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Ceramic Bonding to Biocompatible Titanium Alloys Obtained by Powder Metallurgy

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Abstract: The shear bond strength between a ceramic material (Titankeramik®, Vita Zahnfabrik, Germany) and two biocompatible titanium alloys was investigated. Ti-13%Nb-13%Zr (TNZ) and Ti-35%Nb-7%Zr-5%Ta (TNZT) alloys were obtained based on the blended elemental technique followed by a sequence of cold uniaxial and isostatic pressing and sintering. Characterization involved microstructural analysis (SEM) and crystalline phase identification (XRD). Subsequently, samples were machined to 4 x 4 mm with a base of 5 x 1 mm. The base metals were blasted with Al_2O_3 particles followed by the application of a coupling agent and opaque ceramic. After ceramic firing, the specimens were loaded in a universal testing machine (0,5mm/min). XRD revealed the presence of α and β-phases for TNZ, and peaks related to β phases and Nb and Ta for the TNZT alloy. SEM evaluation (TNZ) depicted remaining pores and biphasic microstructure formation. SEM micrographs of the TNZT alloy revealed good densification and a homogeneous β structure. Shear bond strength data (MPa) were statistically analyzed (one-way ANOVA and Tukey test, α=.05) revealing that TNZT (37.6 ± 2.91) presented significant higher values (p=0.0002) compared to TNZ (26.03 ± 2.92). In conclusion, it seems that Ti alloy composition plays a significant role on ceramic bonding.

Introduction

Continuous efforts to find the ideal metal for use in dental prostheses fabrication has resulted in an increased use of titanium and its alloys due to potential property combination such as high strength-to-weight ratio, good corrosion resistance in physiological environments, fatigue resistance, and low elastic modulus [1-3]. In addition, other peculiarities, including low thermal conductivity, low coefficient of thermal expansion, and their biocompatibility, have rationalized research investments regarding the use of these alloys in implant prosthodontics [1,4].

The interest for the (α+β) Ti-6Al-4V alloy in the biomedical field had a considerable increase in the past five years. However, these alloys, originally designed for aerospace applications have been related to possible harmful effects due to aluminum and vanadium [5-7]. Low elastic modulus titanium alloys such as, Ti-13Nb-13Zr and Ti-35Nb-7Zr-5Ta have received special attention due to their chemical composition, comprising highly biocompatible metallic elements, and improved corrosion resistance compared to cpTi [3,8-11]. For dental clinical use, such as metal-ceramic restorations, these alloys must be able to bond to dental porcelains.

In general, the mechanism of ceramic bond to a metal alloy is attributed to Van-der-Waal's forces, mechanical interlocking between both materials and chemical bonds between the ceramic and an oxide layer. The later mechanism is established during the dental porcelain firing process on the alloy's surface by oxidation of the base metals Bagby et al. [12]. The aim of the present study was to investigate the metal-ceramic shear bond strength (SBS) of Ti-13Nb-13Zr and Ti-35Nb-7Zr-5Ta alloys obtained by powder metallurgy. Also, interfacial failure mode was assessed by scanning electron microscopy (SEM).

Experimental Procedure

Powder metallurgic process

Ti-13Nb-13Zr (TNZ) and Ti-35Nb-7Zr-5Ta (TNZT) alloys were obtained based on the blended elemental (BE) technique followed by a sequence of uniaxial and cold isostatic pressing with subsequent densification by sintering of the starting powders in hydrided state [11].

Titanium powders were obtained by hydriding reaction at 500°C in a vertical furnace for 3 hours under a pressure of 10^{-7} Torr. Temperatures around 800°C was employed in order to obtain Nb, Zr, and Ta powders. After cooling at room temperature, the brittle materials were milled in a rotative mill with titanium balls under vacuum (10^{-2} Torr). The starting powders were weighed and dried for one hour in stove (100°C) and blended for 30 minutes in a rotative mill. After blending, the powders were cold uniaxially pressed under 80 MPa in a cylindrical matrix. Subsequently, the samples were encapsulated under vacuum in flexible rubber molds and cold isostatically pressed (CIP) at 300 MPa during 30 s. Finally, green bodies were sintered in high vacuum condition (Thermal Technology Inc. model Astro 1000 equipment) at 1500 °C with heating rates of 20°C/min. After reaching the nominal temperature, samples were hold at the chosen temperature for 2 h and then furnace-cooled to room temperature. Density was determined by geometrical method. Crystalline phase and microstructure characterizations were performed by X-ray diffraction analyses (XRD, DMAX 2000, Rigaku) and scanning electron microscopy (SEM, Philips XL 30), respectively. Afterwards, all the titanium metallic structures, twenty-four specimens of each group (TNZ and TNZT alloys), were machined to 4 x 4 mm with a base of 5 x 1 mm (Fig. 1a).

Ceramic Application

Prior to ceramic material application, all the metallic structures were cleaned and sandblasted for 10 seconds with 150 μm Al_2O_3 particles at a fixed distance of 2.0 cm and pressure of 2.0 bars. Cleaning of the sandblasted specimens was performed according to the manufacturer's instruction before receiving the bonding agent. After surface preparation, ceramic specimens (Titankeramik, Vita Zahnfabrik, Germany) were fired onto the different metallic surfaces. First, a layer of bonding agent of Titankeramik system was applied onto the flat metallic surfaces, baked, and two layers of opaque ceramic material were applied. After the cycle of firing and cooling, each metallic structure was fitted in one of the ten holes of a metallic matrix (Fig. 1b), with the purpose to help the insertion of 4 mm height of the ceramic. The dentine mass was applied and the sets ceramic/titanium were carefully removed. The samples of the two groups were placed in an oven for ceramic firing completion. A second cycle of ceramic firing was performed in order to compensate the contraction generated in the first cycle. Thus, the samples were fitted again in the matrix in order to insert the missing material. The application of bonding agents, opaque, and dentine ceramics layers were performed following manufacturer's recommendations (Table 1).

Table 1 - Vita Titankeramik® firing procedures.

	Base temp. (ºC)	End temp. (ºC)	Temp. Rate of increase (ºC/min)	Holding Time (min)	Vacuum (bar)
Bonder	400	800	60	1:00	6
Opaque	400	790	110	1:00	4
First dentine	400	770	50	1:00	8
Second dentine	400	770	50	1:00	8
Lustre firing	400	770	100	1:00	4

After these procedures, the samples were stored in distilled water at 37ºC prior to mechanical test.

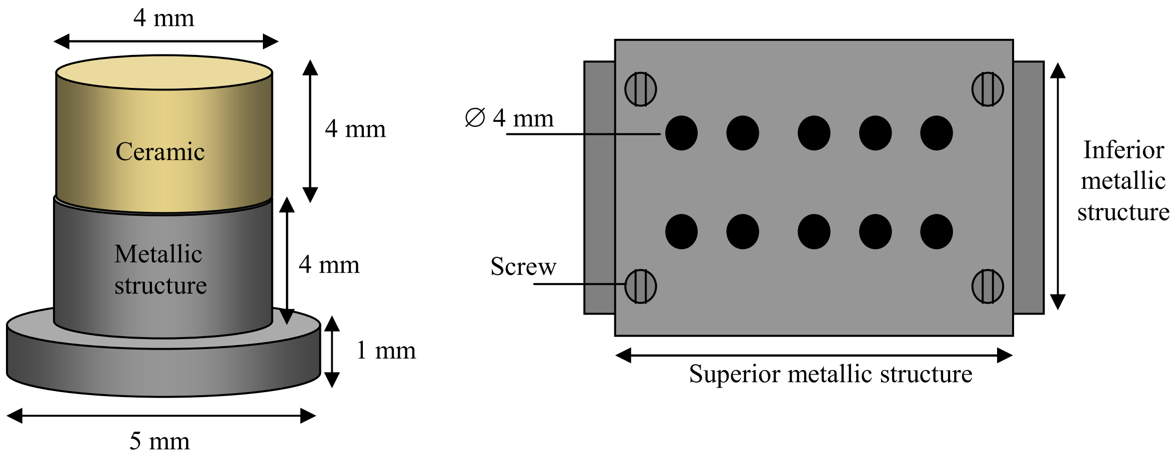
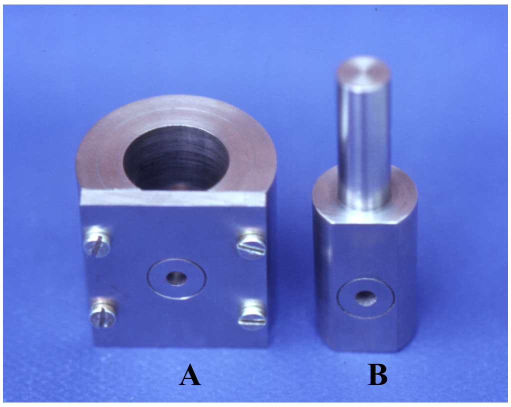


Fig. 1 - a) Schematic illustration of titanium structure/ceramic specimens; b) metallic matrix for ceramic insertion.

Mechanical Testing

For mechanical shear test assessment, a stainless steel device (Fig. 2a) consisting of two independent parts (A and B) was used. Part A, initially cylindrical, underwent an adaptation that generated a 4 mm wide flat surface to allow the insertion of part B in its interior. The internal part (B) of the device followed the same configuration of the external (A) and worked like a piston during mechanical testing. In the flat face of each piece, 4 mm diameter perforations were performed so that the parts dislocated relative to each other during testing (Fig 2b). The alignment between holes allowed the introduction of the specimen through both parts simultaneously. Thus, the ceramic portion of the sample remained lodged into interior of the piston (B), while the metallic part was located in part A. The set up was positioned in a universal testing machine (Instron model 4301 series H0321, Birmingham, UK), with a 500-kg load cell and a crosshead speed of 0.50 mm/min aiming to stress the metal-ceramic interface until failure occurred. Using the metal-ceramic interfacial area, the load at fracture was then converted to the shear bond strength (MPa). The data was subjected to one-way analysis of variance followed by the post hoc multiple range Tukey test (α=.05).



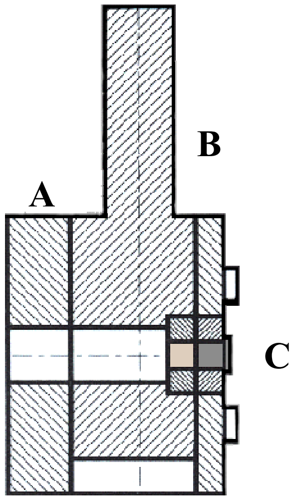


Fig. 2 - a) Stainless steel device for mechanical test, parts A and B; b) Test apparatus: A, external portion; B, internal portion; C, specimen.

Results & Discussion

Titanium alloy characterization

After sintering, the samples presented high densification, approximately 93% for both alloys. X-ray diffraction analysis revealed α and β phase peaks for TNZ alloy. Peaks related to hydrides, oxides, or intermetallics were not found (Fig. 3). The TNZT alloy presented β-phase peaks related to Nb and Ta. SEM showed the presence of residual pores for TNZ (Fig. 4a). The microstructural characteristics of TNZT (Fig. 4b) showed densification, with complete dissolution of alloying elements in the titanium matrix. The results show that a β-homogeneous microstructure was obtained in the whole sample extension.

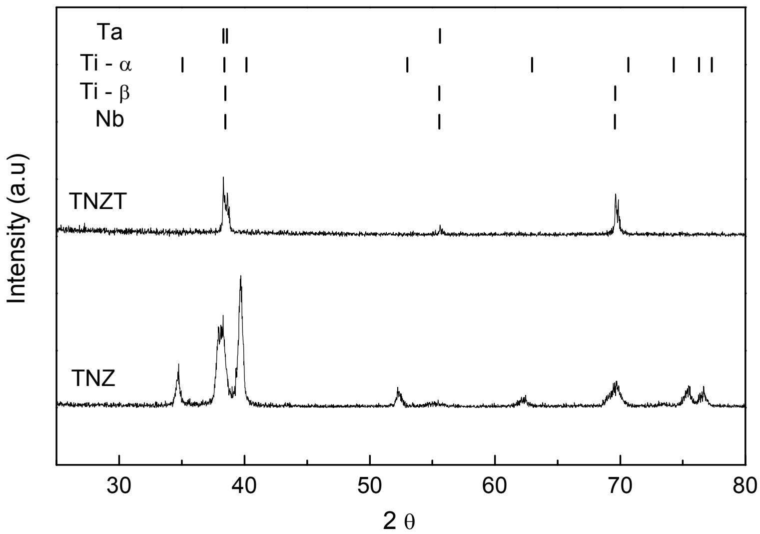


Fig. 3 - X ray diffraction patterns of Ti-13Nb-13Zr (TNZ) and Ti-35Nb-7Zr-5Ta (TNZT) alloys after sintering at 1500 °C/2h.

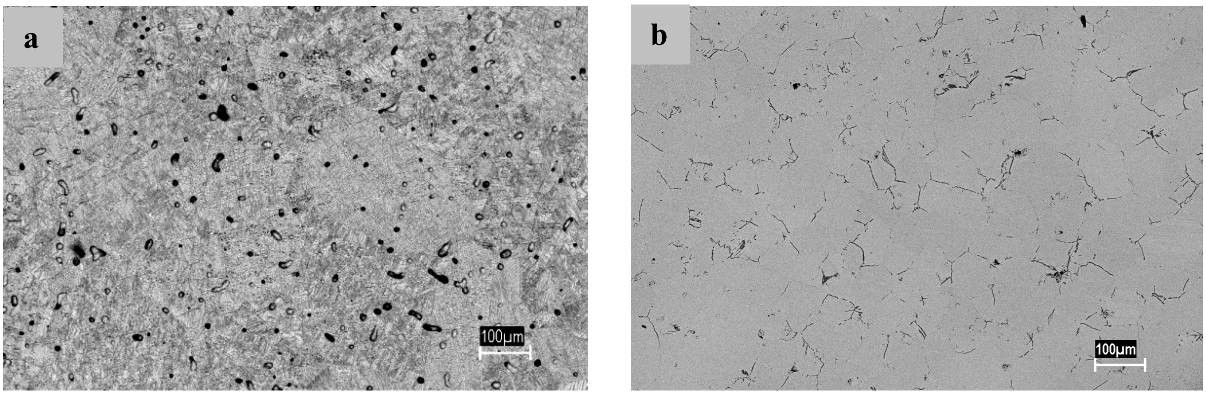


Fig. 4 - SEM micrographs of the powder metallurgic processed Ti-based alloys. a) Ti-13Nb-13Zr alloy and (b) Ti-35Nb-7Zr-5Ta alloy.

Ceramic bonding

One-way ANOVA showed significant difference between titanium-porcelain experimental groups (Table 2). Results of the Tukey's multiple comparison test revealed that TNZT/ceramic had significantly higher bond strength than the TNZ alloy (Fig. 5). The values found for these new and highly biocompatible titanium alloys were considered to be acceptable, since both Ti-alloys developed a ceramic bonding according to the minimum value (25 MPa) described in ISO 9693 [13]. However, given that the SBS values found for the different alloys were significantly different, strong indication that the interphase/interfacial oxide layer formation on these two titanium alloys may be different. This different short- and long- range interactions between substrate alloy and ceramic material may have an influence in shear strength values.

Table 2 - ANOVA for shear bond strength (MPa) by base metal group.

Source	SS	Df	Mean Square	F-Ratio	p-Value
Between groups	1607.3	1	1607.3	5,455	0.0002
Within groups	4636.52	46	100.794	4,856	
Total (Corr.)	6243.82	47			

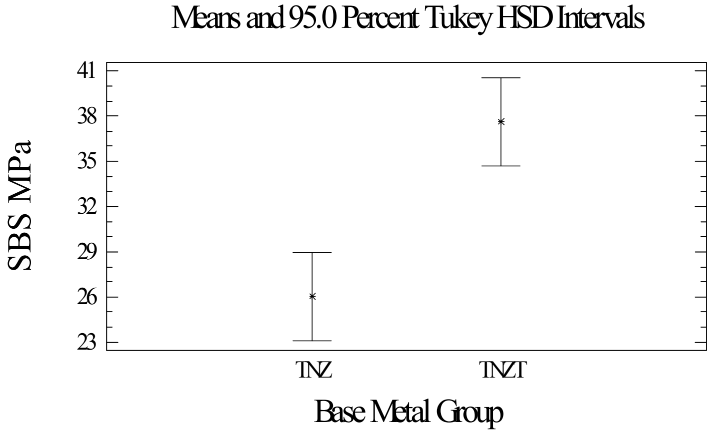


Fig. 5 - Means and standard deviations of the shear bond strength (MPa) for the TNZ and TNZT alloys.

The mean bond strength values found in the present study for both TNZ and TNZT alloys were (26.03 ± 2.92) and (37.6 ± 2.91), respectively, which are comparatively higher than the values reported by Tróia et al. [14] for Ti–6Al–4V/Titankeramik (25.6 ± 3.36) and cpTi/Titankeramik (24.99 ± 2.60) using a three-point flexural test. The greater values associated to the TNZT/Titankeramik specimens are possibly related to post-mechanical testing SEM, where it was observed larger quantities of ceramic adhered to the metal surface compared to TNZ specimens (Fig. 6). The mode of failure was classified as adhesive for failure at the metal-ceramic interface or cohesive for failure within the ceramic material. Representative micrographs indicated that most of the bond failures examined was adhesive for both titanium/ceramic combinations (Fig. 6). The micrograph of the Ti–13Nb–13Zr/Titankeramik surface after shear test also demonstrate residual ceramic adhered on the metal surface. However, these were present in much smaller quantities compared to Ti-35Nb-7Zr-5Ta/Titankeramik group.

The compatibility between thermal expansion coefficients of titanium and ceramics constitutes an excellent factor for adhesion establishment [12]. Several investigations have pointed out the difficulty involved in achieving reasonable bond strengths between low fusing porcelains and titanium due to the fragility of the oxide layer contributing to reduce or to optimize loss of adherence [14-15]. On that regard, more studies should be conducted for a better understanding of important properties such as the coefficient of thermal expansion and the composition of oxide layers related to Ti-13Nb-13Zr (TNZ) and Ti-35Nb-7Zr-5Ta (TNZT) alloys in order to improve the metal-ceramic bonding.

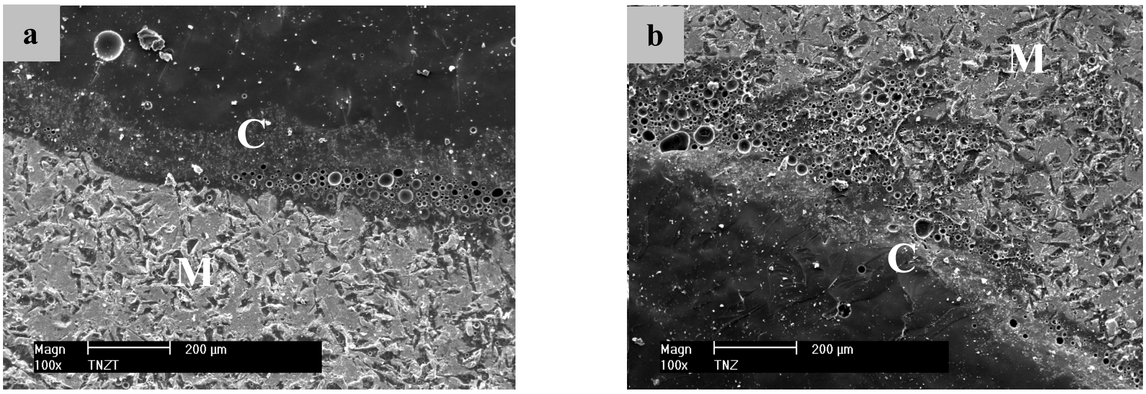


Fig. 6 - SEM micrographs of de-bonded surfaces of the powder metallurgic processed Ti-based alloys. a) Ti-35Nb-7Zr-5Ta alloy and (b) Ti-13Nb-13Zr alloy. Ceramic remnants (C) could be identified on metal as dark areas, in contrast, light regions represented metal surface (M).

Conclusion

The shear bond strength values achieved for both titanium alloys are considered acceptable according to ISO 9693. Also, higher shear bond strength values associated to the TNZT suggest that the oxide layer formed on this titanium alloy may support better integration at the metalloceramic interface/interphase.

Acknowledgements

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