

Article

A Novel Technique for the Connection of Ceramic and Titanium Implant Components Using Glass Solder Bonding

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Abstract: Both titanium and ceramic materials provide specific advantages in dental implant technology. However, some problems, like hypersensitivity reactions, corrosion and mechanical failure, have been reported. Therefore, the combining of both materials to take advantage of their pros, while eliminating their respective cons, would be desirable. Hence, we introduced a new technique to bond titanium and ceramic materials by means of a silica-based glass ceramic solder. Cylindrical compound samples ($\text{\O}10 \text{ mm} \times 56 \text{ mm}$) made of alumina toughened zirconia (ATZ), as well as titanium grade 5, were bonded by glass solder on their end faces. As a control, a two-component adhesive glue was utilized. The samples were investigated without further treatment, after 30 and 90 days of storage in distilled water at room temperature, and after aging. All samples were subjected to quasi-static four-point-bending tests. We found that the glass solder bonding provided significantly higher bending strength than adhesive glue bonding. In contrast to the glued samples, the bending strength of the soldered samples remained unaltered by the storage and aging treatments. Scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) analyses confirmed the presence of a stable solder-ceramic interface. Therefore, the glass solder technique represents a promising method for optimizing dental and orthopedic implant bondings.

Keywords: ceramics; titanium; bonding; glass solder; four-point-bending

1. Introduction

Titanium dental implants have been demonstrated to perform very well for a number of years [1]. Although, the biocompatibility of titanium with differently structured surfaces has been proven [2–4], some problems, such as tissue discoloration and hypersensitivity reactions, have been reported clinically [5–7]. Due to their esthetical appearance and their biocompatibility, ceramics constitute a promising alternative implant material [8,9]. On the other hand, failure with dental implants made of zirconia have been reported for single-part [10] as well as multi-part models [11]. Consequently, it seems likely to combine the advantages and to eliminate the disadvantages of both materials. For several years it has been common practice to join metallic abutments and ceramic crowns and veneers, which is often performed by gluing the respective components together. Thus far, comparable applications within the field of prosthodontics for supporting structures have been limited. However, there are several approaches for the bonding of metallic and ceramic materials in varying areas, including brazing, eutectic joining, diffusion, fusion and friction [12].

For example, the bonding of a silicon nitride ceramic (Si_3N_4) to stainless steel (SUS304) used for electrical and mechanical structures by a copper interlayer via active metal brazing with Ag-Cu-Ti was investigated by Takahashi *et al.* [13]. The interlayer was used to reduce the stress induced by the mismatch of thermal expansion coefficients of ceramics and metals. After subjection to four-point-bending, it was found that the thickness of the interlayer affects the mechanical properties of the structure in different ways, resulting in the determination of an optimal interlayer thickness.

Furthermore, approaches to connect titanium and alumina with a molybdenum coating by means of a gold foil under high temperatures were performed [14]. The bond strength of a veneer ceramic to NiCr and CoCr alloys with or without a TiSiN interlayer was the subject of a further study [15] in which the application of the interlayer was conducted by deposition in a nitrogen-reactive atmosphere with a Ti/Si-cathode, resulting in a positive effect on bond strength between the NiCr alloy and the ceramic layer.

A novel partial transient liquid-phase bonding process for bonding a Cf/SiC composite and titanium was recently proposed by Wang *et al.* [16]. Here, mixed powders of Ti_{54.8}Ni_{34.4}Nb_{10.8} (at%) and Nb metal were used as interlayers, enabling more flexible designs of the joint structure.

For the bonding of ceramics and metals the mechanical properties and thermal expansion coefficient of these materials need to be considered [17]. Especially for applications in dental prosthetics, the bonding has to be investigated under humid conditions, since an oral-like environment can adversely affect the performance of dental implants [18].

The combining of ceramic and titanium materials in an attempt to take advantage of their pros, while eliminating their respective cons, seems promising. Hence, a new concept for bonding of titanium and ceramic materials by means of a glass ceramic solder was introduced [19]. This way, a new concept of modular dental implant solutions could be developed and realized: a ceramic implant comprising a materially bonded titanium screw socket, which enables the connection to a corresponding

abutment via a screwed joint. This would result in a dental implant with an all-ceramic outer appearance in combination with the structural functionality of titanium on the inside. While the glass soldering technique has already been described in terms of a modification for ceramic implant surfaces [20,21], its use for connecting metals and ceramics has not been investigated thus far. In this experimental study, the feasibility of this technique was investigated with respect to its mechanical properties under different test configurations in comparison to a commercially available two-component adhesive glue. Furthermore, the glass solder specimens were subjected to fractographic analysis.

2. Materials and Methods

2.1. Test Specimens

Compound samples made of ceramics and titanium grade 5 were prepared for the mechanical investigations. Cylindrical specimens of alumina toughened zirconia (ATZ) and titanium (Ti6Al4V) were fabricated by Metoxit AG (Thayngen, Switzerland) and Primec GmbH (Rostock, Germany), respectively. Both components measured 10 mm in diameter and 28 mm in length, resulting in a final test compound sample length of 56 mm, which was used for the bending tests. In total, 80 compound samples were produced—40 each with bonding via a glass ceramic solder or a two-component glue—enabling sufficient statistical analysis when subdividing both groups according to four different storage regimes ($n = 10$).

2.2. Bonding Process

A glass ceramic solder was used as the bonding agent, which consisted mainly of SiO_2 (63–68 wt%), Al_2O_3 (5–8 wt%), K_2O (5.5–9 wt%) and Na_2O (5.5–9 wt%). Its thermal expansion coefficient was $10 \times 10^{-6}/\text{K}$, which is in the range of Ti6Al4V ($8.9 \times 10^{-6}/\text{K}$) and ATZ ($9 \times 10^{-6}/\text{K}$), as recommended by Zhang *et al.* [17]. The connecting surfaces of all cylinders were preconditioned in a sandblasting device (P-G 400, Harnisch+Rieth GmbH and Co. KG, Winterbach, Germany) with Al_2O_3 particles (110 μm , 2 bar) followed by steaming, while the titanium surfaces underwent a further coating with fusio connect spray Opak B1 (DCM GmbH, Rostock, Germany) and a curing process at 780 °C for 1 min after preheating under a vacuum atmosphere in a ceramic firing furnace (AUSTROMAT 624, DEKEMA Dental-Keramiköfen GmbH, Freilassing, Germany). The application of the powdery base material of the glass solder dissolved in an alcoholic fluid was performed via airbrushing (IMAGO Layerbrush, steco-systemtechnik GmbH and Co. KG, Hamburg, Germany) onto the preconditioned surfaces. The ATZ cylinder was placed above the titanium one, both aligned along their vertical axes. This structure was placed on a firing tray and was further stabilized with a firing pillow/cotton. For curing, the compound samples were thermally treated with the above-mentioned furnace. In contrast to the application as a sole surface modification, as described by Mick *et al.* [20], the glass solder configuration used in this study was fired at a lower curing temperature (*i.e.*, below 850 °C). Thus, a phase transformation of titanium was avoided. Hence, the temperature rose at a rate of 10 K/min under vacuum up to a value of 800 °C and was held for 5 min. After curing and a slow cooling process (1 K/min), the specimens were cleaned by steaming and ultrasonic bathing (Sonorex RK100H, Bandelin electronic GmbH and Co. KG, Berlin, Germany) in distilled water for 30 min at 80 °C.

As a control, the other ceramic and metallic cylinders were bonded using a two-component adhesive glue (NimeticCem, 3M ESPE AG, Seefeld, Germany). The end faces of the titanium and ATZ cylinders were again preconditioned via sandblasting with corundum followed by steaming. The components of the adhesive were mixed according to the manufacturer's instructions with a plastic spatula on a paper tray. The mixture was applied with the spatula as a thin layer to one of the connecting surfaces. Then, the cylinders were again aligned and placed above each other. Surplus glue was removed using a scalpel. Curing occurred within 1 min without any further treatment due to the autopolymerization of the glue. Compound samples after soldering and gluing are depicted in Figure 1a,b, respectively.



Figure 1. Compound samples after glass soldering (a) and adhesive gluing (b) of the ceramic and titanium components.

2.3. Storage Regimes and Mechanical Testing

Within both bonding groups 10 compound samples were tested without any further treatment (group a), while 20 other compound samples were stored in a glass container filled with distilled water for 30 (group b) and 90 days (group c) at room temperature. Ten additional compound samples were subjected to artificial aging for 14 days at 70 °C and 5 atm/4.9 bar (group d).

All compound samples were subjected to a four-point-bending test using a universal testing machine (Z050, Zwick GmbH and Co. KG, Ulm, Germany). The support span was set to 40 mm and the loading span to 20 mm (see Figure 2) with respect to European standard EN 843-1 (setup B). An axial load was applied at a crosshead speed of 0.7 mm/min. The maximum force applied until sample failure was measured for calculating the bending strength.



Figure 2. Four-point-bending test setup for a soldered compound sample (a); shown schematically (b); indicating supports on the bottom and loading noses on the top (black circles).

Statistical analysis was performed with SPSS Statistics (v20, IBM Corp., Armonk, NY, USA). Data were checked for normal distribution using the Kolmogorov-Smirnov-Test and a two-way analysis of variance (2 (bonding) \times 4 (storage) ANOVA) with post-hoc Bonferroni test was conducted. The level of significance was set to $p = 0.05$.

2.4. Fractographic Analysis

In addition to mechanical testing, the fractured surfaces of the samples were analyzed via scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) utilizing a DSM Gemini 982 (Carl Zeiss AG, Oberkochen, Germany). Prior to investigation, the samples were attached to a special holder and the surfaces of interest were sputtered with carbon. As representing the worst case scenario, two titanium (5_Ti, 10_Ti) and two ceramic cylinders (5_ATZ, 10_ATZ) of two artificially aged compound samples of group (d) (5,10) were examined exemplarily. Each respective fracture surface showed areas comprised of either mostly titanium or glass solder, resulting in eight investigated areas: 5/10_Ti_gs, 5/10_Ti_Ti, 5/10_ATZ_gs, 5/10_ATZ_Ti (Figure 3). For EDX analysis the surfaces were scanned at a magnification of $\times 1000$ within a measuring field of $30 \mu\text{m} \times 25 \mu\text{m}$. The element silicon (Si) was used as an indicator for the detection of glass solder, since SiO_2 is its main component.

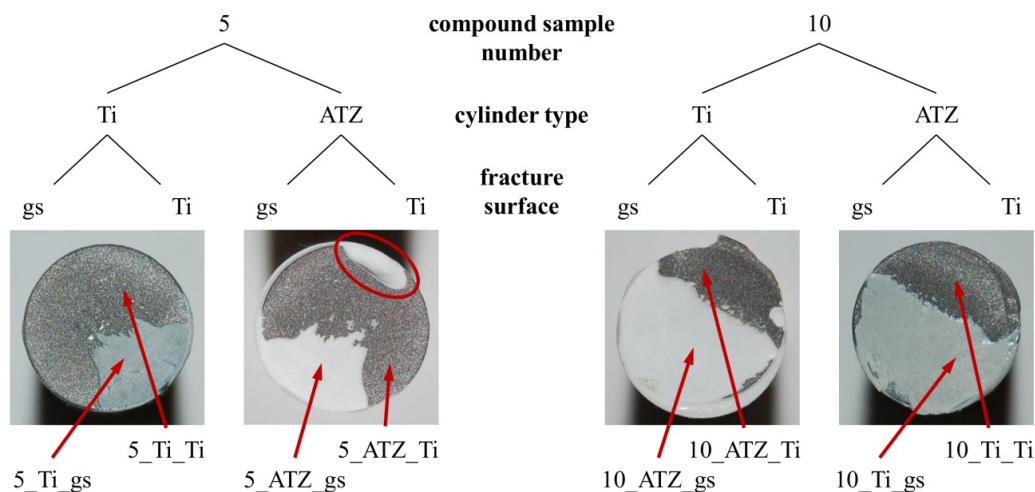


Figure 3. Overview and nomenclature for the investigated fracture surfaces of two exemplary soldered samples; determining the related compound sample number (5, 10), the cylinder type (Ti, alumina toughened zirconia (ATZ)) and the specific fracture surface area (gs (glass solder), Ti). The arrows mark the regions examined for scanning electron microscopy (SEM) imaging and energy-dispersive X-ray (EDX) analysis. The second left image further depicts an area of the ceramic cylinder that cracked due to random forces and motions occurring directly after failure of the samples.

3. Results and Discussion

3.1. Mechanical Testing

For all data sets ($n = 10$) the Kolmogorov-Smirnov-test revealed a normal distribution. With the 2 (bonding) \times 4 (storage) ANOVA no significant interaction effects between the factors bonding and

storage were observed. The bonding method was found to be a significant main effect on the bending strength ($F = 316.057$, $p < 0.001$, $\eta_p^2 = 0.814$). Hence, four-point-bending of the compound samples revealed lower bending strength for glued compound samples in comparison to the soldered ones (Table 1). On the other hand, the storage regime was a non-significant main effect ($F = 1.054$, $p = 0.374$, $\eta_p^2 = 0.042$). However, certain tendencies might be derived. The untreated glued compound samples (a) had higher values than all three other storage conditions (b–d), while (c) was lower than (b) and (d) (Figure 4). The latter finding might be an indication that the long-term storage in humid conditions has a larger influence on the mechanical properties of the adhesive glue than the artificial aging process. Possibly, water diffuses either into the polymer itself or into micro gaps in the interface. Within the soldered compound samples, only group (b) showed lower bending strength, while the others were at the same level. In contrast to the controls, the mean bending strength seemed unaffected by long-term storage under humid conditions or with artificial aging. These findings indicate the advantages of the glass solder fixation technique over conventional methods regarding long-term mechanical stability when applications in prosthodontics are considered.

Table 1. Obtained bending strength (mean value (M) and standard deviation (SD)) for soldered and glued compound samples in native condition (a); after 30 or 90 days in humid condition (b) and (c), respectively; and after artificial aging (d). Furthermore, the mean differences between the bonding methods as well as the boundaries of the 95% confidence interval are listed.

Storage regime	Glass solder M (SD) [MPa]	Adhesive glue M (SD) [MPa]	Mean differences (95% CI) [MPa]
(a)	118 (33)	30 (4)	88 (67–110)
(b)	104 (40)	17 (7)	87 (66–108)
(c)	117 (36)	13 (2)	104 (82–125)
(d)	119 (23)	18 (1)	101 (80–122)

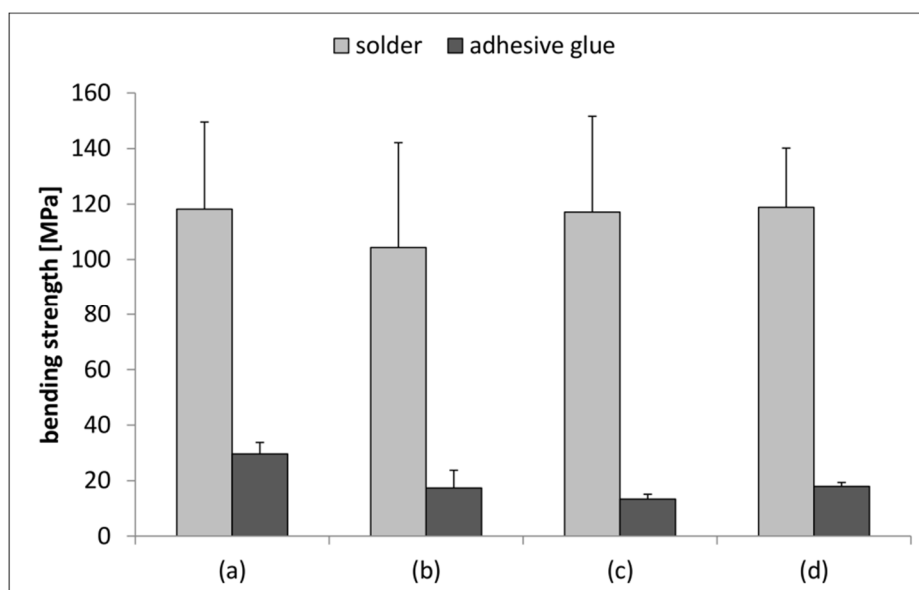


Figure 4. Bending strength values for soldered and glued compound samples in native condition (a); after 30 or 90 days in humid condition ((b) and (c), respectively); and after artificial aging (d).

In general, four-point-bending was preferred to three-point-bending due to a critical load transmission directly at the bonding interface in the latter situation. Furthermore, four-point-bending generates a constant bending moment within the entire loading span, enabling the investigation of a larger volume of the samples for failure occurrences.

3.2. Fractographic Analysis

With fractography, very homogeneous and predominantly defect-free glass solder surfaces were detected. This finding indicates good wettability and an optimized application of the glass solder. The areas of the fracture surfaces comprising mostly titanium tend to be located close to the bottom side of the compound sample, which means that the outer titanium layer is more vulnerable to tensile stress than the ceramic, the glass solder, or the ceramic-solder-interface. In only one case pure ceramic was detected, indicating a generally stable interface between ceramic material and applied glass solder.

Since the investigation of both samples led to similar results, they are only presented for compound sample 5. At the titanium area of the fracture surface of the titanium cylinder of compound sample 5 (5_Ti_Ti) the surface mainly contained titanium and only a few areas of glass solder (Figure 5). Consequently, EDX analysis revealed high levels of titanium/aluminum and less silicon peaks (Figure 6).

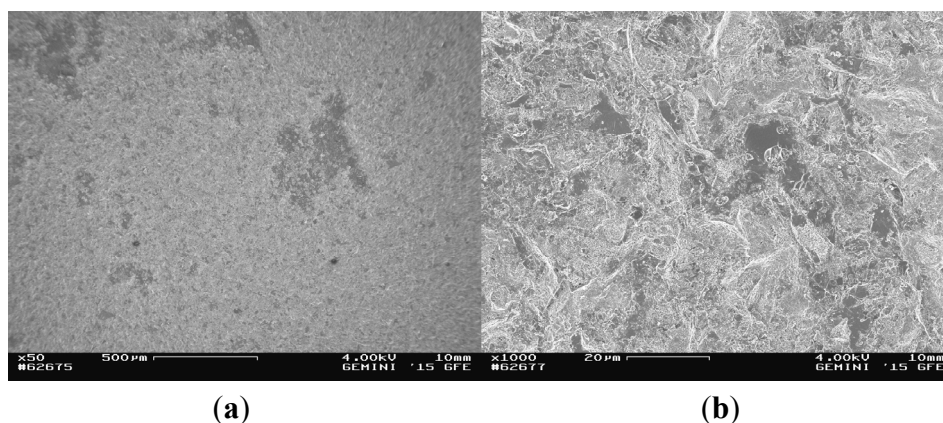


Figure 5. SEM images of the fractured surface of 5_Ti_Ti at magnifications of $\times 50$ (a) and $\times 1000$ (b).

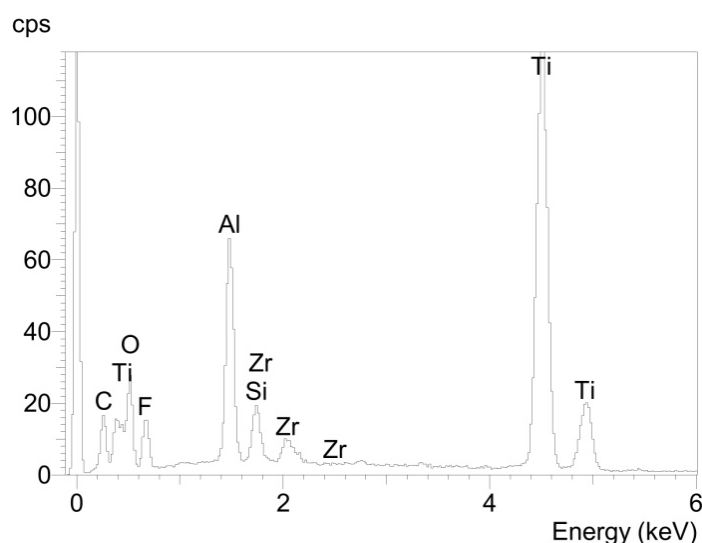


Figure 6. Elemental spectrum for sample 5_Ti_Ti determined using EDX analysis.

The glass solder area of the fracture surface of the titanium cylinder of compound sample 5 (5_Ti_gs) was nearly entirely covered with glass solder material (Figure 7), which was confirmed by EDX analysis (Figure 8), showing a high peak for silicon, while titanium was barely detected at all.

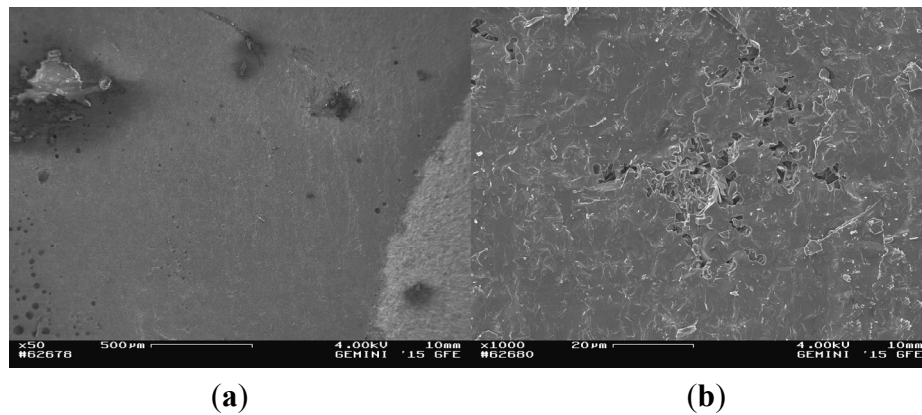


Figure 7. SEM images of the fractured surface of 5_Ti_gs at magnifications of ×50 (a) and ×1000 (b).

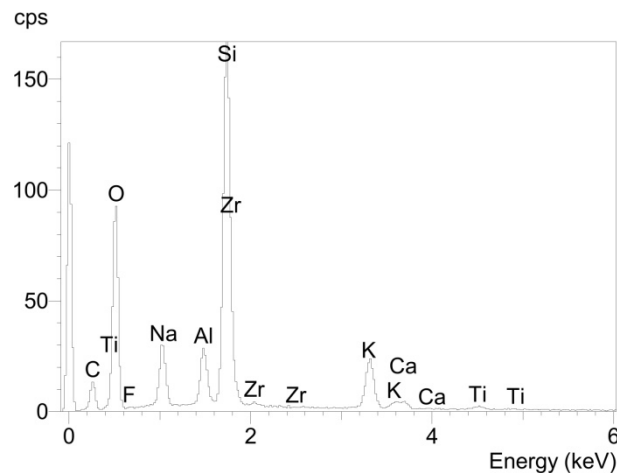


Figure 8. Elemental spectrum for sample 5_Ti_gs determined using EDX analysis.

At the titanium region of the ceramic cylinder of compound sample 5 (5_ATZ_Ti) (Figure 9), the surface was covered nearly entirely by titanium, with only a small amount of glass solder, as confirmed by EDX analysis (Figure 10).

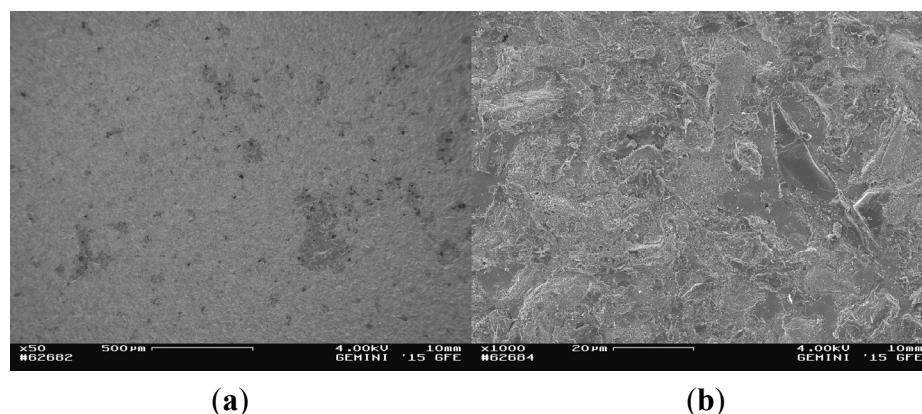


Figure 9. SEM images of the fractured surface of 5_ATZ_Ti at magnifications of ×50 (a) and ×1000 (b).

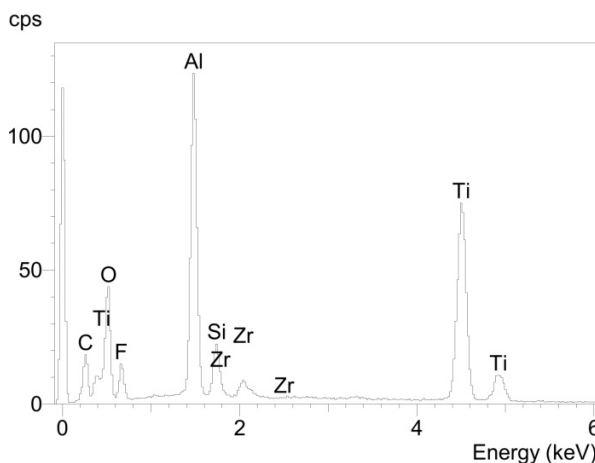


Figure 10. Elemental spectrum for sample 5_ATZ_Ti determined using EDX analysis.

At the glass solder area of the ceramic cylinder of compound sample 5 (5_ATZ_gs), a surface covered nearly entirely with glass solder was observed (Figure 11). This particular material led to a very homogeneous impression and was nearly free of inclusions or bubbles. Again, EDX analysis revealed a high peak of silicon and a negligible amount of titanium (Figure 12). In this case, areas of uncovered ceramic (Zr peak) were also found.

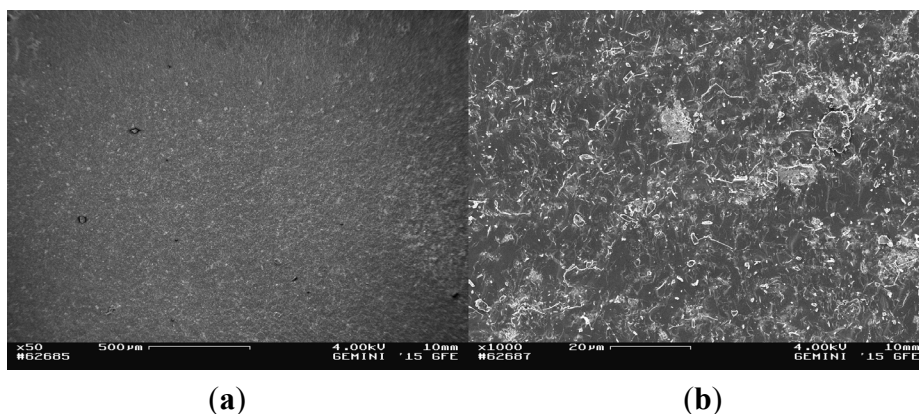


Figure 11. SEM images of the glass solder area of the fractured surface of the ceramic cylinder of compound sample 5 (5_ATZ_gs) at magnifications of $\times 50$ (a) and $\times 1000$ (b).

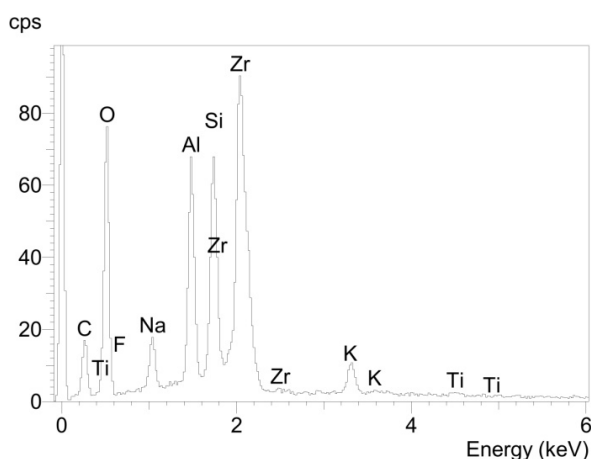


Figure 12. Elemental spectrum for sample 5_ATZ_gs determined using EDX analysis.

Our results indicate that within all compound samples the fractures mainly propagated within the glass solder-filled joint. However, in some regions the oxide layers of the titanium cylinders were also affected. Both visual evaluation and EDX analysis clearly showed that the fracture surfaces of the ATZ cylinders contained more glass solder than the titanium cylinders. This finding, as well as the above-mentioned vulnerability to tensile stress, might be an indication of a certain instability of the glass-solder-titanium interface due to the oxide layers, which the titanium creates during thermal curing of the glass solder. Furthermore, these oxide layers lead to an unaesthetic surface appearance of areas not in contact with the bonding material (Figure 1a). It might be possible that this effect influences the bending strength of the titanium itself. However, the strength of the compound samples is determined by their weakest link, which is clearly the bonding interface. Therefore, a reduction of the titanium strength due to the firing process seems negligible. The oxide formation may be removed by post-processing via light machining, electro-polishing or acid treatment. However, the preferable approach would be an optimized firing process using inert gas for protection since this procedure might also stabilize the critical interface.

Besides the presented results, our experimental study still has some limitations. Mechanical investigations were performed on standard specimen geometries under standard conditions in four-point-bending tests. Moreover, no dynamic, only static, mechanical properties were determined. Therefore, no reliable conclusions regarding the durability of the investigated bonding in real dental implant designs and prosthetic restorations can be drawn. Furthermore, it remains unclear if, and to what extent, the bonding process affects the mechanical properties of the ceramic and titanium themselves, similar to the observations related to the high-temperature coating of ceramics with glass solder [21]. Since the glass solder is suspected to diffuse into the outer layer of the ceramic and, therefore, constitutes a materially bonded connection, an in-depth study of the material science might be of interest but was not performed within the current work. Moreover, challenges to using glass as a filler to join ceramics, like poor toughness, low Young's modulus and susceptibility to stress corrosion were not investigated. Another aspect that was not examined is a possible influence of the bonding on the biological behavior of the surrounding tissue. These topics should be focused in further research studies.

Since the present study is of a basic nature, the findings may be translated to future applications of titanium-ceramic-composites in dental prosthetics. The classical use of adhesive glues could be replaced by newly developed ceramic implants with inner titanium components, combining the aesthetic appearance of ceramics with the functionality of titanium. Another possible field of application lies in orthopedic implant technology. Because the revision surgery of total hip endoprostheses with an intact hip stem bears the risk of fracture of the ceramic ball head applied to a used metal taper of the stem, it is recommended to use either metal ball heads or modular systems [22]. The soldering of a metallic sleeve to the ceramic ball head used for revision surgery could be a possible future application, although further investigations utilizing specific test setups are required.

4. Conclusions

Within the present study we introduced a new technique for bonding of titanium and ceramic implant materials by means of a silica-based glass ceramic solder. Thermal processing of all mating parts lead to a mechanically stable connection. Therefore, this novel technique provides interesting

possibilities for the development of new implant solutions or the modification of existing designs of dental and orthopedic implants.

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Author Contributions

Enrico Mick wrote the manuscript and performed and evaluated the tests. Joachim Tinschert conducted the SEM and EDX analyses. Aurica Mitrovic prepared all of the specimens for investigation. Rainer Bader designed the experimental study and revised the manuscript.

Conflicts of Interest

Enrico Mick, Joachim Tinschert and Rainer Bader declare no conflict of interest. Aurica Mitrovic is a managing partner of ZM Praezisionsdentaltechnik GmbH.

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