. Materials	18
III.2. Methods	19
III.2.1. Fatigue resistance of non-laser welding clasp	19
III.2.1.1. Abutment and Abutment fabrication	19
III.2.1.2. Clasps and Clasp fabrication	21
III.2.1.3. Testing Conditions	28
III.2.2. Fatigue resistance of laser welding clasp	32
III.2.2.1. Abutment and Abutment fabrication	32
III.2.2.2. Clasps and Clasp fabrication	32
III.2.2.3. Testing Conditions	34
III.2.3. Acid etching (pickling)	34
III.2.4. Statistic method	37
IV. Results	
IV.1. Fatigue resistance	42
IV.1.1. Graphs of retentive force and fatigue resistance	42
IV.1.2. Statistic results of fatigue resistance	51
IV.2. Distortion of clasp	55
IV.3. Acid etching (pickling)	56

V. Discussion	
V.1. Materials and methods	58
V.1.1. Materials	58
V.1.2. Methods	59
V.1.2.1. Fatigue resistance	59
V.1.2.1.1. Fatigue resistance of non-laser welding clasp	59
V.1.2.1.2. Fatigue resistance of laser welding clasp	65
V.1.2.1.3. Acid etching (pickling)	67
V.1.2.2. Statistics	68
V.2. Results	70
V.2.1. Fatigue resistance	70
V.2.2. Distortion of clasp	74
V.2.3. Acid etching (pickling)	74
V.3. Clinical Implications	75
V.4. Future Developments	76
VI. Conclusions	78
VII. Tables	
VII.1. Results	79
VII.1.1. Fatigue resistance	79
VII.1.2. Distortion of clasp	89
VIII. References	90
IX. Summary	102
X. Thanks to	103
XI. Curriculum vitae	104

I. Introduction

Titanium and its alloys are attractive for the dental field because of their price and properties. Since titanium is a rich natural resource, its price is not usually affected by the international economic situation, as it happens for other precious metals. Their excellent mechanical properties, like low weight-to-volume ratio, high strength-to-weight ratio, fatigue resistance, and corrosion resistance¹⁰⁰, are desirable in dentistry. But interest is more sharply focused on their excellent biocompatibility. Moreover, as the technology for dental casting of titanium progressed to solve their serious problems, their applications became popular in dental clinics.

The use of titanium and its alloys is also possible due to their benefits. Although the standard material for removable partial denture framework is still cobalt-chromium alloy. The major difference between titanium and cobalt-chromium alloys lies in their modulus of elasticity. It is known that the modulus of elasticity of titanium is about half that of cobalt-chromium^{74,85,90}, which increases its resiliency and makes it more like gold alloys.⁸⁴ This property would allow for the retentive clasp arm of removable partial denture to construct shorter arm length than it is possible with cobalt-chromium and to be placed in deeper undercut on abutment tooth. This characteristic is useful in clinical situations when the abutment tooth is not a molar tooth or has to be concerned about an aesthetic or periodontal health case. On the other hand, the flexibility of a clasp arm affects the retention and function of a removable partial denture.^{55,86,89} If a material is too flexible, the clasp may not provide adequate retention for the removable partial denture when the framework design is based on principles used for cobalt-chromium alloys. However, unalloyed titanium shows low strength, and Ti6Al4V alloy contains cytotoxic vanadium.⁸ Therefore, Ti6Al7Nb alloy was developed.

This study was conducted to determine whether:

1. There are no differences in the retentive forces of titanium grade II, Ti6Al7Nb and cobalt-chromium alloy cast clasps at 10 years simulated clinical use.
2. There are no differences in the retentive forces of titanium grade II, Ti6Al7Nb and cobalt-chromium alloy laser cast clasps at 1 year simulated clinical use.
3. There are no differences in the retentive forces between non- and laser clasps of each material (titanium grade II, Ti6Al7Nb and cobalt-chromium alloy) at 1 year simulated clinical use.
4. There are no differences in the distance between the ending point of lingual bracing arm and buccal retention arm of the clasp before and after test cycles of 10 years simulated clinical use of each material (titanium grade II, Ti6Al7Nb and cobalt-chromium alloy).
5. Titanium grade II and Ti6Al7Nb alloy cast clasps produced by SymbioCast™ provided sufficient quality detected by alpha case layer and porosity.

In the end it has been demonstrated that Ti6Al7Nb alloy is the material of choice for removable partial denture framework.

II Review of literature

II.1. Titanium

II.1.1. History

Titanium is the ninth most common element in the earth's crust and is recovered from TiO₂-rich deposits of rutile, ilmenite and leucoxene that are found on every continent. Since the discovery of titanium in 1974⁴⁰, and up until Kroll's innovative process development in 1936, there had been no practical methods to recover titanium metal from these ores because of its pronounced affinity for oxygen. Modern ore extraction, beneficiation and chemical processes have since then enabled the large-volume manufacturing of high-grade TiO₂, an important pigment for paints and commercial products, and of titanium metal for the production of the CP ("Commercially Pure") titanium grades, titanium-based alloys and other alloys systems.

II.1.2. Biological, chemical and physical characteristics

Biological properties

The literature about the biological reaction to titanium, in vitro and in vivo, is extensive. For example: in theme of corrosion and bioinertness, Ti interaction with cells and proteins, surface modification and healing in bone.²⁵

For clinical performance in corrosion and bioinertness Titanium is a relatively inert, corrosion resistant metal because of its thin (approximately 4 nm), surface oxide layer.²⁵ For this reason titanium and its alloys were required to be used as biomaterials.¹⁴ Moreover it was found that the main difference between Ti6Al4V and Ti6Al7Nb is the fact that niobium oxide (Nb₂O₅) is chemically much more stable, less soluble and more biocompatible in comparison to vanadium oxide (V₂O₅) (Table II.1.2.1.).

Table II.1.2.1. Selected physico-chemical properties of titanium oxide and of oxides of other metals used as alloying elements in titanium alloys.^{18,34,46,59,67,78,80,82}

Element	Most Stable oxide	Charge at pH7	Solubility at pH7 [mol/L]	Charge of dissolved main species ^a	Typical tissue response
Ti	TiO ₂	-	3•10 ⁻⁶	0	Inertness
Nb	Nb ₂ O ₅	-	~10 ⁻⁵	0	Inertness
V	V ₂ O ₅	-	>1	-	Toxicity
	V ₂ O ₄		~10 ⁻⁴		
Cr	Cr ₂ O ₃	±0	~10 ⁻¹¹	+	Toxicity
Co	Co ₂ O ₃	+	~10 ⁻¹² (CoO)	+	Toxicity

^a Charge of main dissolution species at physiological pH.

Chemical and physical properties

Titanium is an allotropic element, meaning that it can exist in more than one crystallographic form. The hexagonal close-packed crystal structure (hcp), also called the alpha phase, exists at room temperature. A transformation to the body-centered cubic (bcc) structure, or beta phase, takes place when titanium solidifies from a liquid or when solid titanium is heated to temperatures above 1621°F (883°C). These two crystal structures are the basis for naming the three generally accepted classes of titanium alloys: “alpha”, “alpha-beta” and “beta”.^{19,28}

By alloying titanium metal with other elements, either crystal structure can be selectively stabilized at room temperature, thus making it possible to manufacture stable alpha, alpha-beta and beta alloys. Fig. II.1.2.1. illustrates the stabilizing preference of these various alloying additions and how material behavior characteristics are affected.²⁹ Common alloying elements used to stabilize the alpha phase include aluminum, tin and oxygen, while those used to

stabilize the beta phase include niobium, molybdenum, tantalum, chromium, iron and vanadium. Many alloys combine a carefully chosen combination of the two types of elements, and these are classified as “alpha-beta” alloys.

- Unalloyed Titanium and Alpha Titanium Alloys

Unalloyed titanium grades and alloys of titanium with alpha stabilizing elements maintain their hcp crystallographic structures at room temperature and hence are classified as alpha titanium grades. These grades exhibit good elevated temperature creep properties, are weldable, and are used in cryogenic applications. Like all the hcp phase materials, they do not exhibit ductile-brittle transformation. Strengthening effects phase materials do not exhibit ductile-brittle transformation. Strengthening effects in alpha alloys are achieved by solid solutioning of the alloying elements.

- Beta Titanium Alloys

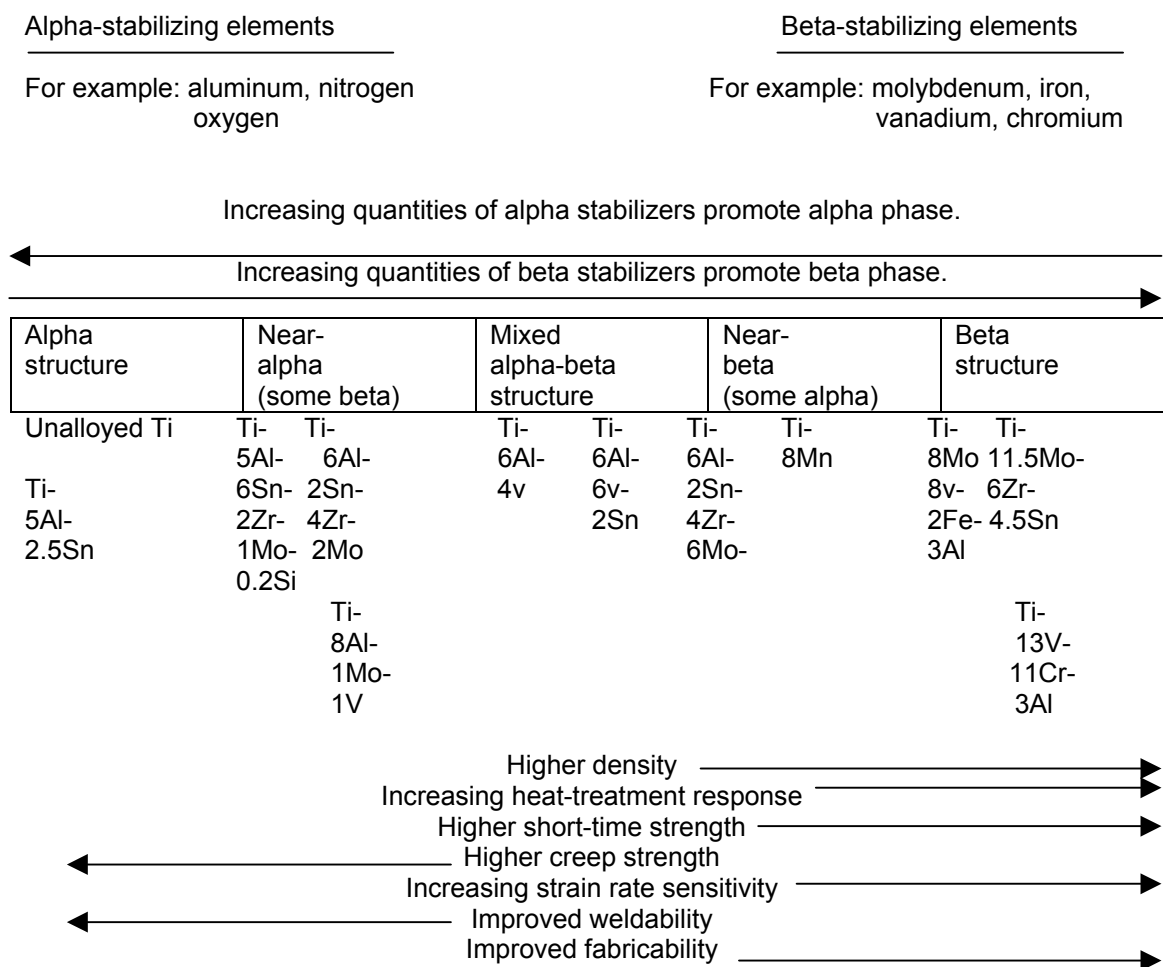
Most beta titanium alloys contain small amounts of alpha stabilizers which permit second phase strengthening to high levels at room to moderate temperatures. The bcc beta phase is ductile, and therefore beta titanium alloys are easily cold formable. Beta alloys are prone to ductile-brittle transformation, and thus are not used for cryogenic applications. The major alloying elements are considered to be very biocompatible, more so than the alpha stabilizing elements like aluminum and tin.

Beta alloys may be strengthened by the solid solutioning effect of the beta stabilizer additions, but large strength increases also result from small volume (typically <5%) second phase precipitation during heat treatment. Because of attractive hot and cold workability properties, much effort has been devoted to creating specialized beta titanium alloys for specific applications. Even though the interest in, and the manufacture of, beta titanium grades is growing, the total worldwide output of titanium mill products includes only a few percent of beta titanium alloys by weight.

- Alpha-Beta Titanium Alloys

Those alloys that combine the metallurgically balanced amounts of both alpha and beta stabilizers are typically used in applications where optimum levels of competing characteristics are desired. This balancing of desired properties of these two phase alpha-beta titanium alloys can be tailored by heat and processing to adjust the microstructure and precipitation states of the beta phase in order to suit the metal temperature(s) for the end use application.

Fig. II.1.2.1. Effects of alloying elements on titanium alloy Structure (Reproduced by permission of ASM International, Metals Park OH, USA).



II.2. Titanium and removable partial denture

Cast titanium and titanium alloys may offer some potential advantages in the fabrication of clasp and metal frameworks for partial removable dentures when compared to cobalt-chromium alloys. For instance, the flexibility of titanium may allow the placement of cast clasps in deeper undercuts than it is advisable for cobalt-chromium alloys.²⁰ It has been shown that the retentive forces of titanium clasps maintained sufficient retention after repeated flexing of the clasp arm during the insertion and removal of the prosthesis.²⁰ Dimensional changes of cast titanium frameworks were considered to be acceptable for partial removable denture framework in a certain range.¹⁶ Titanium is also lighter than cobalt-chromium⁶³ and gold alloys. This might be a potential advantage for the tenure of maxillary partial dentures. However, it has been shown that titanium frameworks 0.7 mm thick had a better castability than 0.35 mm thick frameworks.⁹⁹ Therefore, thicker titanium frameworks may be needed compared to cobalt-chromium ones. The low density of titanium also allows the use of conventional dental X-ray units to detect internal defects (porosity) due to casting procedure.^{20,88,99} Titanium may be an ideal alternative for patients allergic to other metals.^{50,54} On the other hand, the casting technology for titanium needs to be improved still⁶³ and only few laboratories have the appropriate technology for casting titanium frameworks. In addition to this, clinical data on titanium removable dentures are still scarce.^{81,87,99}

II.2.1. Clasp function and its properties

Clasp will be used in conjunction with the words retainer, arm, or assembly whenever possible. The clasp assembly will consist of a retentive arm and a reciprocal or stabilizing clasp arm, plus any minor connectors and occlusal rests from which they originate or with which they are associated. The term bar clasp arm will be used in preference to Roach's name in order to designate this type of extracoronal retainer. It is defined as a clasp arm that originates from the base or framework, transverses soft tissue, and approaches

the tooth undercut area from a gingival direction. In contrast, the term circumferential clasp arm will be used to designate a clasp arm that originates above the height of contour, traverses a portion of the suprabulge portion of the tooth, and approaches the tooth undercut from an occlusal direction. Both types of clasp arms terminate in a retentive undercut lying gingival to the height of contour, and both provide retention by the resistance of metal to deformation rather than frictional resistance of parallel walls.³⁷

Retention and stress in clasp arms are the keys to the long-term success of removable partial dentures (RPDs) without deformation or fracture.^{72,73} Therefore, high strength accompanied by a high flexure fatigue limit is the most desirable property.⁶⁸

For understanding more clearly, we should know the definitions of these technical terms exactly.

1. Retention of the retentive clasp

To determine clasp retention, Applegate⁷ and Lavere⁵⁶ listed five factors which are summarized in the following three categories:

- (1) the fit of the clasp to the abutment,
- (2) the flexibility of the retentive arm, and
- (3) the condition of the abutment.

The conditions of the abutment include the shape of the abutment and the friction coefficient between the abutment and the clasp. The friction coefficient differed in surface condition, surface treatments, abutment materials, and clasp materials.

2. Stress

Stress is the force per unit area in a body which resists an external force.⁶⁸

3. Strength

Strength is the maximal stress required to fracture a structure.⁶⁸

4. Fatigue resistance and fatigue fractures

A word of caution is needed at this point. In fact strength values obtained from any of these "one time" measurements described, may be quite misleading if used for designing a structure that will be subject to repeated or cyclic loading.

For example, in the aircraft industry it has been empirically demonstrated that cyclic loading at stress values well below those determined in ultimate strength measurements can produce abrupt failure of a structure. This type of failure is called fatigue.⁶⁸

Therefore, fatigue behavior is determined by subjecting a material to a cyclic stress of a maximum known value and determining the number of cycles that are required in order to produce failure. A plot of the maximum stress against the cycles to failure enables calculation of a “survive lifetime” and also of an endurance limit – the maximum stress value usable if an infinite fatigue lifetime is required.⁶⁸

In conclusion, fatigue resistance is the ability of a metal to withstand repeated deformation in the elastic region. It can be measured only by cyclical stress tests. Testing should be done in mouth fluid conditions because fatigue failure differs for different corrosive environments.⁶⁸

II.2.2. Casting technology for titanium

When preparing metal frameworks and copings for dental prostheses, the requirements in terms of precision are extremely high, otherwise the prosthesis would not fit or would fit poorly to the prepared abutment teeth or implants with predictable negative consequences. Problems with the use of cast titanium in prosthodontics are related to its high melting point (1668°C) and low specific density.⁶⁰ Titanium is only one fourth as heavy as gold alloys. Thus, it is difficult to force melted titanium into the mold of centrifugal machines.⁶

Consequently, cast titanium thin pieces are prone to porosity. In addition, titanium is highly reactive with oxygen, nitrogen, investment materials (silica) and the ceramic crucibles used during melting.^{62,96} The equipment, materials, and methods for dental casting of titanium presently available appear to control these factors to a large extent. Nevertheless the mechanical properties of a dental casting may differ significantly from the parent material.^{32,93}

New casting machines and investment materials have been developed particularly when complicated structures such as frameworks for removable dentures are being manufactured.^{20,63} Temperature control after titanium casting is also crucial. When cooling from a molting state, titanium crystallizes in the alpha phase below 883°C. At temperatures over 883°C it forms the beta phase characterized by brittleness and greater hardness.^{17,45} Therefore, casting techniques for titanium in dental applications are relatively new and not yet as refined and precise as those developed almost 80 years ago for casting gold alloys.

There are currently two techniques used in order to cast titanium: cold, centrifugal casting, and casting under combined pressure and vacuum.¹

Problems of reactivity of molten titanium with oxygen have been solved by melting and casting in a containment with very little oxygen. This is generally obtained by a combination of primary vacuum and injection of a protective gas like argon. Melting is performed either by an electrical arc, or by an induction system. The crucible is generally made of a solid block of copper, or of ceramics with a very low reactivity with molten titanium. Injection of the molten metal into the mold is obtained either by a combination of gravity, pressure and vacuum or by a centrifugational force. The mold is prepared from special investment with titanium, like for example MgO, Al₂O₃, or CaO, with binders possibly based on phosphate. Beside their reduced reactivity, these investments must also provide enough expansion to compensate the cooling contraction of titanium. Several systems integrating one or the other of these characteristics are now available on the market, each of them allowing its owner to solve with more or less success the main problems associated with forming by casting. Those problems are the following: complete casting of the wax model (castability), internal porosities, and the formation of a superficial reaction layer calls the alpha-case.⁴¹

There are three casting systems. The first one with arc melting in a protective argon atmosphere and casting by pressure and vacuum in a second

chamber below the melting, for example Cyclarc system, by Morita. The second one by arc melting under argon protection, and casting by centrifugation under vacuum, for example Ticast Super R system, by Kobelco/Selec. Finally the third one with an induction melting and centrifugal casting, for example system Titadent, by Eudidant. The makers of those systems provide usually their own investment materials.⁴¹

II.2.3. Surface processing methods

Investment removal⁷¹

After the framework has been cast, all the investment should be removed ultrasonically with airborne particle abrasion or with steam (following the alloy manufacturer's directions).

Oxide removal and metal finishing

During hot working of titanium alloys in air, a continuous oxidation process occurs on the surface of the work-piece. Most of this oxide spalls off as scale, but a small amount may remain on the surface as an oxygen-enriched layer which stabilizes the alpha phase. This layer is known as "the alpha case", a hard and brittle material that must be removed before further cold working and finishing of parts. Grinding or machining are usually sufficient for removing the alpha case, as pickling in a nitric-hydrofluoric acid solution.²⁶

The effects of the surface processing methods can broadly be divided into at least one the following three categories: a) cleaning and/or removal of native surface layers, b) modification of surface structure and topography (smooth, rough or porous surfaces), and c) modification of composition and structure of the oxide layer or controlled formation of a new surface layer.²⁵

Table II.2.4.1. Overview of commonly used surface treatment methods for titanium, and the main effects they have on different surface properties.²⁵

Method	Main effect/ purpose of treatment
Abrading, polishing	Descaling, removal of native layer Smooth surface finish
Abrasive grit blasting, Shot peening	Descaling, removal of native layer Surface roughening Improving adhesion in bonding
Solvent cleaning	Removal of contamination
Pickling/ etching in HF/ HNO ₃ or HCl/H ₂ SO ₄	Descaling, removal of native layer Surface roughening Removal of stresses
Alkaline etching	Hydroxylation Improving apatite formation Surface roughening
Passivation in HNO ₃ or by heat treatment	Oxidation Minimizing ion release
Calcium phosphates and Treatment with other ions	Precipitation of apatite films Modification of surface chemistry
H ₂ O ₂ treatment	Oxidation, hydroxylation Roughening/ etching Cleaning/ sterilization Removal of native layer
Electropolishing	Removal of stresses Creating smooth uniform surfaces
Glow discharge treatment	Surface cleaning Native oxide removal/ etching Sterilization Oxidation, nitriding
Ion implantation	Modification of surface composition Improving wear or corrosion resistance

Mechanical methods all have in common that they involve treatment, shaping or removal of the material surface by means of physical forces applied by the action of another solid material. Mechanical methods for surface treatment can be divided into those involving removal of surface material by cutting or abrasive action, and those where the treated material surface is deformed (and/or partially removed) by particle blasting. Rolling and forging are other important mechanical methods, but they are not treated here since they are not used specifically for surface treatment.²⁵

1. Machining²⁵

Machining (lathing, milling, threading) is commonly used for manufacturing medical devices of titanium. It is not really a surface treatment method, but nevertheless it needs to be mentioned here since it can be used for producing specific surface topographies and surface compositions. The properties of machined surfaces are determined by variables such as work-piece speed, tool pressure and choice of lubricant.

2. Grinding and polishing²⁵

Grinding and mechanical polishing are, in principle, identical methods based on the removal of material by using a hard abrasive medium. Grinding is the preferred term when the medium is coarse and attached to a firm backing, leading to a faster removal and relatively rough surface topographies. Grinding with an abrasive grade 60 leads to R_a values around $1 \mu\text{m}$, and with the coarsest grades surface roughnesses up to values of $5\text{-}6 \mu\text{m}$ can be achieved. If the process is performed unidirectionally, grinding can be used for producing a topography with preferential orientation.

In polishing, the abrasive medium is attached to a soft backing. It involves the use of successively finer abrasive grades, applied in different directions and often in combination with lubrication, to produce smooth surface finishes. Some commonly used polishing media are SiC, alumina and diamond. The finest polishing grades can be used to produce extremely smooth, mirror-like surface finishes on flat specimens, with R_a values of $0.1 \mu\text{m}$ or less. A well known medical example where polishing is a key method, is the bearing

surfaces of artificial joints, where smooth finishes are required in order to minimize the problems of abrasive wear.

Although grinding and polishing are mainly used for producing a desired surface topography (finish), it should be realized that these methods will have other effects on the surface status. The mechanical action will lead to plastic deformation and stresses in the surface region of the material. For soft metals, such as the purest grades of titanium, it is likely that polishing particles will become embedded into the surface. The chemical composition of the surface and the exact nature of the oxide layer can also be influenced, for example, by elevated temperatures or lubricants. All of these effects should be considered if abrasion/polishing is the final surface treatment step before cleaning. Grinding and polishing are, however, generally used as an intermediate step prior to chemical, electrochemical or other methods which will ultimately determine the properties of the finished surface.

3. Blasting²⁵

Grit blasting (also called abrasive blasting) is based on bombardment of the surface by hard particles of high velocity. The particles can be either dry or suspended in a liquid. Upon impact on the surface, the particles lead to local plastic deformation and removal of the material. Blasting is a widely used method for cleaning of gross surface contamination and for surface finishing of manufactured metal components (e.g. removal of oxide scales in welds). A more gentle version of the technique is called shot peening, used primarily for introducing compressive stresses in the material surface. Various types of ceramic particles (alumina, silica, titania) of different sizes can be used for titanium.

In biomedical applications, blasting techniques are commonly used for cleaning and surface roughening of commercial implants which has some general properties of blasted titanium surfaces.

- Controlling the process parameters, of which particle size seems to be the most important factor, can vary the surface topography. For example, alumina particles in the size range of 25-75 μm result in mean surface roughnesses in the range of 0.5-1.5 μm , while roughnesses in the range of 2-6

μm are reported for surfaces blasted with particle sizes of 200-600 μm . In general, abrasive blasting produces surfaces with an irregular topography, often with relatively sharp features. The more gentle shot peening process on the other hand, leads to smoother and more rounded surface topographies.

- Particles are likely to become embedded in the titanium surface during blasting. This is frequently observed with alumina and silica particles. For this reason it is recommended that blasted surfaces are chemically treated in order to remove particle contamination. On the other hand, the blasting particles can be used to intentionally modify the surface chemical composition.

Detailed studies of the composition and thickness of oxide layers on blasted titanium surfaces are lacking. (Reliable oxide thickness measurements are difficult due to the roughness of the surfaces.) Since blasting processes do not involve elevated temperatures and are normally carried out in air or water, it can be expected that the resulting surfaces consist mainly of a thin ($< 10 \text{ nm}$) TiO_2 -like surface oxide, but with traces from the blasting medium.

II.2.4. Laser welding and removable partial denture cast clasp

Basic processing techniques of titanium in dental technology can be divided into casting systems⁷⁹ and alternative procedures including mechanical milling, electrical discharge machining, and CAD/CAM.⁶ Particularly in those alternative methods, suitable fusing techniques are necessary because, as a rule, only single prosthetic units can be produced.

The strong chemical reactivity of titanium and its fast reaction and diffusion rates at high temperatures result in difficulties with casting, brazing, and welding.^{15,52} Oxygen, nitrogen, and hydrogen cause titanium materials to become brittle, and contamination with these elements during the titanium joining process can result in the alteration of the crystal slip behavior.^{21,57,58,61,94,95} This alteration in microstructure has profound effects on the mechanical properties of titanium and its alloys.^{57,58,61}

“Welding is the joining of two or more pieces of metal by applying heat or pressure, or both with or without the addition of filler metal, to produce a

localized union through fusion or recrystallization across the interface.”³ A welded joint is a composite of three regions: the fusion zone, the heat affected zone (HAZ), and the unaffected parent metal. The fusion zone contains material that was melted during welding and usually has a chemical composition similar to that of the base metal. The heat-affected zone consists of material that is not subject to a high enough temperature for fusion but has undergone a thermal cycle that observably alters the microstructure of the parent materials.²

Because of the great affinity of titanium to oxygen^{48,69} and its rapid reaction rate at high temperature,^{94,95} conventional dental soldering methods that use oxygen flame or air torch, are likely to introduce significant concentrations of oxygen into the titanium surface layer and cause embrittlement. Therefore, those methods are undesirable for joining titanium prostheses. Tungsten inert gas (Tig), laser beam welding, and brazing by infrared radiation heating techniques have been used to join metals in protective environment.³⁰ They are potentially suitable for joining titanium dental prostheses, because intensive heat can be generated by these methods in short periods of time. Such conditions can minimize oxygen contamination during joining procedure and preserve original weld metal properties, which makes them the methods of choice for joining high melting-point . However, nowadays we normally use laser welding because it is more practical.

Laser is an acronym for “Light Amplification by Stimulated Emission of Radiation,” and by definition it is a device that transforms various frequencies into an intense, coherent, small, and nearly nondivergent beam of monochromatic radiation within the visible range.³³ The laser beam must be focused to a small spot size to produce a high-power density. This controlled power density melts and with deep penetration welds, vaporizes the metal. When solidification occurs, a fusion zone or weld joint is formed.⁴

Laser beam welding has the following advantages. (1) No direct contact is required with the weld area to permit welding through a glass window, because the heat source is a light beam. (2) It provides precise, well-defined welds. (3) The heat-affected zones are small. (4) The magnetic fields do not cause a detrimental effect on the laser beam.⁹¹

Recent studies on joining titanium with laser beam welding for dental applications concluded that the method is effective; however, the results differed markedly with the intensity of the irradiation⁹⁸ which is also true for other types of alloys.

II.3. Aim of the study

The study was performed because the new titanium casting machine was developed. The mechanical properties of titanium and titanium casting alloys were better, especially the internal porosity and the alpha case layer. In addition to this the biological and physical characteristics of Ti6Al7Nb alloy are interested for making removable partial denture cast clasp. Moreover no one has made this kind of study before.

Therefore, the aim of this study is to inform that titanium grade II and Ti6Al7Nb alloy are materials of choice for removable partial denture framework by measuring the fatigue resistance of cast clasp.

III. Materials and Methods

III.1. Materials

The commercial types of metals used in this study included:

1. Cobalt-chromium alloy (giroBOND[®]NB, Girschbach Dental GmbH, Germany)
2. Unalloyed titanium Grade II (Titan[®], Girschbach Dental GmbH, Germany)
3. Ti6Al7Nb alloy (GiroTAN[®]L, Girschbach Dental GmbH, Germany)

Table III.1.1. Chemical composition and standards for Ti GdII and Ti6Al7Nb.²⁵

Grade Name And Type	UNS Number	ASTM Standard	ISO Standard	Chemical Composition Nominal Weight %
Ti CP-2 (Alpha)	R50400	ASTM F 67	ISO 5832-2	C 0.10 max Fe 0.30 max H 0.015 max N 0.03 max O 0.25 max Ti rem
Ti-6Al-7Nb (Alpha/Beta)	R 56700	ASTM F 1295	ISO 5832-11	Al 6.0 C 0.08 max Fe 0.15 H 0.009 max Nb 7.0 N 0.03 O 0.20 max Ta 0.5 max Ti rem

Fig. III.1.1. The product of CrCo, Ti GdII and Ti6Al7Nb from company.



III.2. Methods

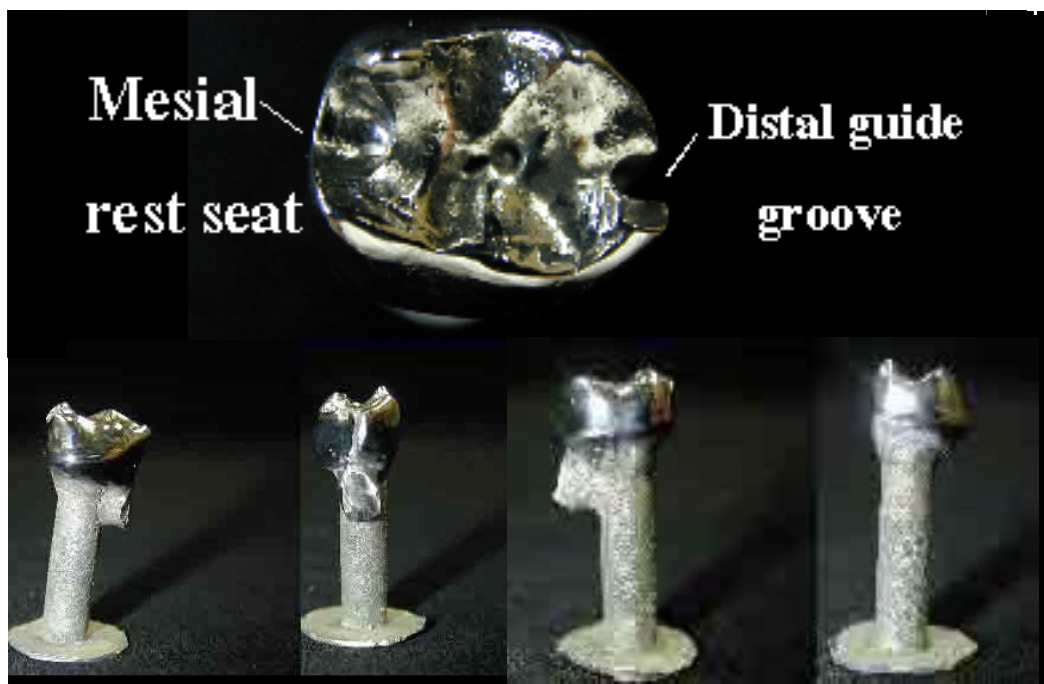
III.2.1. Fatigue resistance of non-laser welding clasp

III.2.1.1. Abutment and Abutment fabrication

Abutment

A model abutment CoCr crown simulates a human mandibular first molar with a mesial guide plane, a mesial occlusal rest seat, a 0.25 mm undercut on the distobuccal cusp and a distal guide groove which is paralleled with mesial guide plane.

Fig. III.2.1.1.1. The CoCr abutment crown.



Abutment fabrication

1.) A tooth was prepared for making an abutment wax.

A human mandibular first molar tooth was surveyed by surveyor (Fraesgeraet F1[®], Degussa, Germany) and labeled for correcting its shape and contour due to the McCracken's removable partial prosthodontics textbook.

A 0.25 mm undercut on the distobuccal surface area was created by measuring it with undercut gauge from Fraesgeraet F1[®] (Degussa, Germany). Then the tooth contour was built up with light cure composite resin, shaped with stone bur and polished with polishing bur. A mesial occlusal rest seat was created with diamond bur. A mesial guide plane and distal guide groove were created with carbide bur from cutting machine (Fraesgeraet F1[®], Degussa, Germany). And then the tooth was polished with pumice and rubber cup.

2.) An abutment wax was made and cast.

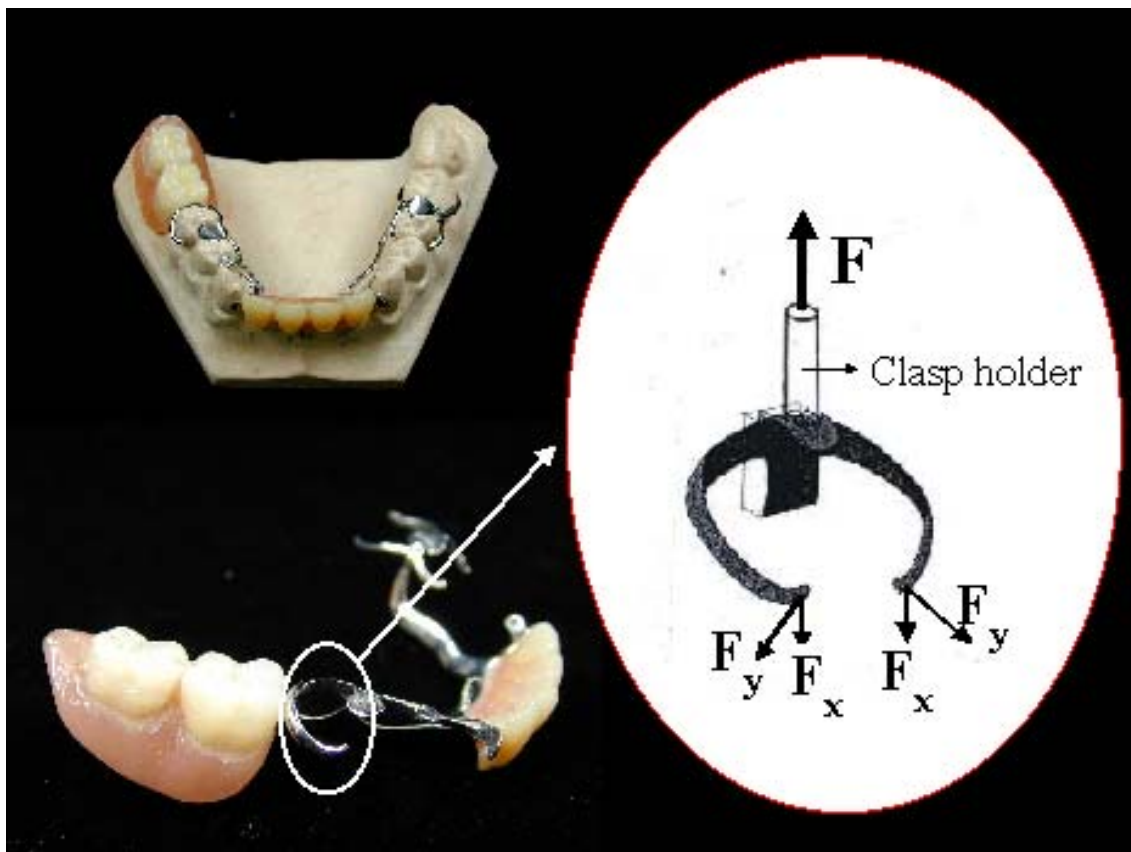
The tooth was duplicated with Polyvinylsiloxane: additional-type (coltene[®], President fast, Swiss). The sculpturing wax (THOWAX[®], YETI Dentalproducte GmbH, Germany) was poured to an impression. An abutment wax was removed from the impression and connected with a 5 mm diameter tube at the cervical part of the wax crown. And 1.5 cm round plate wax was connected to the other ending side of the tube. Then the abutment wax with tube and plate wax was invested with investment material: C 130-Mo[®] (Feguramed GmbH, Germany), baked in oven (Vorwarm-Oven typ 5636, Kavo EWL, Germany) and cast with CrCo by casting machine (BEGO Nautilus MP, Germany). Then an abutment cast was cut and finished with carbide and stone burs and polished with pumice and rubber cup.

III.2.1.2. Clasps and Clasp fabrication

Clasp

Each specimen was cast with a mesial rest, a mesial guide plan, a 10 mm long lingual bracing arm, a 12.5 mm long buccal retention arm at the 0.25 mm undercut and a 3 mm diameter clasp-holder above the mesial rest which is paralleled with the mesial guide plane.

Fig.III.2.1.2.1. The clasp specimen.



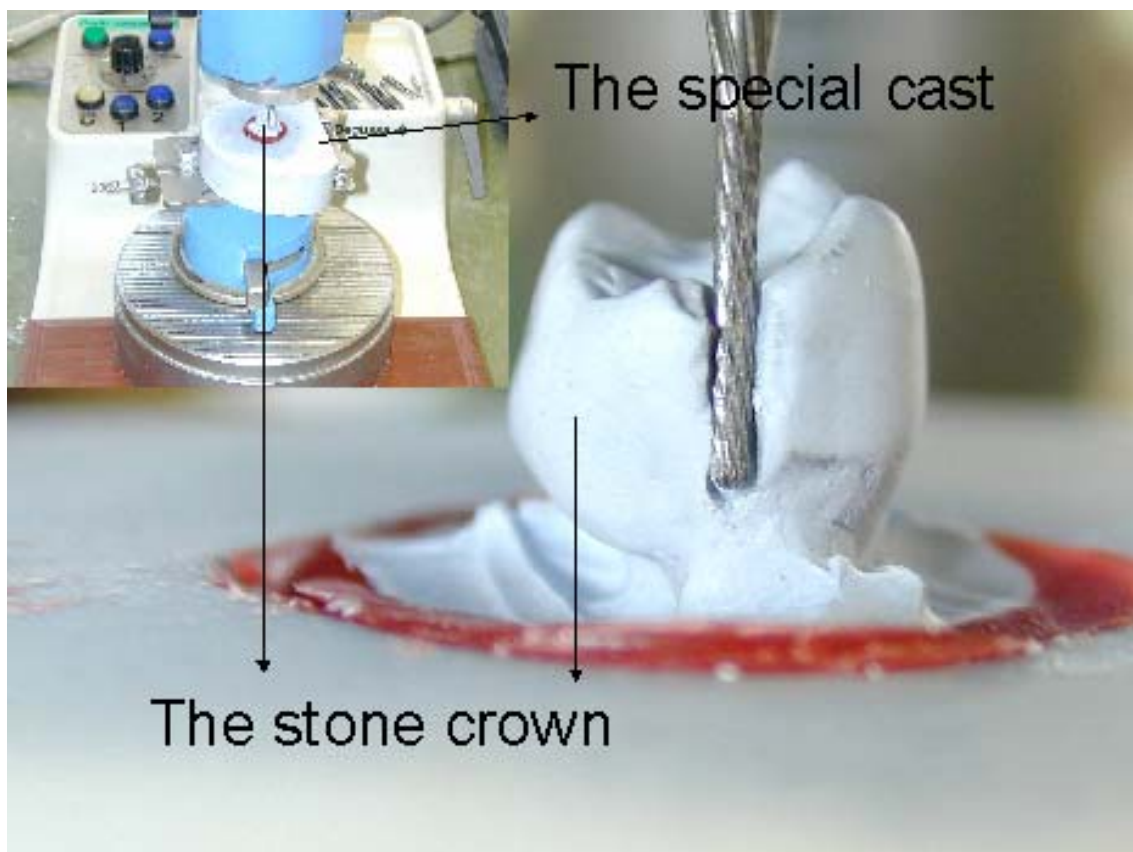
Clasp fabrication

1.) The stone crown that was partially waxed was made.

The crown of metal abutment tooth was duplicated with the additional silicone. An abutment stone was made by means of pouring stone type IV into an impression.

A special stone cast was made with a half-round hole in the center (diameter 12 mm, 20 mm depth and approximately 5° flare surrounding wall). The hole was lined by vaseline. Acrylic resin was poured into the hole for fixing the abutment stone.

Fig. III.2.1.2.2. The special cast and abutment stone tooth fixed by acrylic resin.



The cast was fixed to the surveyor. The position of the cast was adjusted by using the pin rod of the surveyor to transfer the path of the distal guide groove from the abutment stone tooth. A black survey line around the stone tooth was drawn by the surveyor.

A 0.25 mm undercut point was labeled on the distobuccal surface area by undercut gauge from the surveyor. A border line of the retentive clasp, the reciprocal clasp, the proximal plate and the occlusal rest seat was drawn by hand with red color for ideal shape of circumferential clasp due to the McCracken's removable partial prosthodontics textbook .

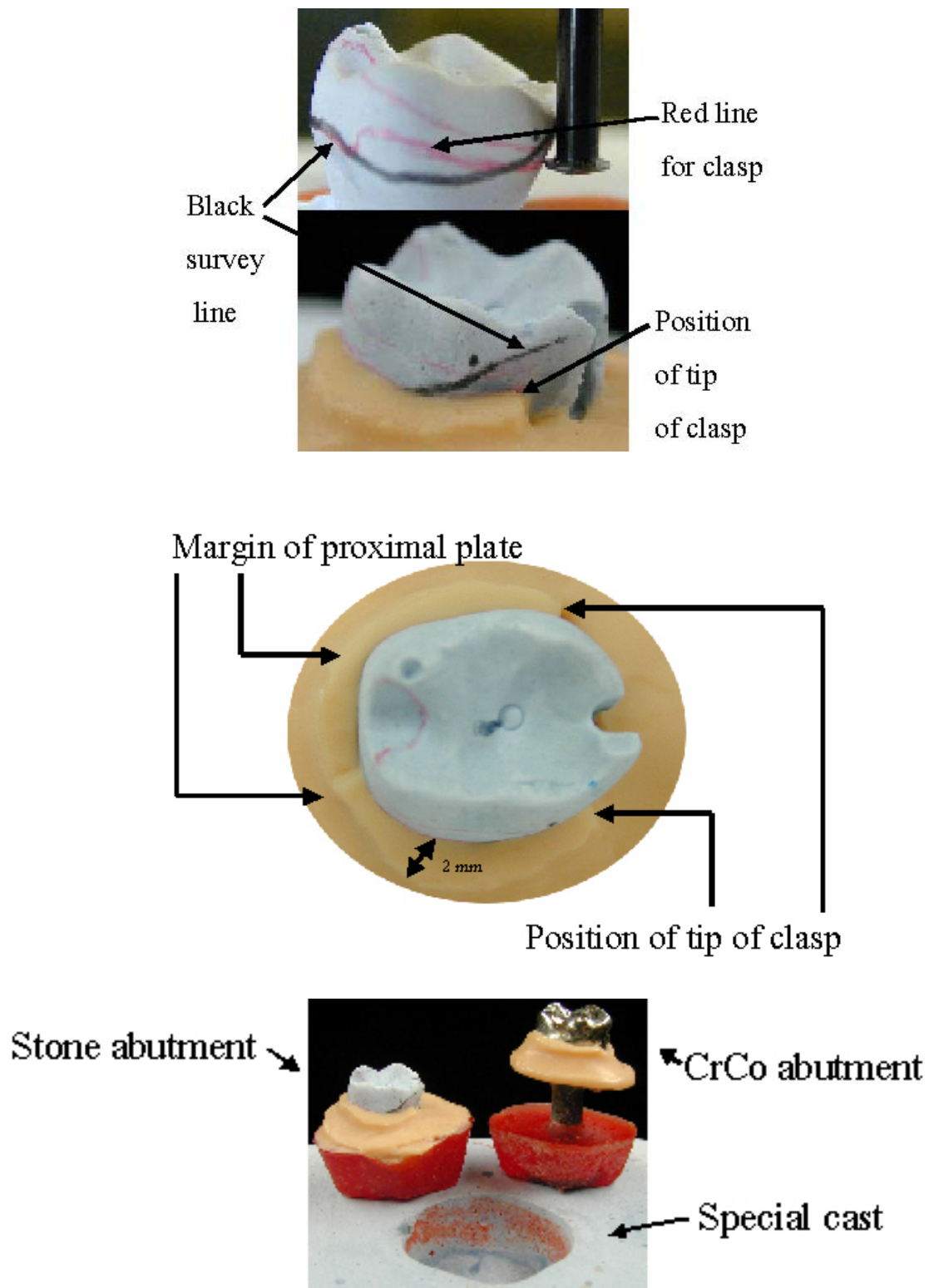
The crown was blocked out with the sculpturing wax (THOWAX[®], YETI Dentalproducte GmbH, Germany) below the red line and waxed up at this line with approximately 2 mm surrounding thick. Then the crown was duplicated with silicone.

The abutment stone tooth fixed by acrylic resin was removed from the special cast. The hole was lined with vaseline. Acrylic resin was poured into the hole for fixing the metal abutment tooth. The impression from the waxed stone crown was fixed to the metal abutment tooth. Then wax was poured into the impression in order to fulfil the space which is blocked out and waxed up wax from the stone crown.

2.) 18 investment teeth were made from the metal abutment tooth with partially waxed up.

The waxed metal crown was duplicated with the additional silicone 18 times. 6 investment teeth were made for each metal by means of pouring investment to the duplicated silicone. Girovest[®] TM (Degussa, Germany) investment was used for Ti Gd II and Ti6Al7Nb. And C 130-Mo[®](Feguramed GmbH, Germany) was used for CoCr.

Fig. III.2.1.2.4. The process of making investment crown.



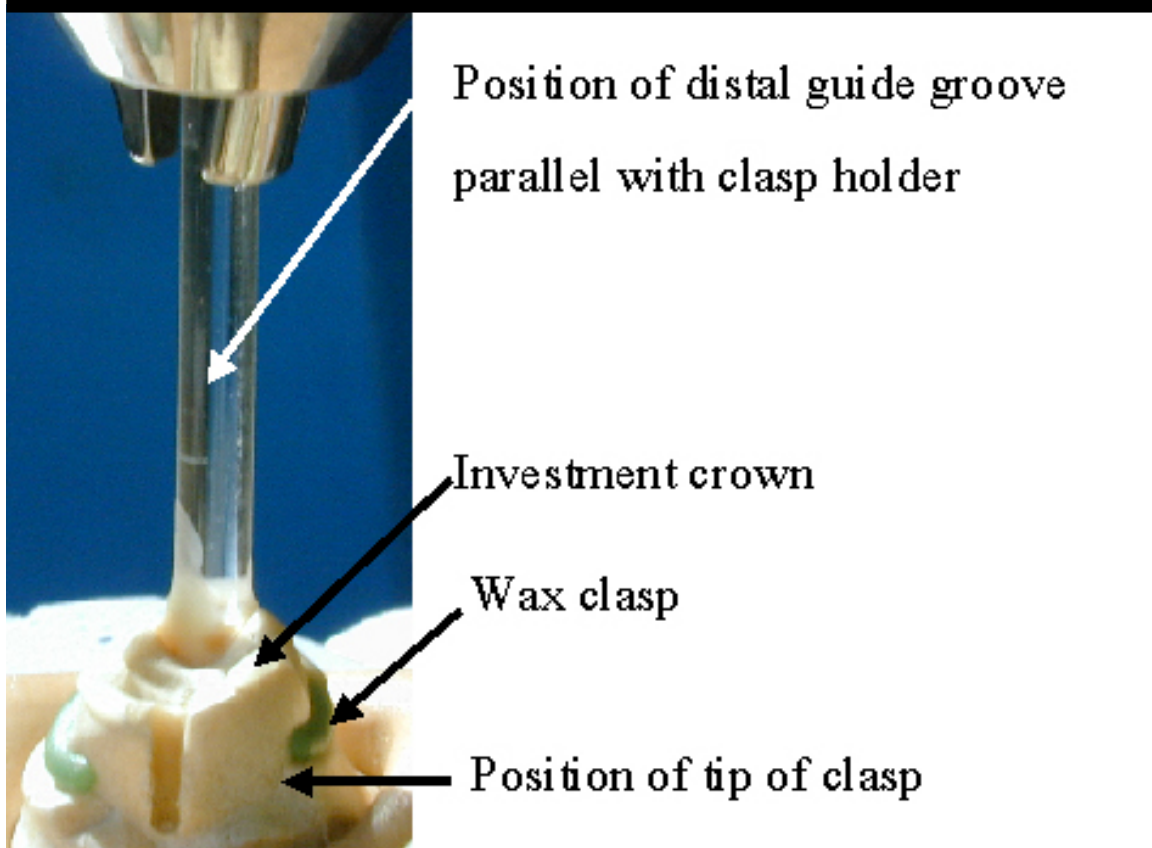
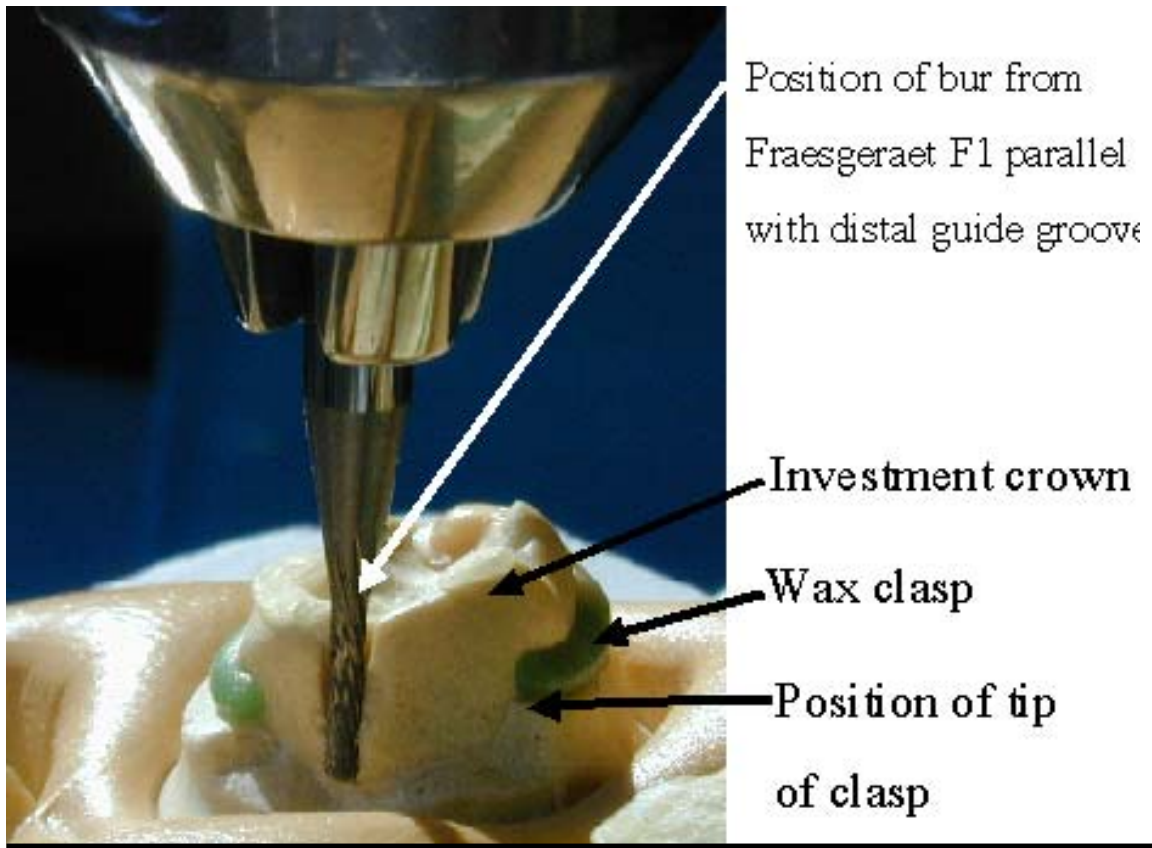
The investment teeth were baked for Ti GdII and Ti6Al7Nb in the oven (Vorwarm-Oven typ 5636, Kavo EWL, Germany). Then they were dipped with beeswax and waited until drying like the manual from Girrbach company.

3.) The wax clasp specimens were made.

The wax pattern (CONSEQUENT Multiklammer[®] for molar teeth, Yenti, Germany) was attached to the investment crown for making the circumferential clasp. The proximal plate and occlusal rest seat were waxed up on the investment crown by hand.

The waxed stone crown was removed from the special cast. And the investment crown with wax clasp, proximal plate and occlusal rest seat was fixed to the cast with the additional silicone. Then the cast was fixed to the surveyor. The position of the cast was adjusted by using the pin rod of the surveyor to transfer the path of the distal guide groove. The 3 mm diameter plastic rod (Kunststoff-Gusskanal-Stifte, Degussa, Germany) was attached to the upper part of the surveyor. The rod was fixed to the investment crown with the wax.

Fig. III.2.1.2.5. The fixing process of the clasp-holder.



4.) The wax patterns were invested and cast.

A wax-pattern sprue was made. Girovest[®] TD (Girrbach, Germany) was poured for investing the pattern of Ti GdII and Ti6Al7Nb clasps, whereas C 130-Mo[®] (Feguramed GmbH, Germany) was poured for investing the pattern of CoCr clasps. Oven (Vorwarm-Oven typ 5636, Kavo EWL, Germany) was used for baking the investments. SymbioCast[™] (Girrbach Dental Systems, Germany) was used for casting Ti GdII and Ti6Al7Nb clasps and BEGO Nautilus MP casting machine (Germany) for CoCr clasps.

Symbiocast is a chamber-casting machine with arc melting in a protective argon atmosphere. Its injection technique of the molten titanium and its alloy into the mold is obtained by a combination of gravity, pressure and vacuum. (www.girrbach.de)

Fig.III.2.1.2.6. SymbioCast[™] (Girrbach Dental Systems, Germany).



5.) All clasps were cut from sprue by carbide bur, and the investment material and oxide layer were removed. The clasps were then finished, polished and checked fit to the abutment by air-abrasion, stone, carbide and rubber bur.

Careful examination of the internal aspect of the framework may reveal small investment particles. Several cycles of ultrasonic cleaning may be required to eliminate all residual investment. If air-abrasion is used for investment removal, it should be used carefully to prevent the removal of metal and investment. The oxide layer that has been formed on the metal surface during casting must be removed with either acid or air-abrasion.⁷¹

Care is needed when grinding the internal surface to avoid dragging the metal over itself, which could entrap grinding debris. Finishing the surface in one direction and using light pressure will help avoid trapping debris between folds of the metal. Carbide burs also may be used safely. After the surface has been smoothed by stone, carbide and rubber bur, it should be air-abraded with a fine grit alumina. This will create a satin surface.⁷¹

III.2.1.3. Testing Conditions

1.) The distance between the ending point of lingual bracing arm and buccal retention arm of each clasp was measured by microscope and optic software.

Each clasp specimen attached to the testing machine was then placed on the corresponding abutment crown that was fixed on the lower part of machine with Cold-curing resin (Palavit® G Co. KG, Germany). The test conditions were maintained at room temperature and wet condition (distilled water).

2.) The maximum and the mean retentive force [mN] for each cycle needed to remove the clasp in 15000 cycles was measured with a testing machine called Beisser Ver: 10.2002 (produced by Mr. G. Wenedig) (Fig. III.2.1.3.1.). This machine was used to measure pressure and withdrawal force. It consists of a pneumatic metal cylinder tube which can be moved vertically by

approximately 20 mm. This vertical movement was measured by inductive distance-sensor (< 0.2 mm). Force was detected by load cell (< 20 gram). A microprocessor controls the specimen from insertion and withdrawal by a pneumatic direction control valve. The force was continuously detected by load cell and saved by microprocessor at the same time. For serial interface, this machine was connected with a personal computer. Labview[®] is a software program which is the controlling program of PC controls the machine and read out the saved data. The data was showed as diagram in PC and saved into another form of data which was used for this research.

3.) The distance between the clasp arms again after 15000 tested cycles was measured by microscope and Image-Pro[®]Plus software and compared with the data from this clasp before tested cycle.

Fig. III.2.1.3.1. A testing machine: Beisser Ver: 10.2002 (produced by Mr. G. Wenedig).



Fig. III.2.1.3.2. The position of the clasp specimen during testing.

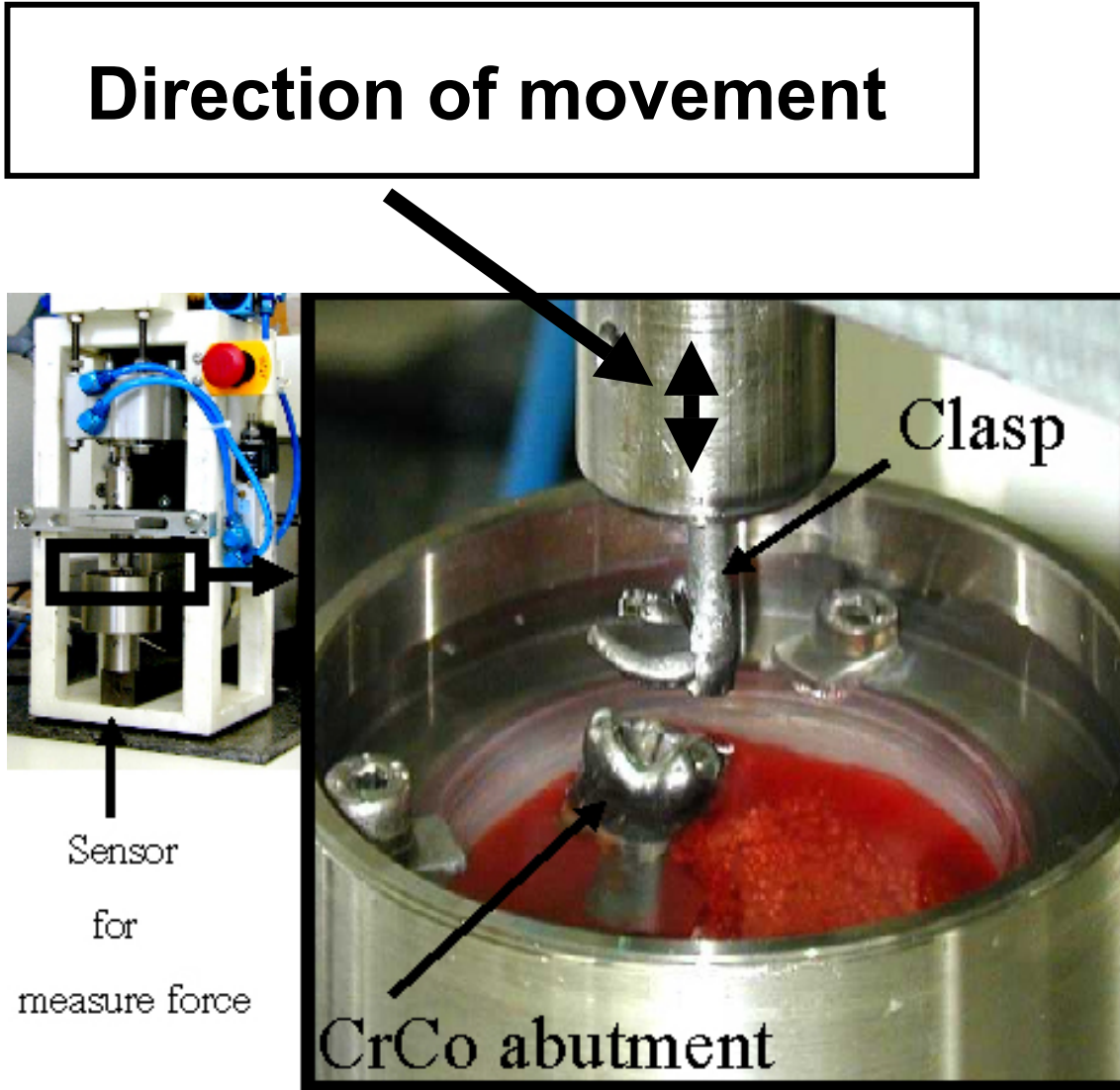
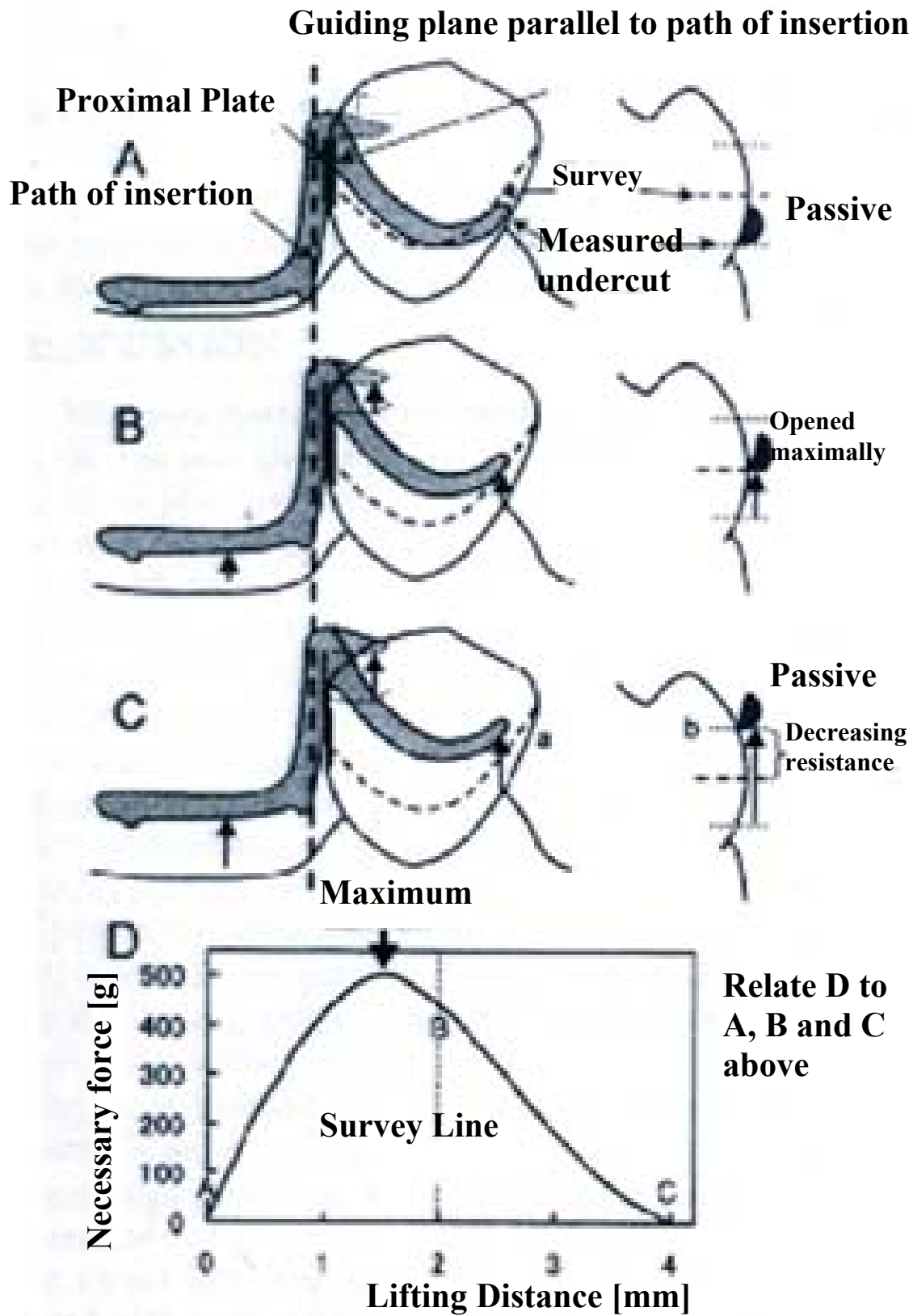


Fig. III.2.1.3.3. The maximum and the mean retentive force [mN] for each cycle needed to remove the clasp was measured with a testing machine.



III.2.2. Fatigue resistance of laser welding clasp

III.2.2.1. Abutment and Abutment fabrication

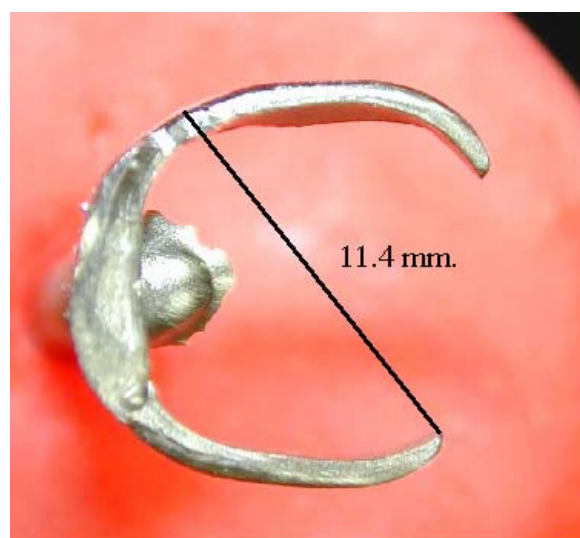
The same process as III.2.1.1. was used.

III.2.2.2. Clasps and Clasp fabrication

1.) The cutting point for laser was found.

Seven clasps for each material were made according to III.2.1.2. Testing cycle was done according to III.2.1.3. until fatigue failure for three clasps (one clasp for each material). The fracture lines of the three clasps were found. The distance of the end of reciprocal clasp to the fracture line of each clasp was measured by microscope and Image-Pro[®]Plus software and the mean value was calculated to be 11.4 mm. The distance between the ending point of lingual bracing arm and buccal retention arm of each clasp was measured by microscope and optic software. The microscope and optic software were used to label the line that will be cut and connected by laser welding due to the mean value.

Fig. III.2.2.2.1. The distance of the end of reciprocal clasp to the cutting line.



2.) The clasp was cut and repaired by laser welding.

Each clasp was fixed with hard stone die which has space from the cutting line of approximately 5 mm. The clasp was cut with 0.1 mm thin fine disc. The outer surface of buccal retention arm was repaired by laser welding from Neolaser L[®] (Girrbach Dental Systems, Germany) with 190 V, 7.0 ms, 1.0 mm diameter and 1.0 Hz for Ti Gd II and Ti6Al7Nb alloy and 200 V, 10 ms, 1.1 mm diameter and 1.0 Hz for CoCr alloy. The clasp was removed and cleaned from stone. The inner surface of buccal retention arm was lasered with the same conditions for each material.

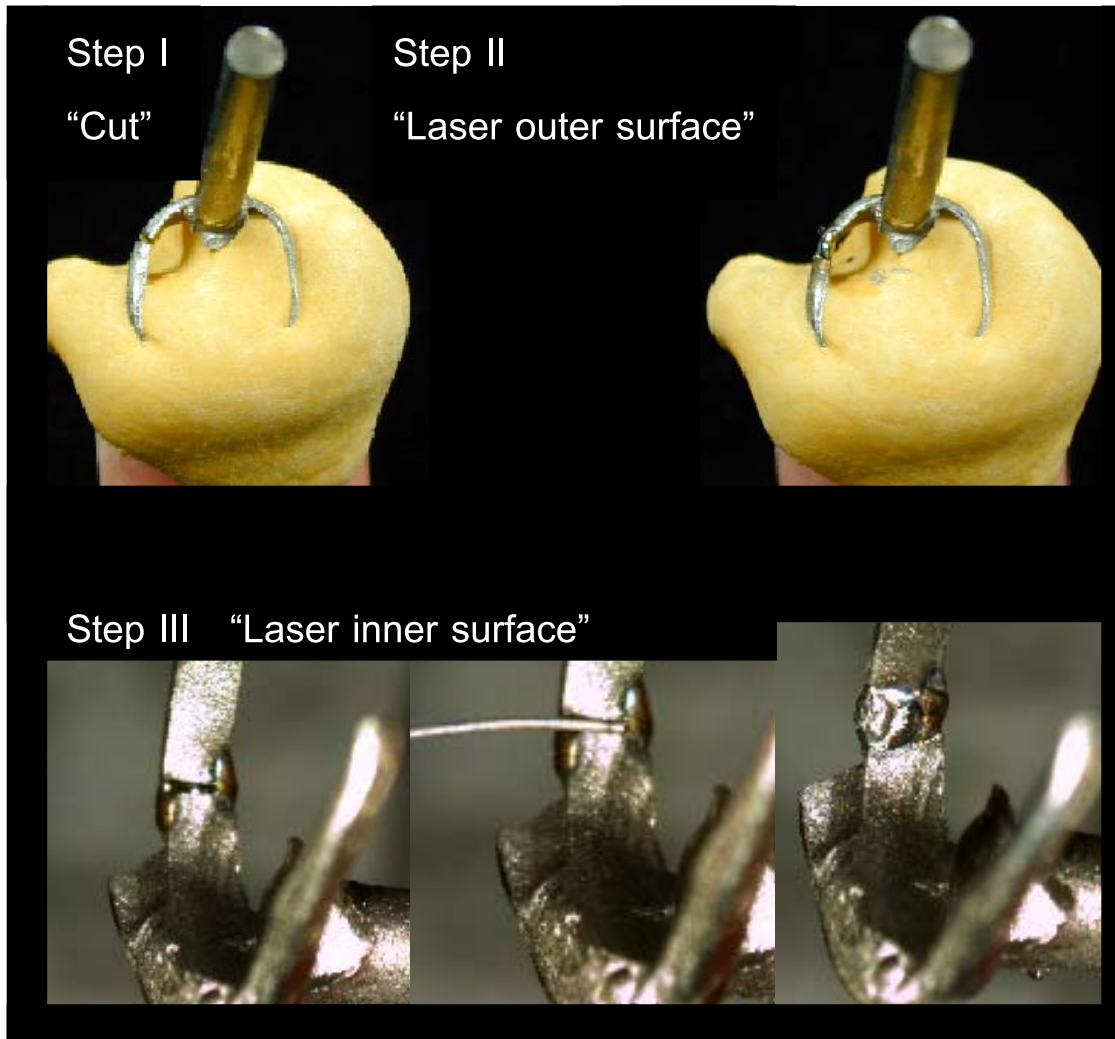
3.) The distance between the arms was measured again after laser welding and compared with the distance before laser welding.

4.) Each clasp was finished and polished according to III.2.1.2.

Fig. III.2.2.2.2. Neolaser L[®] (Girrbach Dental Systems, Germany).



Fig. III.2.2.2.3. The process of repairing the clasp by means of laser welding.



III.2.2.3. Testing Conditions.

The same testing conditions as III.2.1.3. were used but only for 1500 cycles.

III.2.3. Acid etching (pickling).

Pickling is the technical term for etching when used for removing oxide scales in order to obtain clean and uniform surface finishes. The most commonly used and recommended standard solution for acid pickling of titanium and titanium alloys consists of⁹: 10-30 volume-% of nitric acid HNO_3 (69 mass-%) and 1-3 volume-% of hydrofluoric acid HF (60 mass-%) in distilled water. The actual effect is due to the hydrofluoric acid, which readily attacks the TiO_2 and reacts with Ti to form soluble titanium fluorides and hydrogen.

Absorption of hydrogen into the titanium can cause embrittlement of the surface layer. The ratio of nitric acid to hydrofluoric acid should therefore be maintained at 10:1, since this minimizes the formation of free hydrogen.⁹

The extent of pickling/etching depends on the acid concentration, temperature (normally RT), and treatment time. Agitation can also be used for enhancing the process and for preventing gas bubbles from sticking to the surface where they can cause uneven results. The main surface characteristics of acid pickled/etched titanium surfaces can be summarized as follows.

The surface topography of acid etched titanium surfaces is dependent on the previous surface condition and on the extent of material removed. "Mild" treatments preserve the main features of the previous topography. If significant amounts (relative to the pre-existing surface roughness) of material are removed, the topography will be determined mainly by the etching process. In such cases the topography will reflect the microstructure of the bulk material, with clearly visible grains and grain boundaries. The faceted surface reflects the fact that the different crystalline directions are etched at different rates, ultimately leading to a surface which mainly exposes crystal surfaces oriented in low-index directions. For alloyed titanium containing α and β phases, the differences in etching rates for the different phases lead to a surface topography where the β phase protrudes from the α phase, which is etched faster. Surfaces which have been blasted prior to acid etching will in general show a more irregular surface topography than the examples shown above.^{22,76} Surface roughnesses in the range from a few 0.1 μm up to several microns have been reported, and are clearly dependent on pretreatment and process conditions.^{49,65,76,77,83}

1.) Specimens were made and prepared for pickling.

Two clasps were made according to III.2.1.2. (one clasp for Ti GdII and one for Ti6Al7Nb). Each clasp was fixed with acrylic resin. The specimens were grinded until both center of clasp arms appear like Fig. III.2.3.1. by using grinding machine (TG 200, Buehler-Wirtz GmbH, Germany) with sand paper until SiC 4,000.

Fig. III.2.3.1. The clasp in the acrylic resin block.



2.) The specimens were etched.

The solution of 40 ml of nitric acid HNO_3 (1.40 conc.) and 10 ml of hydrofluoric acid HF (40% conc.) in 50 ml distilled water was used for acid pickling of titanium and titanium alloys.³⁵ The specimens were etched at normal room temperature and 10 second of treatment time. Agitation was used for enhancing the process and for preventing gas bubbles from sticking to the surface where they can cause uneven results. The surface of specimens was cleaned by Ultrasonic for 5 min.

3.) The surface characteristics of acid pickled/etched titanium surfaces were studied and measured the α -case layer by Stereo-microscope and Optic Image Plus software.

III.2.4. Statistical process.

Planning

There are three null hypotheses for this study.

1. There are no significant differences in the retentive forces of titanium grade II, Ti6Al7Nb and cobalt-chromium alloy cast clasps at 10 years simulated clinical use.
2. There are no significant differences in the retentive forces of titanium grade II, Ti6Al7Nb and cobalt-chromium alloy laser cast clasps at 1 year simulated clinical use.
3. There are no significant differences in the retentive forces between non-laser and laser clasps of each material (titanium grade II, Ti6Al7Nb and cobalt-chromium alloy) at 1 year simulated clinical use.

Design

The sample size is six specimens for each material. Research designs are experimental, prospective and longitudinal. The number of groups of observations for the first, the second and the third hypothesis are 3, 3 and 2 respectively. The type of data for all hypotheses is continuous data. And all hypotheses are independent groups of object. For the first and the second hypothesis which are independent groups, parametric methods require the observations within each group to have an approximately Normal distribution, and the standard deviations in each group should be similar.

Execution (data collection) and data processing

- 1.) The graph of the results was plotted.

Raw data were collected from every clasp in every cycle (e.g. Fig. III.2.4.1.). The criterion that 1460 test cycles of 1 year simulated clinical use was created. And we assumed that the insertion and the withdrawal cycles of removable partial denture were 4 times per day (3 meals and before sleep).

Therefore, a 1460 (4x365) test cycle was used to simulate 1 year of use in this study.

2.) The means of the range cycles suitable for duration of each graph were calculated (Table III.2.4.1. and III.2.4.2.).

3.) The means of forces in 11 selected range cycles were calculated according to Table III.2.4.1. and III.2.4.2.

4.) The means of forces from 6 clasps in these range cycles were calculated. Using data from the second and the third step created the graph of results (e.g. Fig. III.2.4.2.).

5.) The graphs and the tables were used according to Fig. III.2.4.2. for data presentation (see Results and Tables). Then the data were checked and screened.

Fig. III.2.4.1. A sample of raw data from 1 clasp showed in every cycle.

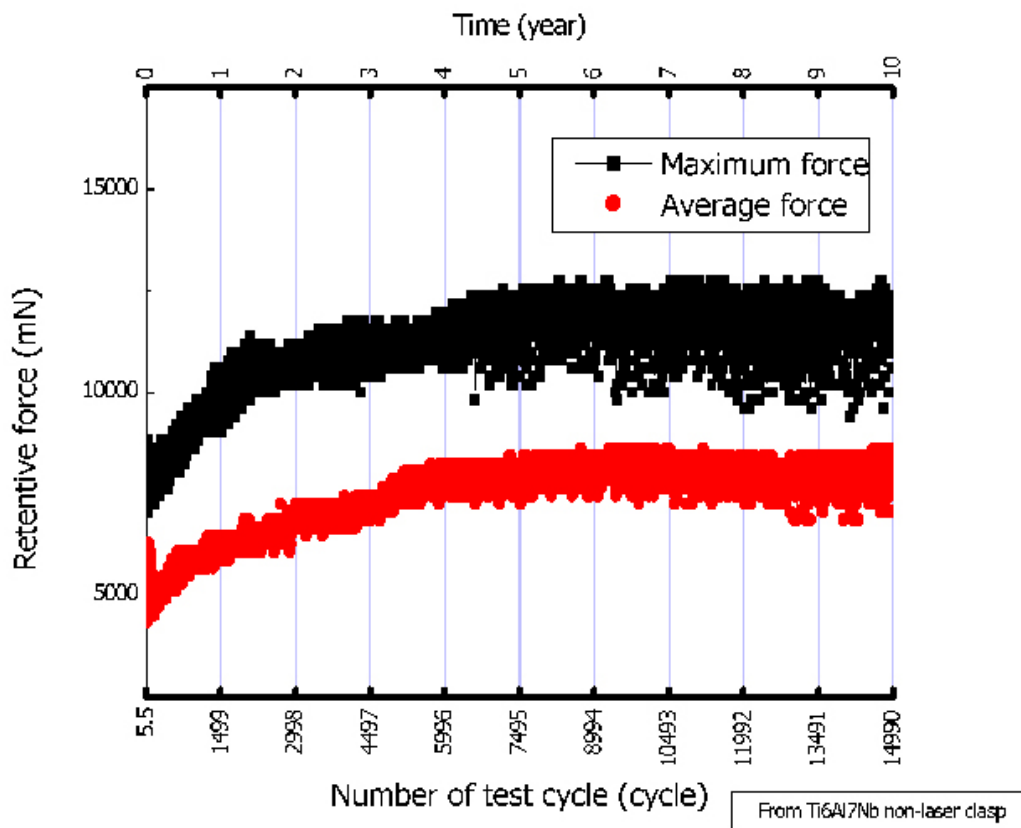


Table III.2.4.1. The range of test cycles of 10 years simulated clinical use and its mean.

Range of test cycles simulated 10 year	Mean of range of test cycles simulated 10 year	Time [year]
1-10	5.5	0
1500-1509	1504.5	1
2999-3008	3003.5	2
4498-4507	4502.5	3
5997-6006	6001.5	4
7496-7505	7500.5	5
8995-9004	8999.5	6
10494-10503	10498.5	7
11993-12002	11997.5	8
13492-13501	13496.5	9
14991-15000	14995.5	10

Table III.2.4.2. The range of test cycles of 1 year simulated clinical use and its mean.

Range of test cycles simulated 1 year	Mean of range of test cycles simulated 1 year	Time [week]
1-10	5.5	0
146-155	150.5	5
291-300	295.5	10
436-445	440.5	16
581-590	585.5	21
726-735	730.5	26
871-880	875.5	31
1016-1025	1020.5	36
1161-1170	1165.5	42
1306-1315	1310.5	47
1451-1460	1455.5	52

Fig. III.2.4.1. A sample of data from 1 clasp calculated in 11 serial test cycles of 10 years simulated clinical use.

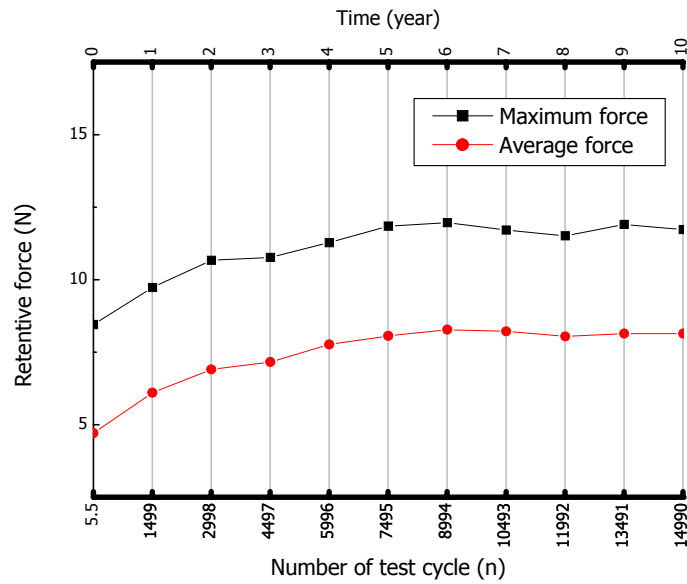
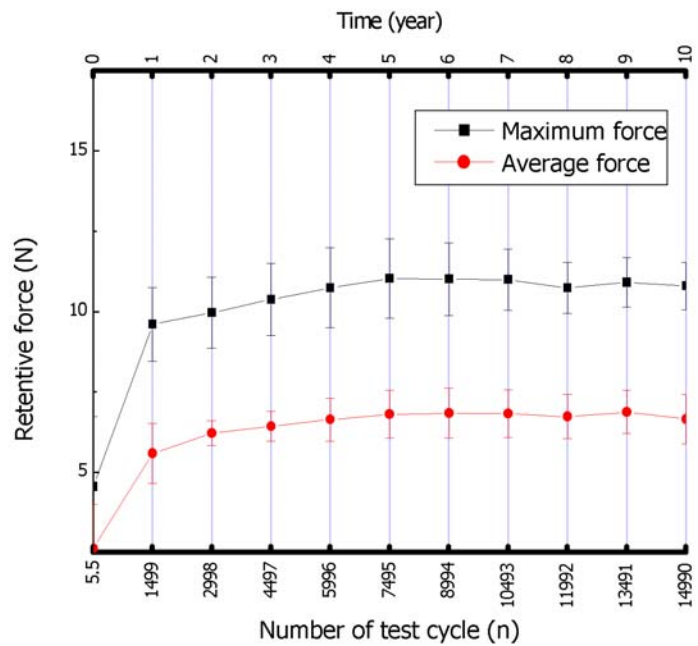


Fig. III.2.4.2. A sample of data from 6 clasps calculated in 11 serial test cycles of 10 years simulated clinical use.



Data analysis

When choosing an appropriate method of analysis there are several aspects of the data, relating to the design of the study, the nature of the data, and the purpose of the analysis that we must consider.³¹

The standard deviation is one of the key quantities in statistical analysis. Its value for describing variability is conditional on the distribution of the data. Although it is always valid to calculate the standard deviation we can infer that about 95% of the observations were in the interval $\text{mean} \pm 2\text{SD}$ only if we know (or assume) that the distribution of the data was reasonably symmetric.³¹

One-way ANOVA ($p=0.05$) was used for the null hypotheses:

- There are no significant differences in the mean of retentive forces of titanium grade II, Ti6Al7Nb and cobalt-chromium alloy cast clasps at 10 years simulated clinical use.
- There are no significant differences in the mean of retentive forces of titanium grade II, Ti6Al7Nb and cobalt-chromium alloy laser cast clasps at 1 year simulated clinical use.

Then additional statistical analysis (Two sample t test, $p=0.05$) was used to analyze rejected hypothesis cases.

Two sample t -test ($p=0.05$) was used for the null hypothesis:

- There are no significant differences in the retentive forces between non-laser and laser clasps of each material (titanium grade II, Ti6Al7Nb and cobalt-chromium alloy) at 1 year simulated clinical use.

Presentation and interpretation

In this study, “S” and “N” were used for the presentation and the interpretation of the results. S shows significant difference between means of them. And N shows no significant difference between means of them.

IV. Results

IV.1. Fatigue resistance

IV.1.1. Graphs of retentive force and fatigue resistance

Fig IV.1.1.1. Titanium Grade II laser clasp (From Table VII.1.1.1.).

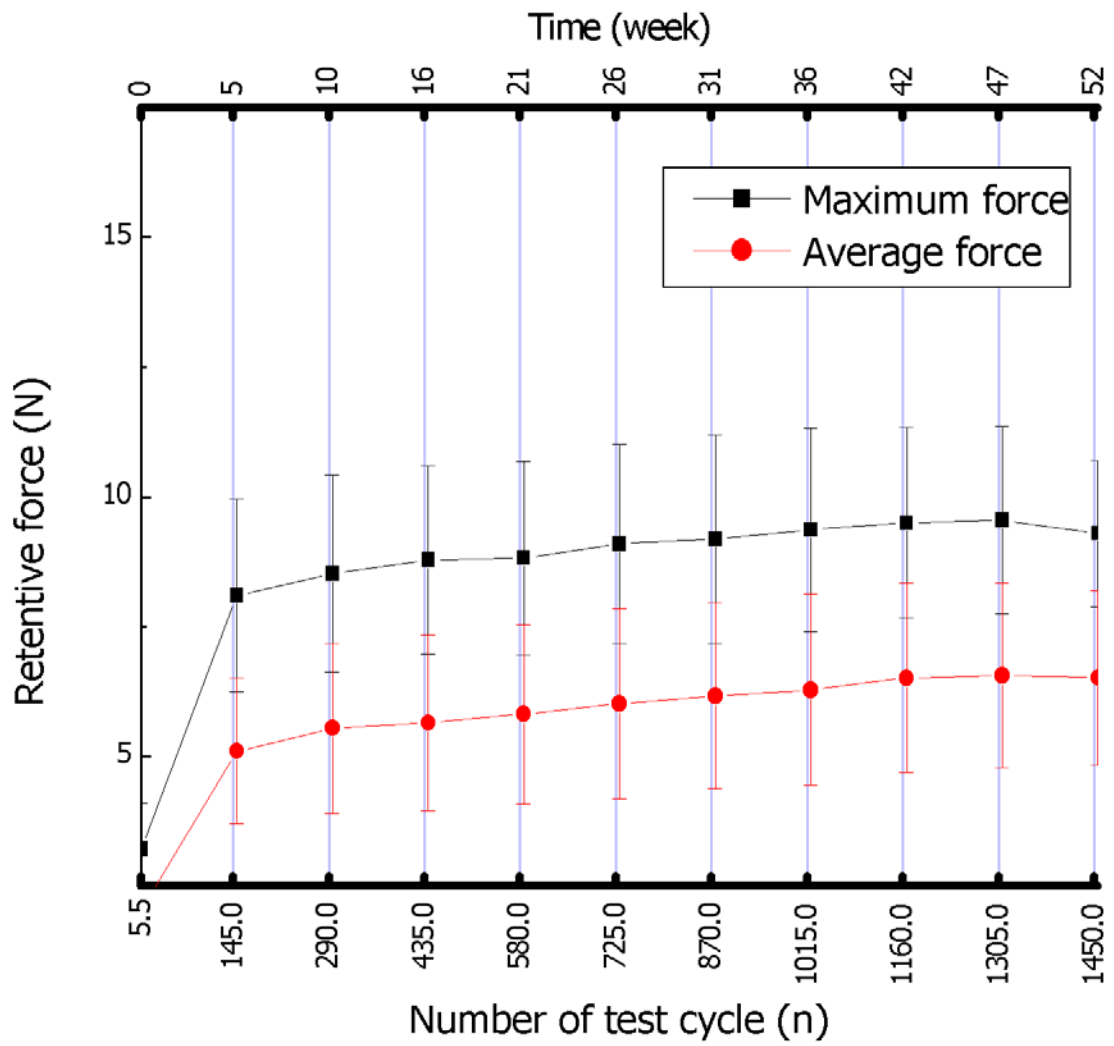


Fig IV.1.1.2. Titanium Grade II non-laser clasp (From Table VII.1.1.2.).

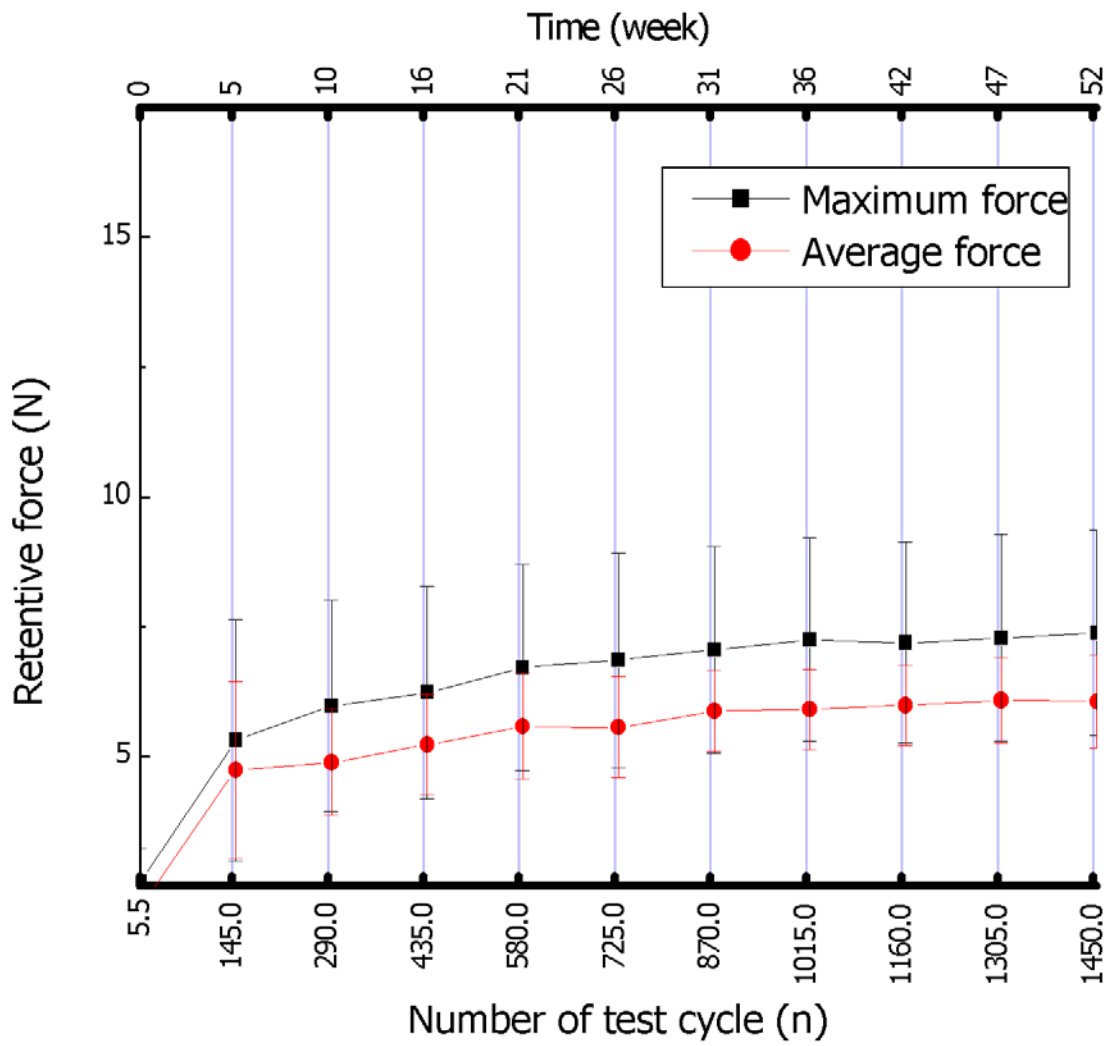


Fig IV.1.1.3. Titanium Grade II non-laser clasp (From Table VII.1.1.3).

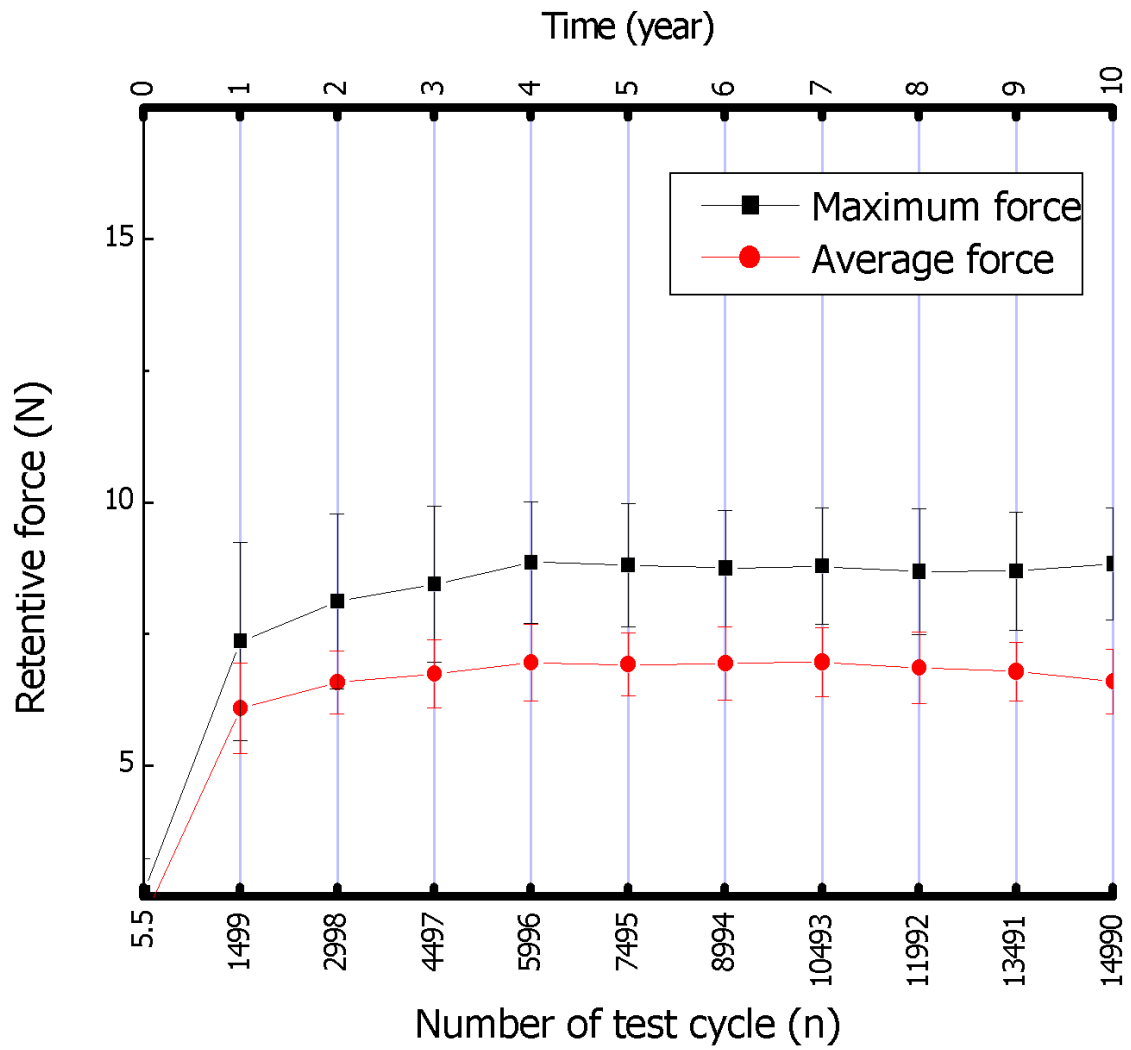


Fig IV.1.1.4. Cr-Co laser clasp (From Table VII.1.1.4.).

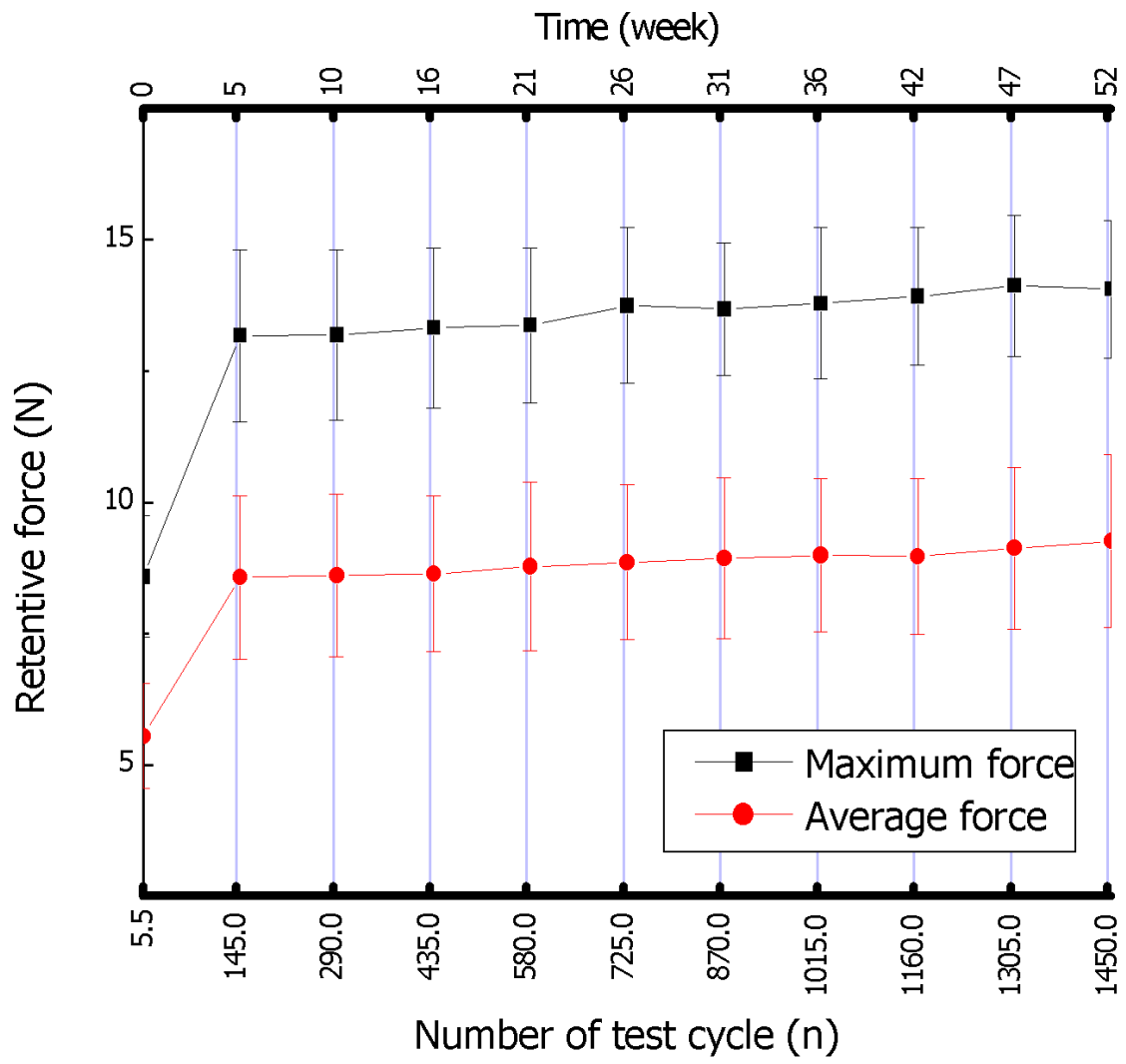


Fig IV.1.1.5. Cr-Co non-laser clasp (From Table VII.1.1.5).

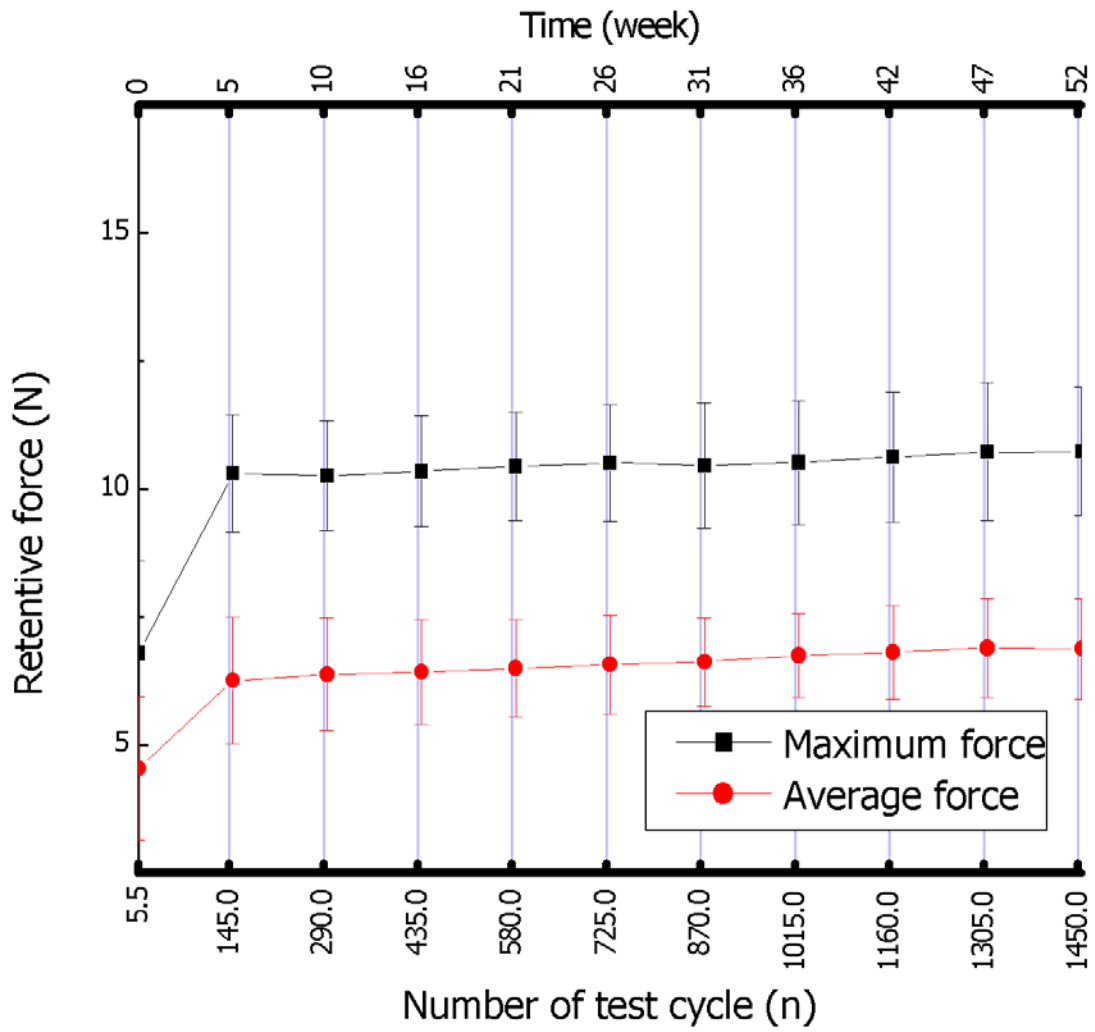


Fig IV.1.1.6. Cr-Co non-laser clasp (From Table VII.1.1.6.).

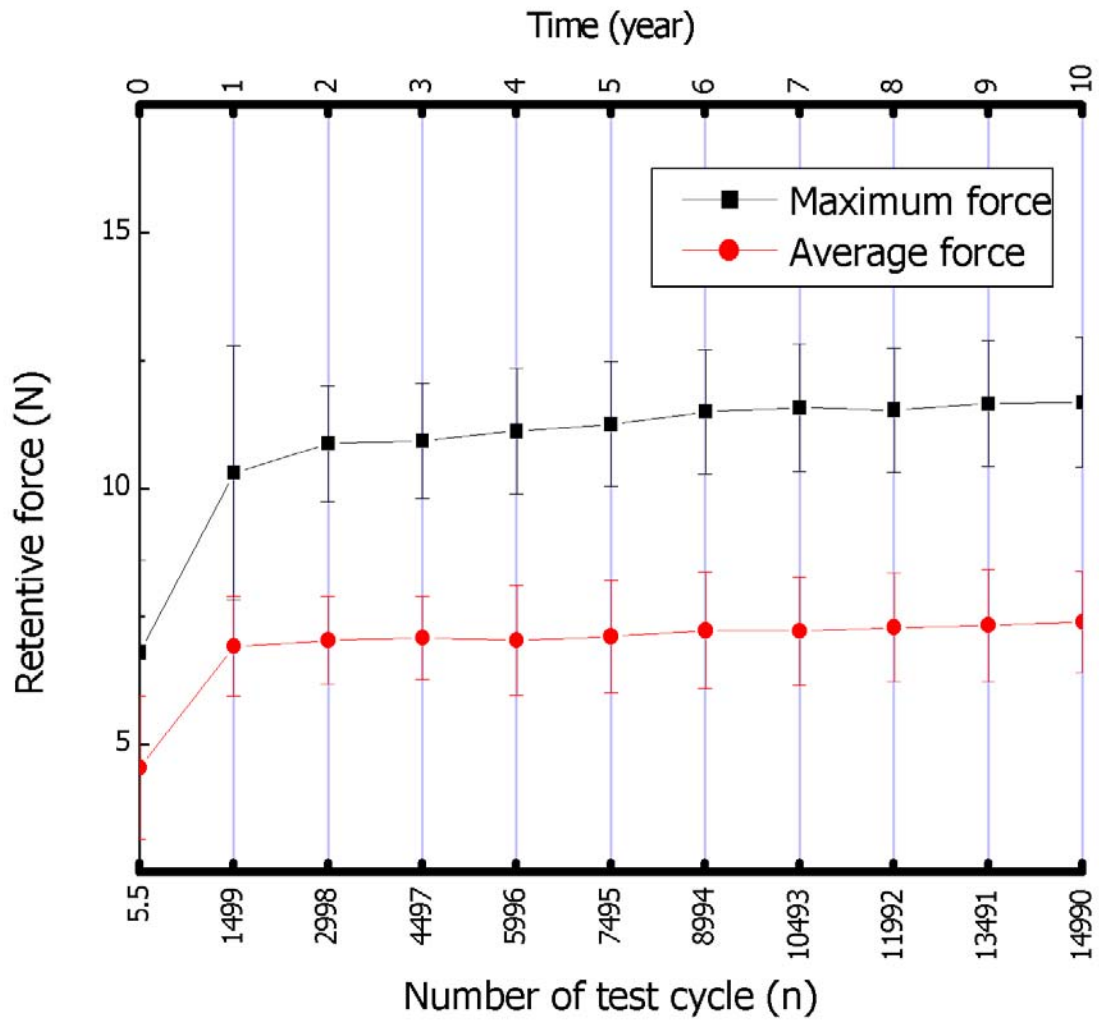


Fig IV.1.1.7. Ti6Al7Nb laser clasp (From Table VII.1.1.7.).

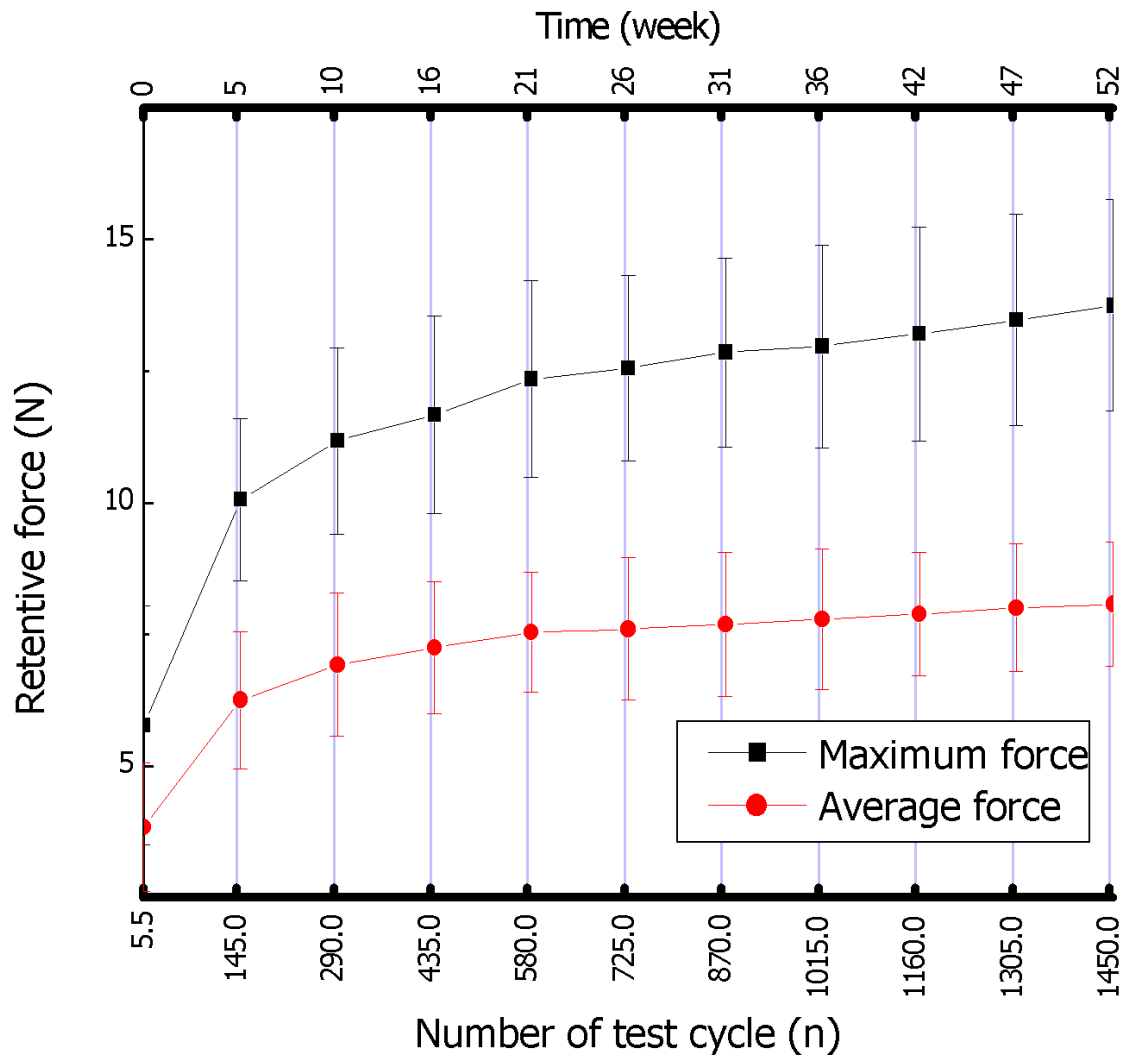


Fig IV.1.1.8. Ti6Al7Nb non-laser clasp (From Table VII.1.1.8.).

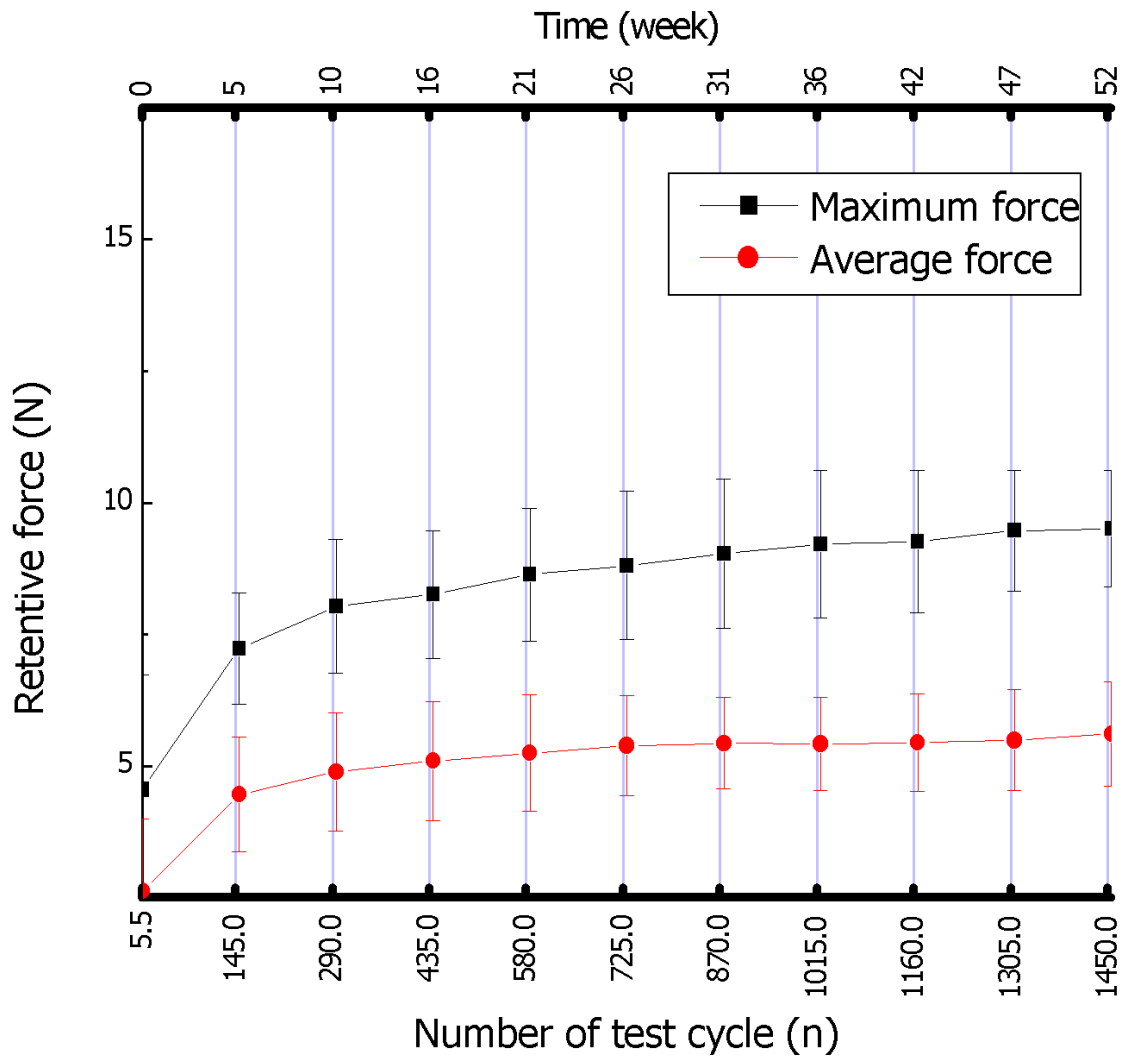
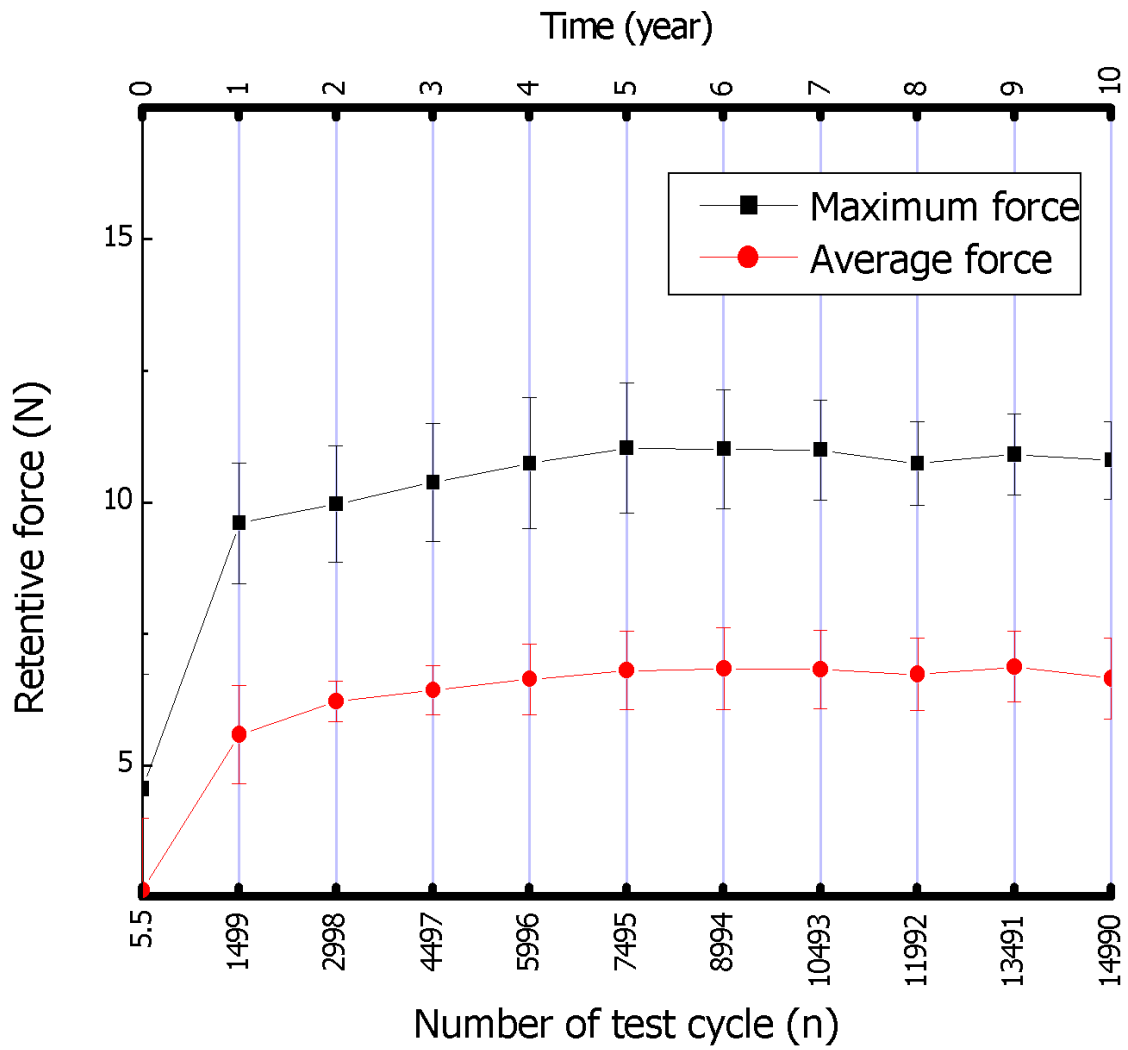


Fig IV.1.1.9. Ti6Al7NbI non-laser clasp (From Table VII.1.1.9.).



IV.1.2. Statistical results of fatigue resistance

1. For the null hypothesis, there are no significant differences between the means of retentive forces of titanium grade II, Ti6Al7Nb and cobalt-chromium alloy cast clasps at 10 years simulated clinical use (Table IV.1.2.1.).

One-way ANOVA for the maximum retentive force of the three materials non-laser cast clasp at 10 years simulated clinical use showed no significant differences between means of three materials ($p=0.05$).

One-way ANOVA for the average retentive force of the three materials non-laser cast clasp at 10 years simulated clinical use showed no significant differences between the means of the three materials ($p=0.05$).

2. For the null hypothesis, there are no significant differences in the retentive forces of titanium grade II, Ti6Al7Nb and cobalt-chromium alloy laser cast clasps at 1 year simulated clinical use (Table IV.1.2.1.).

One-way ANOVA for the maximum retentive force of the three materials laser cast clasp at 1 year simulated clinical use showed no significant differences between means of three materials ($p=0.05$).

One-way ANOVA for the average retentive force of the three materials laser cast clasp at 1 year simulated clinical use showed significant differences between means of three materials ($p=0.05$).

Table IV.1.2.1. The means of maximum and average retentive forces of laser and non-laser clasp between three tested materials at 1 and 10 years simulated clinical use respectively are not significant different except for the average force of non-laser (One way ANOVA, $p=0.05$).

	Laser	Non-laser
Maximum force	S	S
Average force	S	N

S = Significant different between means of samples.

N = Not significant different between means of samples.

Additional statistical analysis to assess the rejected hypothesis cases from 1. and 2.

1. Two sample *t* test for the maximum retentive force at 1 year simulated clinical use of laser cast clasp between two materials ($p=0.05$) (Table IV.1.2.2.).

1.1. Two sample *t* test for the maximum retentive force at 1 year simulated clinical use of laser cast clasp between Cobalt-chromium and Ti6Al7Nb showed no significant difference between means of clasp type ($p=0.05$).

1.2. Two sample *t* test for the maximum retentive force at 1 year simulated clinical use of laser cast clasp between Cobalt-chromium and Ti Grade II showed significant difference between means of clasp type ($p=0.05$).

1.3. Two sample *t* test for the maximum retentive force at 1 year simulated clinical use of laser cast clasp between Ti Grade II and Ti6Al7Nb showed significant difference between means of clasp type ($p=0.05$).

2. Two sample *t* test for the maximum retentive force at 10 years simulated clinical use of non-laser cast clasp between two materials ($p=0.05$) (Table IV.1.2.2.).

2.1. Two sample *t* test for the maximum retentive force at 10 years simulated clinical use of non-laser cast clasp between Cobalt-chromium and Ti6Al7Nb showed no significant difference between means of clasp type ($p=0.05$).

2.2. Two sample *t* test for the maximum retentive force at 10 years simulated clinical use of non-laser cast clasp between Cobalt-chromium and Ti Grade II showed significant difference between means of clasp type ($p=0.05$).

2.3. Two sample *t* test for the average retentive force of non-laser cast clasp between Ti Grade II and Ti6Al7Nb showed significant difference between means of clasp type ($p=0.05$).

3. Two sample *t* test for the average retentive force at 1 year simulated clinical use of laser cast clasp between two materials ($p=0.05$) (Table IV.1.2.2.).

3.1. Two sample *t* test for the average retentive force at 1 year simulated clinical use of laser cast clasp between Cobalt-chromium and Ti6Al7Nb showed significant difference between means of clasp type ($p=0.05$).

3.2. Two sample *t* test for the average retentive force at 1 year simulated clinical use of laser cast clasp between Cobalt-chromium and Ti Grade II showed significant difference between means of clasp type ($p=0.05$).

3.3. Two sample *t* test for the average retentive force at 1 year simulated clinical use of laser cast clasp between Ti Grade II and Ti6Al7Nb showed no significant difference between means of clasp type ($p=0.05$).

Table IV.1.2.2. The means of maximum and average retentive forces of laser and non-laser clasps between two tested material are significantly different except those between CoCr and Ti6Al7Nb and the average force of laser clasp between TiGdII and Ti6Al7Nb (Two sample *t* test, $p=0.05$).

	Maximum force & Laser clasp	Maximum force & Non-laser clasp	Average force & Laser clasp
CoCr-Ti6Al7Nb	N	N	N
CoCr-TiGdII	S	S	S
TiGdII-Ti6Al7Nb	S	S	N

S = Significant different between means of samples.

N = Not significant different between means of samples.

3. For the null hypothesis, there are no significant differences between means of the retentive forces of non-laser and laser clasps in each material (titanium grade II, Ti6Al7Nb and cobalt-chromium alloy) at 1 year simulated clinical use. (Table IV.1.2.3.)

Two sample *t* test for the maximum retentive force of Titanium Grade II cast clasp at 1 year simulated clinical use showed no significant difference between means of clasp type ($p=0.05$).

Two sample *t* test for the maximum retentive force of chrom-cobalt cast clasp at 1 year simulated clinical use showed significant difference between means of clasp type ($p=0.05$).

Two sample *t* test for the maximum retentive force of Ti6Al7Nb cast clasp at 1 year simulated clinical use showed significant difference between means of clasp type. ($p=0.05$)

Two sample *t* test for the average retentive force of Titanium Grade II cast clasp at 1 year simulated clinical use showed no significant difference between means of clasp type. ($p=0.05$)

Two sample *t* test for the average retentive force of chrom-cobalt cast clasp at 1 year simulated clinical use showed significant difference between means of clasp type. ($p=0.05$)

Two sample *t* test for the average retentive force of Ti6Al7Nb cast clasp at 1 year simulated clinical use showed significant difference between means of clasp type. ($p=0.05$)

Table IV.1.2.3: The means of maximum and average retentive force between laser and non-laser clasps of Ti Grade II are not significant different (Two sample *t* test, $p=0.05$).

	Ti GdII	CrCo	Ti6Al7Nb
Maximum force	N	S	S
Average force	N	S	S

S = Significant different between means of samples.

N = Not significant different between means of samples.

IV.2. Distortion of clasp

The differences in the distance between the ending point of lingual bracing arm and buccal retention arm of the clasp before and after test cycles simulated 10 years simulated clinical use for each material (titanium grade II, Ti6Al7Nb and cobalt-chromium alloy) are small. Moreover the mean differences between before and after cycles in each material are very little (Table IV.2.1.-3.).

Table IV.2.1. The distance [mm] between the ending point of lingual bracing arm and buccal retention arm of Co-Cr clasps before and after 15000 testing cycles.

	No.1	No.2	No.3	No.4	No.5	No.6	Mean	SD
Before	6.8	7.3	7.3	7.0	6.8	6.5	7.0	0.3
After	6.8	7.3	7.4	7.0	6.8	6.5	7.0	0.3
The difference	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0

Table IV.2.2. The distance [mm] between the ending point of lingual bracing arm and buccal retention arm of cpTi clasps before and after 15000 testing cycles.

	No.1	No.2	No.3	No.4	No.5	No.6	Mean	SD
Before	7.5	7.3	7.3	6.9	7.2	7.3	7.3	0.2
After	7.5	7.3	7.3	6.9	7.2	7.3	7.3	0.2
The difference	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Table IV.2.3. The distance [mm] between the ending point of lingual bracing arm and buccal retention arm of Ti6Al7Nb clasps before and after 15000 testing cycles.

	No.1	No.2	No.3	No.4	No.5	No.6	Mean	SD
Before	7.3	7.5	7.3	7.2	7.5	7.3	7.4	0.1
After	7.3	7.5	7.3	7.2	7.6	7.4	7.4	0.1
The difference	0.0	0.0	0.0	0.0	0.1	0.1	0.0	0.0

In conclusion, all three materials were recommended to used for 10 years in this condition have good retention without distortion of clasp for 15000 insertion and withdrawal cycles.

Moreover, in this research no clasp was broken during both types of testing cycles.

IV.3. Acid etching (pickling)

The surface characteristics of acid pickled/etched cpTi and Ti4Al7Nb alloy investigated by Stereo-microscope are similar. The α -case layer (25-30 μ m) was found at the edge of both specimens (Fig. IV.3.1.) whereas the crystal structure was found in the middle (Fig. IV.3.2.).The porosity of both specimens was found (Fig. IV.3.1 and IV.3.3.).

Fig IV.3.1. SEM image showing the alpha case layer and porosity of cp-Ti.

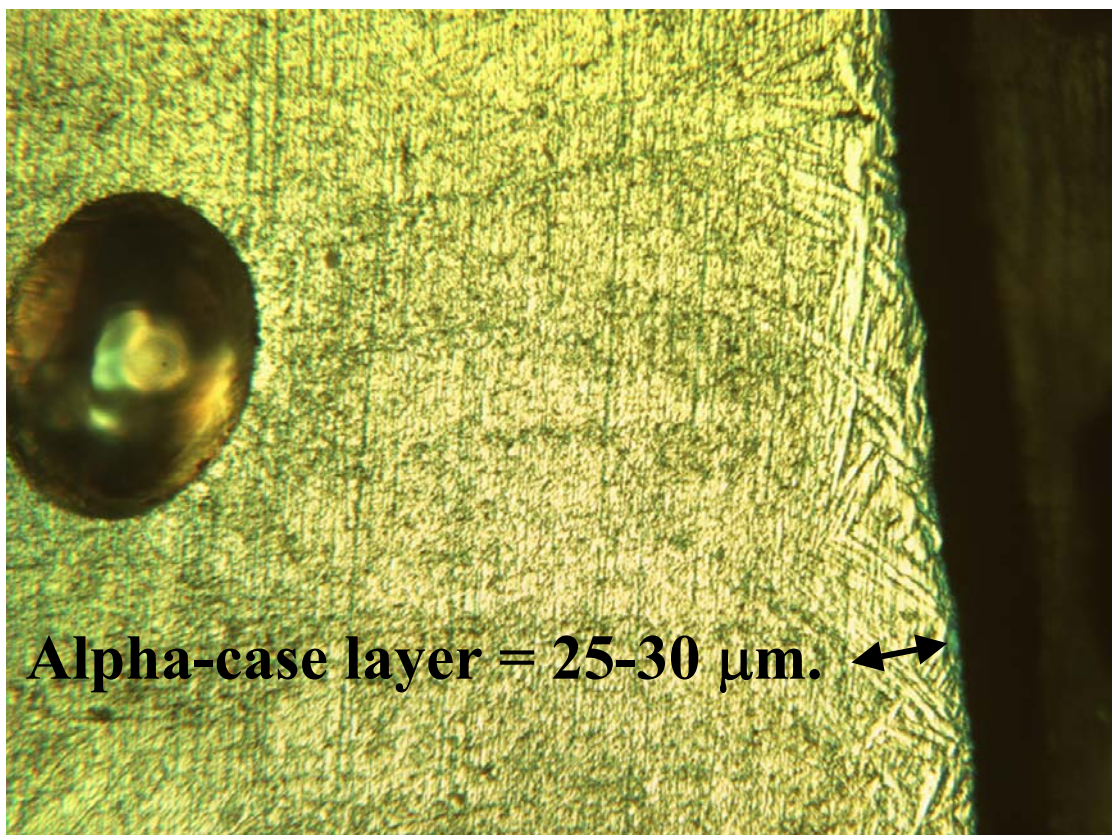


Fig IV.3.2. SEM image showing crystal surface of Ti6Al7Nb.

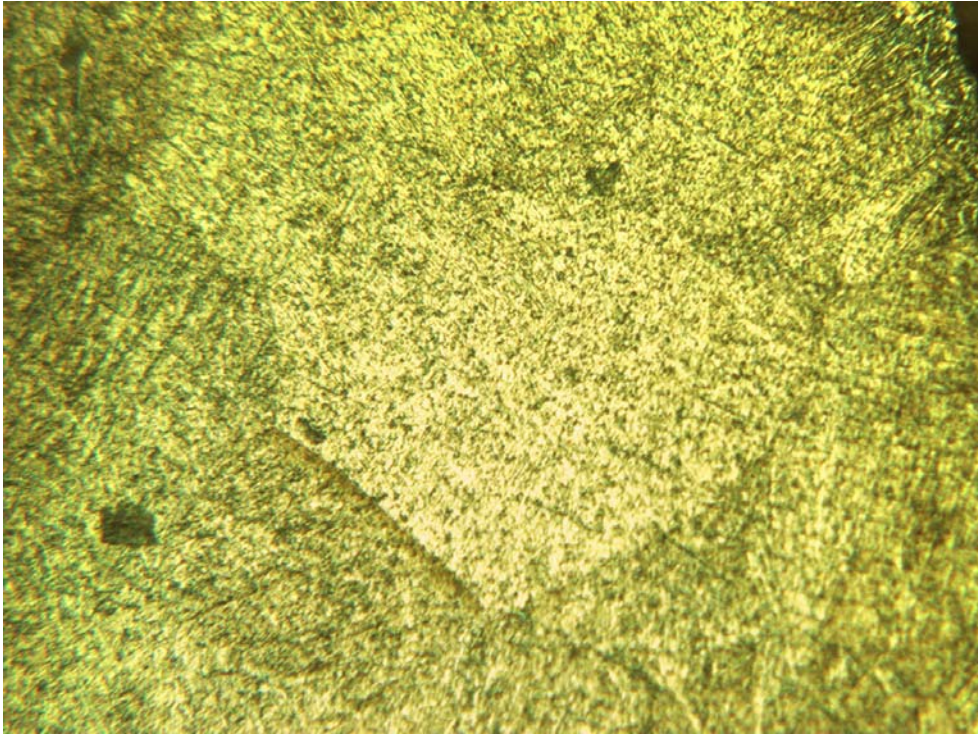
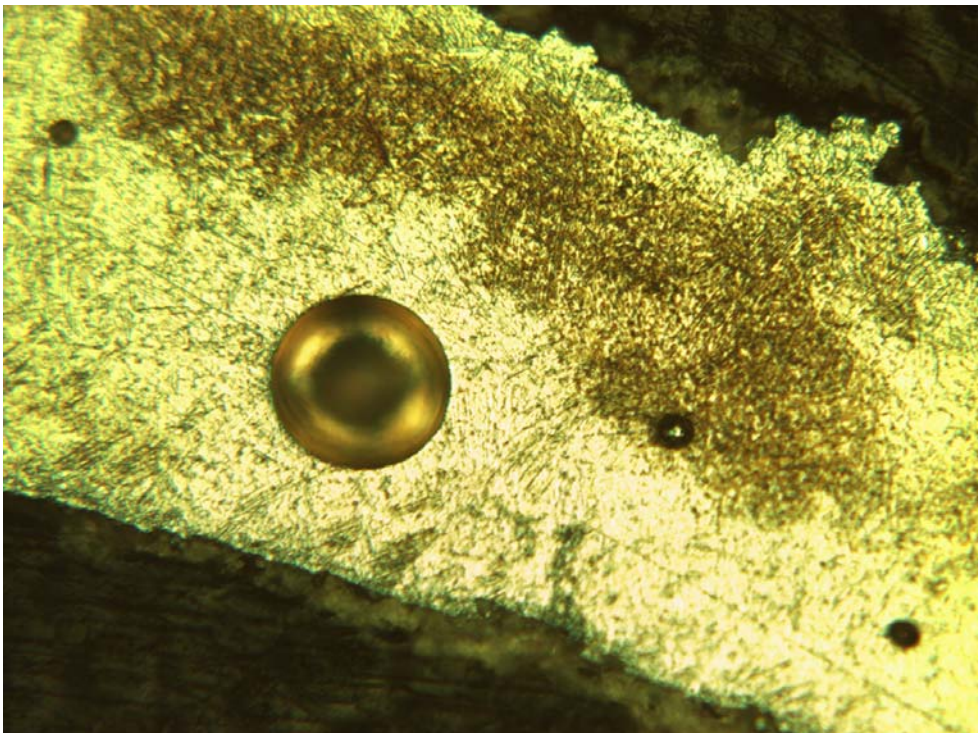


Fig IV.3.3. SEM image showing the alpha case layer and porosity of Ti6Al7Nb.



V. Discussion

V.1. Materials and methods

V.1.1. Materials

Material for removable partial denture should have enough flexibility for clasp and rigidity for other components of partial denture. Because their flexibility is proportionate to their bulk. The disadvantage of cast gold partial dentures is that their bulk must be increased to obtain needed rigidity at the expense of added weight. It cannot be denied that greater rigidity with less bulk is possible through the use of Co-Cr alloys.⁶⁸ Therefore, using Co-Cr for the denture is more popular than gold. However, titanium (as well as its alloys) which is a highly biocompatible non-allergenic and cheap metal has attracted a lot of interest since it could replace noble alloys in many prosthetic applications. For an excellent review on titanium for prosthetic applications, the reader is referred elsewhere.⁹⁰ Moreover, their excellent mechanical properties are attractive for removable partial denture cast clasp (Table V.1.1.1. and see Introduction).

Table V.1.1.1. Physical properties of Dental alloy for Metal base denture.³⁹

	Tensile strength [MPa]	Elongation [%]	Hardness [VHN]	Fatigue Life Ave. [number]
CPTi Grade1	240	24.0	100	2.502
CPTi Grade2	345	20.0	110	4.249
CPTi Grade3	450	18.0	150	4.187
CPTi Grade4	480	9.6	251	4.226
Ti6Al7Nb	933	7.0	300	10.338
Co-Cr Alloy A	938	8.3	365	2.055
Co-Cr Alloy B	715	2.3	432	1.131

For these reasons, in this study Co-Cr alloy served as the control group while unalloyed titanium Grade II and Ti6Al7Nb Alloy served as the first and the second test group respectively.

V.1.2. Methods

V.1.2.1. Fatigue resistance

V.1.2.1.1. Fatigue resistance of non-laser welding clasp

Abutment and Abutment fabrication

There are three reasons to use only one model of abutment CoCr crown. The first reason is that the vicker hardness of CoCr is higher than that of unalloyed titanium Grade II and Ti6Al7Nb alloy (Table V.1.1.1.). This is important because the hardness of a material is one of the properties that influences its resistance to abrasion.⁶⁸ The second reason is that the number of clasp specimens is not too high and their test cycles are also not extremely many. The third reason is the high risk of dimensional change of test clasps from different abutments due to laboratory procedure. From these points of view, this research ignored changing of abutment contour due to attrition during insertion and withdrawal of the clasps.

There are two reasons to use a human mandibular first molar for making the abutment. The first reason is that the human tooth represents a real contour of tooth which has influence on the shape of the clasps. The difference of shape of clasp affects its mechanical properties; for example, retention and flexibility. The second reason is some motivations for clasp design (as explained below). In fact, in order to create the abutment for this research, first of all we need to design clasp due to its type, length, undercut and material.

- Type of the test clasp: Circumferential clasp arm

Although a thorough knowledge of the principles of clasp design should lead to a logical application of those principles (see Introduction), it is better to consider some of the more common clasp designs individually. The circumferential clasp will be considered first as an all-cast clasp.³⁷

The cast circumferential clasp is usually the most logical clasp to use with all tooth-supported partial dentures because of its retentive and bracing

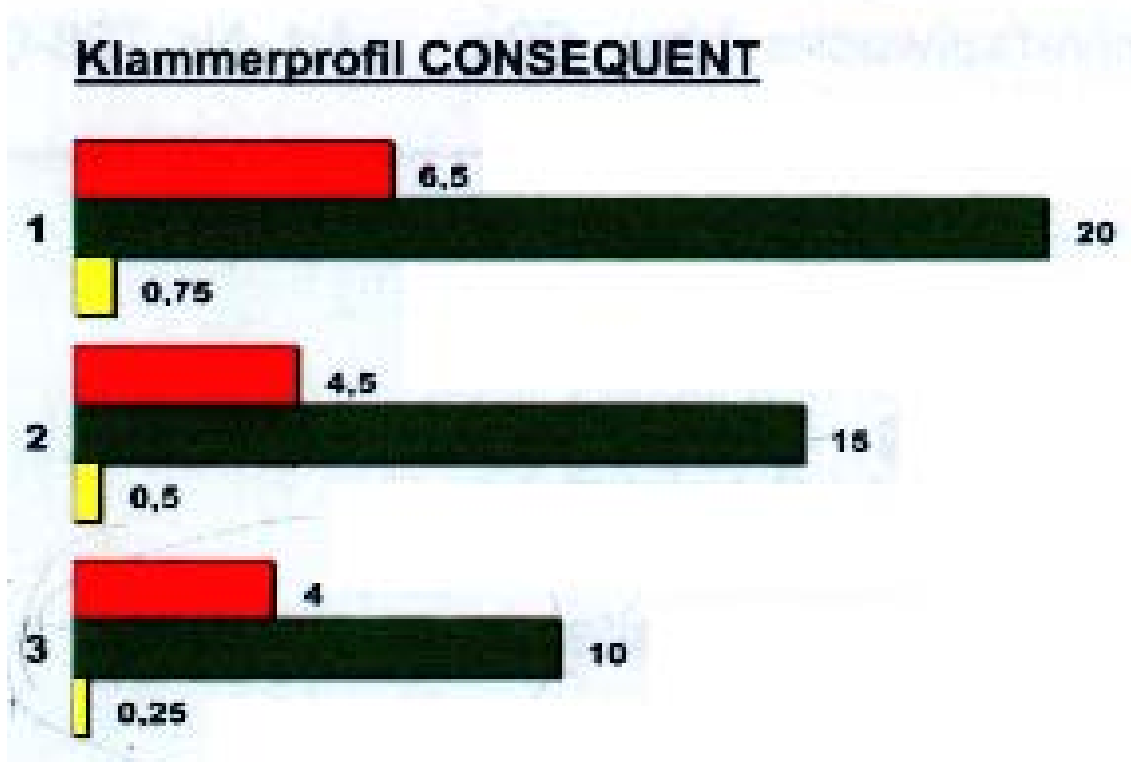
ability. Only when the retentive undercut may be approached better with a bar clasp arm or when esthetics will be enhanced should the latter be used.³⁷

The basic form of the circumferential type clasp is a buccal and lingual arm originating from a body and occlusal rest area. One of them is a retentive clasp arm, opposed by a nonretentive reciprocal arm on the opposite side. Cast circumferential retentive clasp arm originates on or occlusally to the height of contour its terminal third then crosses and engages retentive undercut progressively as its taper decreases and its flexibility increases.³⁷

- Length, undercut and material of the test clasp

There are four reasons to design clasp which has to be tested in the elastic region. Firstly the flexibility of Cr-Co alloy is lower than Ti and Ti6Al7Nb.²⁰ Secondly Yeti company's information which was represented by Cr-Co. (Fig. V.1.2.1.1.) Thirdly the cast circumferential clasp is usually the most logical clasp to use with all tooth supported partial dentures because of its retentive and bracing ability.³⁷ And fourthly the nonmetal abutment indicated higher friction coefficient under the wet condition.⁷² However, the relationship between friction coefficient and retentive force is still unclear, because the flexibility of the clasp arm^{11,92} and the shape of the abutment^{10,37,75} affect the relationship.

Fig. V.1.2.1.1. Yeti company's information which was represented by Cr-Co.



	1	2	3
■ Retentive force [N]	6,5	4,5	4,0
■ Clasp length [mm]	20	15	10
■ Clasp undercut [mm]	0,75	0,5	0,25

Thus we need the biggest crown to simulate real shape of crown and the proper undercut to create retentive circumferential cast clasp arm for representing retentive force in the elastic region. That is why a human mandibular first molar and 0.25 mm undercut was selected for 12.5 mm retentive clasp arm.

The mesial occlusal rest seat served as a stop for insertion and as an additional way to ensure a straight line of withdrawal.

The mesial guide plane served as a plane to ensure a straight line of insertion and withdrawal.

The distal guide groove served as a reference path of insertion and withdrawal of the mesial guide plane to create the clasp-holder.

Abutment fabrication by selective grinding and contour build-up was simulated from clinical use.⁷¹ The modification of tooth contour with composite resin is a conservative, simple, durable and effective way of creating undercut for clasping where no, or inadequate, undercut exists.²⁷

Despite its disadvantages, the cast circumferential clasp arm may be used effectively by proper design. For example, adequate mouth preparations will permit its point of origin to be placed far enough below the occlusal surface in order to avoid poor esthetics and increased tooth dimension.

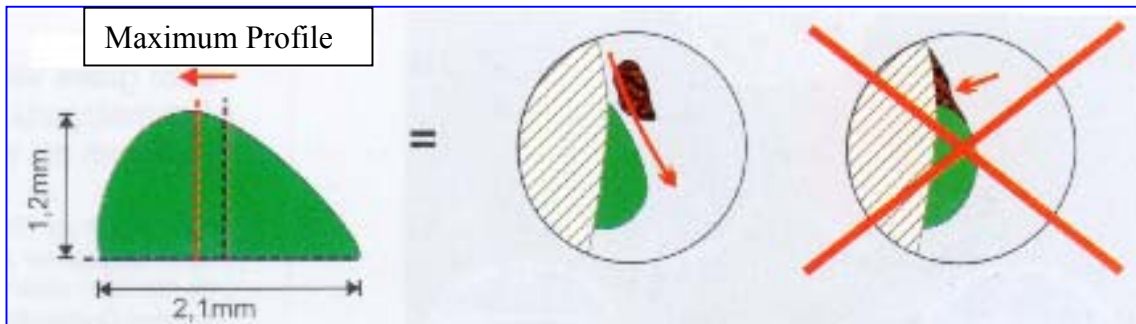
Polyvinylsiloxane (additional-type) (coltene[®], President fast, Swiss) was used because of its dimensional stability.⁷¹

Clasps and Clasp fabrication

Wax patterns (CONSEQUENT Multiklammer[®] for molar teeth, Yenti, Germany) were used because their profile is better for oral hygiene (Fig. V.1.2.1.2.).

Six clasps for each material were tested in order to provide sufficient data for statistics.

Fig. V.1.2.1.2. Wax pattern(CONSEQUENT Multiklammer® for molar teeth, Yenti, Germany)



Wax Profile
In
cross section

Food debris
can go through
“Consequent clasp”

Food debris
is collected
at the clasp

A higher pressure, a bigger vacuum, a greater purity of atmosphere, a shorter way from the melting place of metal to investment and a more inert investment material are needed in order to produce titanium casting with better shape and less alpha-case layer. This is because titanium has a high reaction with oxygen. All of the above can fulfill with SymbioCast™ (Girrbach Dental Systems, Germany) with its 1.6 l mini-casting chamber (140x120 mm diameter). It can produce very fast vacuum and high pressure. And processing time is reduced by the short way from the Cu crucible to investment. Moreover, the metal that is melted by electrode on the crucible can be poured directly to the hole in the investment very fast and stable. And because the size of metal mold is controlled from company. Thus, the parameter for casting can be controlled which can produce the same good quality of casting product (www.girrbach.de).

Testing Conditions

Retention and stress in clasp arms are the keys to the long-term success of removable partial dentures (RPDs) without deformation or fracture.^{72,73} Thus the distance between the ending point of lingual bracing arm and buccal retention arm of each clasp was measured by microscope and image software before and after testing condition. This process is modified to test deformation of clasp. By the way, this procedure cannot be considered the real distortion of clasp, because it can measure only one dimension. The real situation is three-dimension distortion (see Introduction).

Testing should be done in mouth fluid conditions because fatigue failure differs for different corrosive environments.⁶⁸ The test conditions were maintained as wet conditions (distilled water). The fact that both water and artificial saliva reduce the fatigue strength of cobalt-chromium alloy, is explained by corrosion of the alloy in the wet environment.⁵³

The maximum retentive force [mN] and mean of retentive force for each cycle [mN] needed to remove the clasp were chosen. The maximum retentive force should always be below the elastic limit. However, there are a lot of factors connected to the elastic limit. For this research, I could find only the approximate force of the maximum retentive force under these conditions. Total resistance to removal of the clasp reaches its greatest magnitude as the retentive tips reach the greatest diameter of the tooth (survey line) and diminish beyond this position as the clasp tips approach the occlusal surface of the abutment. Maximum retention occurs when a retentive clasp tip is lifted to near the survey line.⁷²

V.1.2.1.2. Fatigue resistance of laser welding clasp Clasps and Clasp fabrication

For this study, I used the mean of the distances between the fracture point and the tip of reciprocal clasp arm which is 11.4 mm, as a reference for cutting and laser welding (Table V.1.2.1.2.1.).

Table V.1.2.1.2. 1. The distance between the fracture point and the tip of reciprocal clasp arm.

Material	The distance [mm]
CoCr	11.3
Ti GdII	11.5
Ti6Al7Nb	11.5

A method for eliminating distortion during assemblage of the appliance is the use of laser welding to join the cast units. The claimed advantages, in addition to superior fit of the appliance, are that the welding can be made directly on the master stone cast without damage to the cast or adjacent resin or porcelain and the rapidity of the procedure.⁴⁷

The joining of titanium and its alloys by conventional brazing is complicated by the tendency of titanium to oxidize. An inert gas environment could be used to prevent excessive oxidation; however, oxygen is also required for combustion of a flame. Techniques of electrical resistance soldering, infrared soldering, and plasma soldering have been reported, but heat-releasing procedures are still required to minimize oxidation.⁹⁸ Therefore, titanium welding is more common.

With laser welding, it is possible to join parts by the self-welding of the metal parts themselves. Laser welding of titanium offers several advantages over the soldering methods. Because the latter can be focused on a relatively small spot, the effect of heat on the titanium is weaker than that of exposure to a flame. The process is less time-consuming because no investment material is needed. Since the joint is formed by the original metal melted together without

an intermediary of solder, there should be little problem with reduced corrosion resistance.

The following factors that affect the titanium joining should be considered: (1) joint design, (2) adequate energy delivery to areas to be joined, (3) method of energy delivery, (4) cooling rate, and (5) amount of contamination during joining procedure.⁹¹

The clinical significance of incomplete laser-welded joints for fixed and removable titanium prostheses is important. Because of the limited depth of laser-fused seams in the peripheral area of a joint, aggressive conventional dental grinding and polishing of laser-welded joints of a titanium prosthesis should be avoided. Joint preparation is critical for laser welding. Preparation of intimate and even contact to be joined is essential, because only small localized fusing zones can be created when two pieces of titanium are welded together by laser beam. The conventional hand grinding method for prostheses to be joined by laser welding is not acceptable because of lack of precision. All fusion zones in a laser-welded prosthesis should be overlapped⁹⁸; otherwise small unwelded areas between fusion zones may act as microcracks, which would weaken joints that are subject to fatigue loading during chewing. Further evaluation of the properties of joints made using laser energy and refinement of the instrumentation necessary.⁶⁸

From above, this study is the same as V.2.2.2 in Materials and methods.

Ideally, the strength of a joined prosthesis should be as good as that of the original material. The tensile strength of the laser welding group of titanium was though significantly inferior to the non-laser group.⁹¹ Moreover, the tensile strength of laser-welded cast gold alloy joints has been found to be comparable to that of soldered joints. The ability of the alloy to age harden is not significantly altered by the rapid heating and cooling during the laser welding. However, occasionally, microcracking does appear in the center of the fusion zone.⁶⁸

In comparison to the native substrate, laser welding induced comparable decreases (approximately 20%) in resistance to both motonic tensile and fatigue loading. Hence, in the case of laser welds, an increase of approximately 50% in Hv hardness had no effect on mechanical resistance.⁹⁷

The quality of the welds appeared to be the most important factor in determining the strength of welded titanium. The fractography of titanium samples indicated that strength depends primarily on flaws and not on the properties of the metal in the weld zone. The samples from literature that had the lowest values had large pores. Some samples fractured both in the weld and the adjacent zone, which indicates that the metal in the weld zone is equal to or greater in strength than the rest of the sample and that pores in the weld are solely responsible for lowering the strength. In conclusion, welding of titanium lead to a significant reduction of ductility of the materials.¹²

The most common type of flaw observed on the fracture surface were pores in the welded specimens. Data from literature show that the fractures most probably occurred in the area with the largest pores or other flaws. A wide variation of ductile behavior was observed in the fracture region as indicated by large reductions of the area at the fracture site, microvoids that formed during loading, shear lips on the fracture surface (which also from during loading), and the presence of deformed grains. On the other hand, the cast titanium specimens that were not welded showed minimal porosity. In conclusion, the presence of large pores in the repaired joint appears to be the most important factor in controlling the strength of the weld in cast titanium.¹²

From above, I assume that laser welding titanium cast clasp has a lower fatigue resistance compared with the non-laser cast clasp due to porosity. Thus this research studies suggest to use the laser cast clasps for simulating 1 year of use.

V.1.2.1.3. Acid etching (pickling)

The clasps were put into the acrylic resin block, because it is easier for holding during grinding and for studying with the microscope.

The specimens were grinded until both center of clasp arms appeared by using grinding machine (TG 200, Buehler-Wirtz GmbH, Germany) with sand paper until SiC 4,000 for creating a good surface topography without the alpha case layer on the surface (see Introduction).

V.1.2.2. Statistics³¹

The analyses covered in this study are better done by computer. Since we are reaching the limit of what is practicable for “hand calculation”.

Data screening

When analyzing the data we have a choice between methods that make distributional assumptions, called parametric methods, and those which make no assumptions about distributions, called distribution-free or non-parametric methods.

For many purposes it is not necessary to do more than checking the Normal plot by eye, but if something more is required then a more useful approach is based on measuring the straightness of the Normal plot.

One way of measuring non-Normality is to calculate what are called “the higher moments” of the distribution of data. We can measure shape by means of quantities which are obvious extensions to the formula for the variance. From these we can derive a quantity called skewness, which is a measure of the asymmetry, and kurtosis, which is a measure of the flatness or the peakedness. For example, the Shapiro-Wilk W test for Normality is available in several statistical computer programs.

In the analysis of continuous data the calculation of means plays a prominent part, and so we need to consider the distribution of the mean for smaller samples. (large sample is more than 100).

The mean of a sample from a Normal distribution with unknown variance has a distribution that is similar to, but not quite the same as, a Normal distribution. W.S. Gossett called it the t distribution.

We use the t distribution for estimation and hypothesis testing relating to the means of one or two samples. The t distribution has one parameter, a quantity called the degrees of freedom. In general the degrees of freedom are calculated as the sample size minus the number of estimated parameters. The degrees of freedom for the t distribution relate to the estimated standard

deviation, which is calculated as variation around the estimated mean. Hence for a single sample of n observations we have $n-1$ degrees of freedom. Likewise, we use the t distribution to calculate confidence intervals.

For the case with more than two samples, we need the method called analysis of variance, for which we use the F distribution rather than the t distribution. All these parametric methods make assumptions about Normality.

Use of Two sample t test ($p=0.05$) for the null hypothesis: There are no significant differences in the retentive forces between non-laser and laser clasps of each material (titanium grade II, Ti6Al7Nb and cobalt-chromium alloy) after 1 year simulated clinical use.

Because there are two independent groups of observations and parameters.

Use of One-way ANOVA ($p=0.05$) for the null hypotheses:

- There are no significant differences in the retentive forces of titanium grade II, Ti6Al7Nb and cobalt-chromium alloy cast clasps at 10 years simulated clinical use.
- There are no significant differences in the retentive forces of titanium grade II, Ti6Al7Nb and cobalt-chromium alloy laser cast clasps at 1 year simulated clinical use.

Because there are three independent groups of observations, one factor classifying the observations and parameters. With several groups of observations it is obviously possible to compare each pair of groups using t tests, but this is not a good approach. It is far better to use a single analysis that enables us to look at all the data in one go, and the method we use is called one way analysis of variance (sometimes abbreviated to anova). Then the additional statistical analysis (Two sample t test, $p=0.05$) was used to analyze rejected hypothesis cases.

V.2. Results

V.2.1. Fatigue resistance

In the case of dental appliances and restorations, a high value for the elastic limit is a necessary requirement for the materials from which they are fabricated, since the structure is expected to return to its original shape after it has been stressed. Usually a high modulus of elasticity is also required, since a small deformation is usually desired under considerable stress.⁶⁸

There are instances, however, in which a larger strain or deformation may be needed with a moderate or slight stress, as in the case of retentive clasp arm of removable partial denture. The maximal flexibility is defined as the strain which occurs when the material is stressed to its proportional limit. It can be expressed mathematically as follows.⁶⁸

Let E = Modulus of elasticity

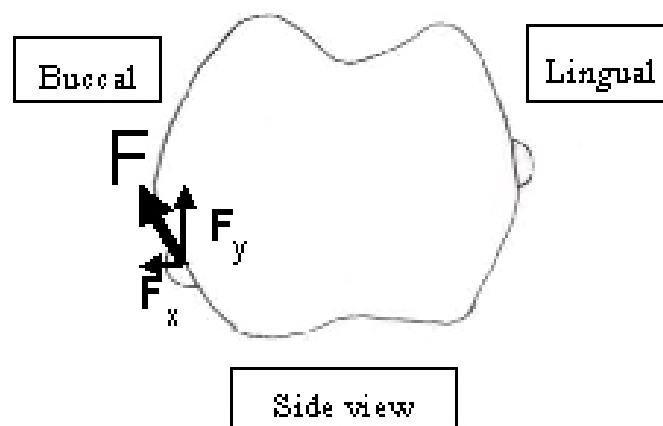
P = Proportional limit

ϵ_m = Maximal flexibility

From equation (I), $E = P/\epsilon_m$

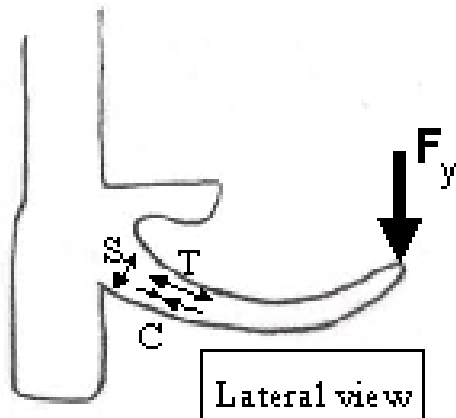
For this study, the complex force that moves retentive clasp arm from 0.25 mm undercut abutment crown can be showed:

F = Force that moves retentive clasp arm from 0.25 mm undercut.



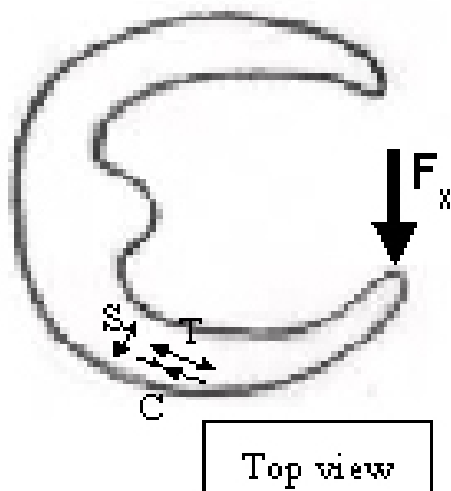
F_y = Vertical force that moves the retentive clasp arm from 0.25 mm undercut.

F_x = Horizontal force that moves the retentive clasp arm from 0.25 mm undercut.



Lateral view

S = Shear stress
 T = Tensile stress
 C = Compressive stress



Top view

As can be seen, compressive, tensile, and shear stresses are present in various parts of the structure. However, we have been discussing mechanical forces which are applied constantly for a finite time and are called static loads or stresses. The stresses in the retentive clasp arm during insertion and removing are not of this type. These stresses usually exist for only an instant; they are the result of a force created by the motion of insertion and removing of denture appliance. They are known as dynamic forces in contrast to static forces. Since

the dynamic forces exist for an infinitesimally short time, the resulting deformation or strain cannot be measured.⁶⁸

The explanation about the characteristics of the retentive clasp arm of removable partial denture can be done with this example: when an acrobat falls or jumps onto a trapeze net, the energy of his fall is impact, so that its energy at the time of maximal deformation is equal to the energy of the acrobat at the instant of impact. When the energy of the net is released, the acrobat is thrown into the air again, and a second impact occurs, and so on. Fortunately, part of the energy is dissipated, otherwise he would never stop rebounding. The amount of energy absorbed by a structure when it is stressed not to exceed its proportional limit, is known as resilience.⁶⁸

Resilience in this context : Elastic energy which is stored by (and which is recoverable from) the retentive clasp.

For the retentive tip of a cobalt chromium clasp to flex 0.25 mm without deformity permanently, it needs to be about 15 mm in length. This can usually be achieved with an occlusally-approaching clasp on a molar tooth.²⁷

Base metal alloys such as Co-Cr and Co-Cr-Ni alloys is normally used to constructed removable partial denture framework. The popularity of these alloys may be attributed to their low density, high modulus of elasticity, and low cost in comparison with gold alloys. These characteristics are considered advantageous, especially for major connectors of the framework including lingual and palatal bars. However, the choice of an appropriate retentive clasp material appears to be somewhat complex. Retentive clasp arms must be capable of flexing and returning to their original form and should retain a denture satisfactorily and yet not stress the tooth unduly or be distorted permanently during service.⁵¹

The results of this study can imply that force of non- and laser clasp of CrCo is equal to Ti6Al7Nb, whereas Ti GdII is less than CrCo. It shows the same result like the study from Edwin and Ulrike Lenz in 2002.

Although the retentive force of Ti6Al7Nb is equal to that of CrCo, other properties of Ti6Al7Nb are better than those of CrCo especially corrosion and biocompatibility. Therefore, Ti6Al7Nb was suggested to be used for clasp instead of CrCo.

The study about laser welding and suprastructure framework can be concluded as following:

- When producing a laser-welded titanium framework, prefabricated components are soldered by laser-welding to form a metal frame which is then manually controlled.⁴⁴ A special stereo laser welder is used for joining the prefabricated components by simultaneously fusing their junctions with opposed laser beams. In other words, the components are soldered simultaneously from both buccal and lingual surfaces in order to decrease potential distortions induced by conventional welding procedures. By the way, the idea of this method is not spread. Several designs have been tested to improve the mechanical strength of the framework.⁴⁴ Follow-up studies, comparing the performance of laser-welded titanium frameworks with that of conventional cast gold-alloy frameworks over a 5-year period, have shown that laser-welded superstructures were affected by more than double the number of framework fractures.^{13,66} The fractured superstructures can be easily repaired by laser-welding in a second time.

- A recent randomized 2-year follow-up study showed comparable results among laser-welded prostheses and conventional cast suprastructures in edentulous maxillas.⁴³ These improvements can be partly explained by technical refinements that occurred after the initial development period. On the other hand, with the exception of an in vitro investigation⁷⁰, no data have been presented suggesting an improved fit for laser-welded titanium frameworks when compared to conventional cast superstructures.⁴²

By the way, no literature about laser welding in clasp can be found. Theoretically, the retentive force of non-laser and laser clasp from the same material and shape should be equal. But the results of this study indicate that force of Ti6Al7Nb and CrCo of non-laser clasp is smaller than that of laser

clasp, whereas force of Ti GdII of non-laser clasp is equal to that of laser clasp. Thus it is possible that after laser welding the clasp was distorted in three direction which cannot be detect by one dimension measurement. However, There is no clasp which was broken during 1 year simulated clinical use. Therefore, laser welding was recommended to repair for clasp for use in 1 year.

V.2.2. Distortion of clasp

From the results, the distances between the ending point of lingual bracing arm and buccal retention arm before and after 15000 test cycles of all three materials are too small in order to change their retentive force. It can be implied that the clasp design for three tested materials is properly due to their maximum retentive forces under the elastic limit. By the way, these data cannot represent the real distortion of clasp because of one dimension measurement.

In conclusion, all three materials were recommended to use as a cast clasp for 10 years without distortion of clasp.

V.2.3. Acid etching (pickling)

The high solubility of oxygen in titanium may have negative consequences. At high temperatures, the affinity of titanium for oxygen creates not only a superficial oxidation, but also some hardening of the surface, by solid solution, on some depth, due to the diffusion of oxygen into titanium. After the binary phase diagram Ti-O, the allotropic transformation β/α disappears for oxygen concentrations from 5 to 13%. For all temperatures, the system then becomes α -monophased. This is the reason why this hardened, superficial layer has been named “ α -case”.³⁶

This hardened layer is not desired, since it reduces ductility and fatigue resistance of the material. Its formation remains one of the most important problems in the casting procedure for dental prostheses. During melting and casting of titanium, the crucible, the atmosphere, and mainly the investment, are potential “providers” of oxygen- or other impurities-, which shall react with the

metal at the surface of the casting. The thickness of the “ α -case” vary with the thickness of the casting itself, it is about 50-100 μm ³⁸ and it may reach 0.2 mm. The necessary elimination of it shall always produce a loss of precision of the casting.³⁶

In this study, the α -case layer (approximately 25-30 μm) which is in its normal range was found in the surrounding of the edge of both specimens.

The α grain was found in the middle of cpTi whereas the α and β grain were found in Ti6Al7Nb according to their chemistry and structure. The grains or crystal structures were found only in the middle of the specimen. This is because the degree of decreasing temperature in the middle is slow enough for crystallization.

The porosity shows the need to improve casting technique and can imply that the physical properties of the testing clasps are decreases.

Clinical Implications

The mechanical properties of welded titanium connectors were shown to be comparable to the parent metal.⁶⁴ According to the present findings, the tensile strengths of welded titanium connectors are higher than those of conventional soldered connectors of a high noble, a noble, or a base metal alloy.^{23,24,64} Thus the clinical performance of welded titanium connectors should be promising. By comparing the mechanical properties obtained by both techniques, and in view of the difficulty in brazing titanium, welding would be the better technique in fabricating connectors.

It should also be noted that the stereographic laser welding technique was also designed with the intention of minimizing distortion. Although a higher energy input might produce a weld with better mechanical strength, more distortion will ensure it.⁵

Future Developments

1. Materials

Low melting (900 to 1100°C) binary and ternary titanium alloys that would avoid many casting problems, retaining the biocompatibility and corrosion resistance of commercially pure titanium could be another future development for titanium in prosthetic applications.

Titanium alloys should improve for higher viscosity during melting.

2. Casting machine

Titanium and its alloys are very light, therefore they need higher pressure than other metals and alloys during casting and low vacuum during melting.

Reducing considerably the mold temperature before casting titanium is another way of decreasing the thickness of the alpha case layer. Oxidation of titanium becomes actually less important, but the accelerated rate of cooling created defects in the casting, like porosities, not visible to the naked eye, but which decreases the mechanical strength of the casting.³⁶

3. Investment material

In order to reduce the addition of oxygen, investments with highly stable oxides (so stable in fact that titanium cannot extract oxygen from them) should be used. The free enthalpy of formation ΔG of the oxides, which is a thermodynamic measure of the stability of a compound, gives some indication. High negative values for ΔG correspond to very stable compounds. From the literature, some oxides are less stable (e.g. SiO_2) than TiO_2 , and molten titanium may oxidize at their contact. Some oxides are more stable than TiO_2 , as for example Al_2O_3 , LiO_2 , and CaO . The use of these oxides is suggested for investment materials. Other very stable oxides could also be considered as

refractory materials. Unfortunately, they possess adverse properties like toxicity (BeO, ThO) or high cost (Y_2O_3). Moreover, they do not have the property of reversible thermal expansion known with the silica (cristbalite, quartz).³⁶

VI. Conclusions

The fatigue resistances of titanium grade II, Ti6Al7Nb and chrom-cobalt alloy laser cast clasps were investigated and compared with the resistances of the same materials without any joining process. The fatigue resistance of the laser cast clasp was compared within these three materials as well as that of the non-laser. The differences of the clasp distance before and after 10 years simulated test cycles were compared between these three materials. Moreover, this study investigated whether titanium grade II and Ti6Al7Nb alloy cast clasps produced by SymbioCast™ provided sufficient quality detected by the alpha case layer and porosity. Within the parameters of this study design, the following conclusions may be drawn:

1. The maximum force of non-laser and laser clasp of CrCo is equal to that of Ti6Al7Nb, whereas Ti GdII is less strong than both of them.

2. The average force of non-laser clasp of CrCo, Ti6Al7Nb and TiGdII are equal.

3. The average force of laser clasp of CrCo is equal to that of Ti6Al7Nb and the force of Ti6Al7Nb is equal to that of TiGdII, whereas that of CrCo is higher than that of Ti GdII.

4. The maximum and average forces of Ti GdII of non-laser clasp are equal to those of laser clasp.

5. The maximum and average forces of CrCo of non-laser clasp are smaller than those of laser clasp.

6. The maximum and average forces of Ti6Al7Nb of non-laser clasp are smaller than those of laser clasp.

7. There is no distortion of clasp during 10 years simulated clinical use for the three materials.

8. The α -case layer (approximately 25-30 μm) which is in its normal range was found in the surrounding of the edge of both specimens (Ti GdII and Ti6Al7Nb) in the same quantity.

9. The porosity was found in both specimens (Ti GdII and Ti6Al7Nb) in the same quantity.

VII. Tables

VII.1. Results

VII.1.1. Fatigue resistance

Table VII.1.1.1. The retentive force of Titanium Grade II laser cast clasp.

Number of test cycle [Cycle]	Maximum force [mN]	SD of maximum force [mN]	Average force [mN]	SD of average force [mN]
5.5	3211.9	877.9	2024.3	793.6
150.5	8100.0	1862.6	5099.5	1403.1
295.5	8519.8	1897.1	5543.0	1639.0
440.5	8781.5	1819.5	5647.2	1696.5
585.5	8821.2	1866.9	5814.2	1730.4
730.5	9091.2	1920.5	6014.0	1839.8
875.5	9182.5	2012.2	6164.1	1793.0
1020.5	9366.0	1953.1	6278.6	1844.7
1165.5	9499.5	1831.4	6507.0	1829.0
1310.5	9552.8	1800.3	6554.9	1778.9
1455.5	9293.5	1407.8	6510.2	1685.0

Table VII.1.1.2. The retentive force of Titanium Grade II non-laser cast clasp.

Number of test cycle [Cycle]	Maximum force [mN]	SD of maximum force [mN]	Average force [mN]	SD of average force [mN]
5.5	2582.5	640.8	2082.3	696.6
150.5	5309.8	2329.9	4736.3	1701.1
295.5	5971.8	2043.8	4882.6	1024.2
440.5	6227.6	2040.3	5225.6	970.2
585.5	6708.9	1995.7	5577.5	1019.8
730.5	6852.5	2065.8	5556.9	970.3
875.5	7052.9	1984.0	5876.0	774.2
1020.5	7252.0	1959.5	5905.4	769.3
1165.5	7192.3	1939.8	5982.7	771.6
1310.5	7284.6	1995.9	6079.6	820.1
1455.5	7384.6	1974.7	6055.7	898.3

Table VII.1.1.3. The retentive force of Titanium Grade II non-laser cast clasp.

Number of test cycle [Cycle]	Maximum force [mN]	SD of maximum force [mN]	Average force [mN]	SD of average force [mN]
5.5	2582.4	640.9	2082.2	696.6
1504.5	7356.6	1885.7	6088.5	856.8
3003.5	8112.5	1659.3	6578.9	592.9
4502.5	8445.1	1484.4	6739.3	646.9
6001.5	8858.3	1153.1	6957.2	728.5
7500.5	8806.9	1171.1	6919.1	597.1
8999.5	8746.7	1103.3	6933.2	696.4
10498.5	8784.0	1109.5	6967.0	653.5
11997.5	8682.8	1199.0	6857.0	673.5
13496.5	8690.6	1128.4	6787.2	555.6
14995.5	8830.1	1064.0	6596.2	607.8

Table VII.1.1.4. The retentive force of Cr-Co alloy laser cast clasp.

Number of test cycle [Cycle]	Maximum force [mN]	SD of maximum force [mN]	Average force [mN]	SD of average force [mN]
5.5	8587.8	1152.8	5549.6	1002.4
150.5	13173.5	1637.3	8570.6	1550.3
295.5	13186.6	1616.5	8613.8	1544.4
440.5	13324.5	1525.3	8639.3	1477.8
585.5	13373.4	1475.6	8780.5	1602.2
730.5	13746.2	1485.7	8858.3	1477.6
875.5	13678.1	1257.7	8933.3	1529.0
1020.5	13789.4	1436.0	8993.0	1463.2
1165.5	13925.3	1316.3	8973.9	1482.5
1310.5	14124.8	1342.0	9126.3	1539.1
1455.5	14058.8	1309.9	9264.4	1653.1

Table VII.1.1.5. The retentive force of Cr-Co alloy non-laser cast clasp.

Number of test cycle [Cycle]	Maximum force [mN]	SD of maximum force [mN]	Average force [mN]	SD of average force [mN]
5.5	6798.8	1797.0	4545.1	1405.4
150.5	10305.8	1145.8	6270.5	1234.1
295.5	10261.0	1072.6	6382.1	1099.1
440.5	10351.9	1084.0	6432.1	1017.3
585.5	10449.9	1055.9	6502.4	947.2
730.5	10512.6	1141.7	6573.7	965.5
875.5	10460.8	1217.1	6630.5	860.4
1020.5	10519.9	1210.1	6749.5	827.1
1165.5	10628.0	1268.2	6814.4	920.6
1310.5	10723.1	1343.8	6899.9	965.9
1455.5	10733.8	1251.5	6886.3	983.1

Table VII.1.1.6. The retentive force of Cr-Co alloy non-laser cast clasp.

Number of test cycle [Cycle]	Maximum force [mN]	SD of maximum force [mN]	Average force [mN]	SD of average force [mN]
5.5	6798.9	1797.0	4545.1	1405.4
1504.5	10307.6	2479.2	6915.7	974.3
3003.5	10884.0	1128.9	7033.5	863.0
4502.5	10932.8	1118.4	7087.6	807.0
6001.5	11122.8	1235.8	7038.9	1074.8
7500.5	11257.1	1219.7	7107.8	1096.2
8999.5	11501.4	1208.1	7228.2	1141.4
10498.5	11580.5	1240.7	7218.2	1053.7
11997.5	11534.0	1215.8	7290.1	1058.1
13496.5	11662.2	1224.8	7330.0	1095.9
14995.5	11686.1	1270.3	7394.6	995.5

Table VII.1.1.7. The retentive force of Ti6Al7Nb laser cast clasp.

Number of test cycle [Cycle]	Maximum force [mN]	SD of maximum force [mN]	Average force [mN]	SD of average force [mN]
5.5	5778.1	2264.1	3539.6	1060.5
150.5	10061.9	1536.4	5793.8	762.5
295.5	11174.7	1766.9	6438.8	944.1
440.5	11671.6	1873.8	6746.3	727.8
585.5	12349.9	1867.7	7041.3	810.9
730.5	12556.5	1766.5	7075.3	852.5
875.5	12855.5	1788.8	7169.3	1018.2
1020.5	12972.3	1924.5	7273.7	1056.0
1165.5	13205.0	2034.2	7381.3	1020.5
1310.5	13473.0	2007.1	7496.4	1082.2
1455.5	13745.6	2006.2	7575.8	1227.6

Table VII.1.1.8. The retentive force of Ti6Al7Nb non-laser cast clasp.

Number of test cycle [Cycle]	Maximum force [mN]	SD of maximum force [mN]	Average force [mN]	SD of average force [mN]
5.5	4556.4	2174.5	2629.1	1365.5
150.5	7229.3	1055.6	4464.6	1093.3
295.5	8036.4	1266.8	4893.5	1124.1
440.5	8260.8	1210.5	5100.7	1131.6
585.5	8636.9	1264.5	5251.1	1110.2
730.5	8811.4	1412.0	5392.3	947.7
875.5	9037.9	1417.4	5436.4	867.1
1020.5	9213.6	1401.2	5419.7	882.2
1165.5	9260.1	1355.5	5446.2	929.6
1310.5	9472.7	1141.9	5493.0	956.1
1455.5	9509.6	1100.5	5610.5	996.7

Table VII.1.1.9. The retentive force of Ti6Al7Nb non-laser cast clasp.

Number of test cycle [Cycle]	Maximum force [mN]	SD of maximum force [mN]	Average force [mN]	SD of average force [mN]
5.5	4556.4	2174.6	2629.1	1365.5
1504.5	9604.4	1148.2	5587.8	932.1
3003.5	9965.8	1102.5	6220.4	380.9
4502.5	10377.3	1126.3	6428.8	466.9
6001.5	10745.7	1245.9	6641.6	672.4
7500.5	11030.9	1236.8	6802.9	746.6
8999.5	11013.0	1131.0	6842.9	778.1
10498.5	10994.5	950.2	6822.3	745.1
11997.5	10736.0	791.2	6731.5	690.4
13496.5	10911.9	769.4	6874.1	673.7
14995.5	10799.4	736.3	6652.7	761.8

Table VII.1.1.10. The retentive force [mN] of Titanium Grade II cast clasp.

	Laser (at 1 year)		Non-laser (at 1 year)		Non-laser (at 10 years)	
	Maximum force	Average force	Maximum force	Average force	Maximum force	Average force
No 1.	7537.1	5187.7	10434.2	6590.1	9748.2	6158.4
No 2.	11061.7	7669.0	8394.6	5707.6	10535.0	6843.5
No 3.	8826.0	6080.0	4865.5	4491.4	8333.0	6315.2
No 4.	8276.9	5118.8	5706.6	6570.5	7802.9	6040.9
No 5.	10855.0	9375.3	7508.4	5966.4	8331.4	6526.4
No 6.	9204.6	5630.7	7398.4	7008.4	8229.9	7692.7
Mean	9293.5	6510.2	7384.6	6055.7	8830.1	6596.2
SD	1407.8	1685.0	1974.7	898.3	1064.0	607.8

Table VII.1.1.11. The retentive force [mN] of Cr-Co alloy cast clasp.

	Laser (at 1 year)		Non-laser (at 1 year)		Non-laser (at 10 years)	
	Maximum force	Average force	Maximum force	Average force	Maximum force	Average force
No 1.	15220.0	11061.8	9139.7	6062.3	9692.5	6542.1
No 2.	15592.6	9689.4	11368.7	6569.7	12496.4	6976.1
No 3.	14847.4	11101.1	10355.8	6492.0	12199.2	7904.1
No 4.	12637.2	7202.5	9610.6	6040.8	10493.0	6099.6
No 5.	13261.1	8828.3	11486.8	7658.0	12532.6	8455.4
No 6.	12794.2	7703.3	12441.2	8494.9	12702.7	8390.3
Mean	14058.8	9264.4	10733.8	6886.3	11686.1	7394.6
SD	1309.9	1653.1	1251.5	983.1	1270.3	995.5

Table VII.1.1.12. The retentive force [mN] of Ti6Al7Nb cast clasp.

	Laser (at 1 year)		Non-laser (at 1 year)		Non-laser (at 10 years)	
	Maximum force	Average force	Maximum force	Average force	Maximum force	Average force
No 1.	10983.2	7335.4	9689.1	6080.0	11728.8	8139.5
No 2.	15749.7	8845.6	8178.9	6099.6	10395.0	6138.9
No 3.	16357.4	8669.2	9113.5	5387.1	11192.6	6446.3
No 4.	13288.2	6472.5	10896.5	3678.7	10739.6	6169.4
No 5.	13533.1	8276.9	8550.7	6138.6	9609.8	6275.8
No 6.	12562.2	5855.1	10628.6	6279.1	11130.8	6746.0
Mean	13745.6	7575.8	9509.6	5610.5	10799.4	6652.7
SD	2006.2	1227.6	1100.5	996.7	736.3	761.8

VII.1.2. Distortion of clasp

Table VII.1.2.1. The distance [mm] between the ending point of lingual bracing arm and buccal retention arm of Co-Cr clasps before and after 15000 testing cycles.

	No.1	No.2	No.3	No.4	No.5	No.6	Mean	SD
before	6.795	7.300	7.307	7.002	6.793	6.519	6.953	0.312
after	6.822	7.338	7.363	7.047	6.844	6.566	6.997	0.314
The difference	0.027	0.038	0.056	0.045	0.051	0.047	0.044	0.010

Table VII.1.2.2. The distance [mm] between the ending point of lingual bracing arm and buccal retention arm of cpTi clasps before and after 15000 testing cycles.

	No.1	No.2	No.3	No.4	No.5	No.6	Mean	SD
before	7.506	7.280	7.335	6.885	7.220	7.282	7.251	0.204
after	7.514	7.306	7.338	6.901	7.223	7.286	7.261	0.202
The difference	0.008	0.026	0.003	0.016	0.003	0.004	0.010	0.009

Table VII.1.2.3. The distance [mm] between the ending point of lingual bracing arm and buccal retention arm of Ti6Al7Nb clasps before and after 15000 testing cycles.

	No.1	No.2	No.3	No.4	No.5	No.6	Mean	SD
before	7.251	7.470	7.278	7.221	7.545	7.349	7.352	0.130
after	7.277	7.474	7.280	7.239	7.558	7.352	7.363	0.127
The difference	0.026	0.004	0.002	0.018	0.013	0.003	0.011	0.010

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IX. Summary

All three materials were recommended to be used as a cast clasp for 10 years without distortion of clasp. However, although the retentive force of Ti6Al7Nb is equal to that of CrCo and greater than that of Ti GdII, other properties of Ti6Al7Nb are better than those of CrCo and Ti GdII especially flexibility, corrosion and biocompatibility. Therefore, Ti6Al7Nb was suggested for use for clasp instead of CrCo.

Theoretically the retentive force of non-laser and laser clasp from the same material and shape should be equal. Thus it is possible that after laser welding the clasp was distorted in three directions which cannot be detected by one dimension measurements. By the way, The retentive force of the laser clasp is greater than that of the non-laser one. Even then the non-laser clasp can provide adequate retention for the removable partial denture. Since no clasp was broken during 1 year of use. Laser welding was definitely recommended for repairing of clasp in that period of time.

It is concluded that the quality of this casting machine and technique can be accepted for the alpha-case layer, whereas it is still necessary to improve the porosity of specimen.

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XI. Curriculum Vitae

Mali Palanuwech, DDS.



Nationality:	Thai
Status:	Single
Gentle:	Female
28.02.1974	Born in Munic, Germany Father: Thanong Palanuwech (“Dipl.-Ing” from Munic), born in Bangkok, Thailand; Engineer and business man Mother: Rudee Palanuwech (“Germanistic” from Munic), born in Bangkok, Thailand; Lecturer at TU
1981-1986	Primary school: studied at St. Joseph Convent school, Bangkok, Thailand
1987-1992	Secondary school: studied at Sainampeung school, Bangkok, Thailand
1993-1998	University: studied at the Dentistry faculty, Chulalongkorn university, Bangkok, Thailand (www.chula.ac.th)
1993	Awarded the silver medal of badminton competition at Chulalongkorn University
1993-1998	Representative from dental faculty for being committees and/or player of badminton competition: in dental faculty of Chulalongkorn University, between faculties in Chulalongkorn University and between dental faculties in Thailand

- 1996 Awarded the 1st prize of student researches in dental faculty, Chulalongkorn university
- 1997 Publications: C. Wiwatworapan, B. Pukkavej, P. Chinnanpongsanont, M. Palanuwech: Fluoride release from a resin-modified glass ionomer cement and a polyacid-modified composite resin. CU Dent J 1997; 20: 73-82
- From 1997 Member of treatment programs for rural supported by the Lion Bangkok Arawan Rotary
- 1998-1999 Representative from dental faculty for being a committee of documentation and ceremony of graduated student in 1998 supported by and cooperated with Chulalongkorn University
- 1998-1999 Representative from dental faculty, Chulalongkorn University for being a committee to organize and control the selection for all vacant dental positions of state hospitals in Thailand in 1999 at Embassy hotel supported by and cooperated with state
- 19.03.1999 Awarded the Doctor of Dental Surgery degree (DDS.).
- From 04.1999 Lecturer at the Dentistry faculty and treatment at dental hospital, Thammasat University, Pratumthani, Thailand (www.tu.ac.th)
- From 1999 Member of the Thai Dental Society
- From 1999 Member of the Thai Dental Implant Society
- 1999-2000 Treatment at private clinic: Discovery building branch, Denta-Joy Clinic, Bangkok, Thailand.
- 06-07.2000 Studied german language: Basic course(G3) at Goethe school, Freiburg, German and 1st visit to Tuebingen university
- From 23.02.01 Received a scholarship from German government: Deutscher Akademischer Austauschdienst (DAAD)
- 04-09.2001 Studied German language: Intermediate to advance courses (Oberstufe-DSH) at Speak and Write, Marburg supported by DAAD

- From 10.2001 Studying for doctoral degree (Dr.med.dent.) in the section of Material and Technology of Medicine (Director: Prof. Dr. J. Geis-Gerstorfer) and attending as a visitor dentist for Prosthetic and Implant at the Prosthetic department, Tuebingen University (Director: Prof. Dr. H. Weber), supported by DAAD
- From 2001 Member of the Thai student in German Society. (www.thai-students.de)
- From 2002 Representative from dental study for being a committee of the 1st Thai Student Academic Conference supported by and cooperated with state and private organizations.