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Anodic bonding of titanium alloy with bioactive glass

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ABSTRACT

The aim of this paper is to report the use of the anodic bonding technique to bond titanium alloy and two different bioactive glasses aiming the medical application of these biomaterials. Ti alloy and bioactive glasses 52S4.6 and 45S5 were successfully bonded using anodic bonding technique for range of temperature and applied potential. The effects of anodic bonding parameters over the total charge transferred and the bonding time were evaluated. The adhesion of Ti alloy and bioactive glasses was measured by shear test. Due to polishing process, titanium alloy samples shown a slightly rounding and consequently the bonding area was limited to part of the sample area. It was found the temperature and potential have effect with statistical significance over the total transferred charge and the bonding time. The results herein discussed suggest the viability of anodic bonding added to process versatility and material compatibility for the use of bioglass and Ti alloy bonded together on medical application.

1. Introduction

Bioactive glasses have been used in medical applications since they were introduced by Hench [1]. Among all bioactive materials, bioactive glasses show the best-known bioactive behavior [2,3]. This family of bioactive materials was originally developed by Hench based on the SiO_2-P_2O_5-CaO-Na_2O composition system [1]. Thus, bioactive glasses are typically silicate glasses with silica content below 60 wt%. This is an important requirement since glasses with silica contents greater than 60 wt% are no longer bioactive [4]. Since the introduction of bioactive glass, a great number of bioactive glass (and glass–ceramic) compositions have been developed and studied in order to tune their bioactivity and to adjust their properties for specific applications [5]. However, due to their poor mechanical properties, bioactive glass materials cannot be used in load bearing applications such as hip replacements and osteosynthesis, where pure metals and metal alloys are the materials of choice. On the other hand, attention has been given to non-load bearing applications where bioactive glass materials have been used in bone defects repair mainly through the development of scaffolds [6,7].

Titanium and its alloys possess the good mechanical properties for load-bearing medical applications, but show no bioactive responses when in contact with living tissues [8]. Several surface treatments have been proposed to improve important characteristics such as increase in roughness and porosity, change in chemical composition and crystal structure at the surface, in order to promote a surface modification of titanium implants aiming the bioactivity [9].

One of the many ways to turn titanium surface bioactive is to coat it with an osteoinductive material as bioactive glass by means of plasma spray technique [5,10]. Investigations show that the plasma spray process does not compromise the bioactivity of bioactive glasses. On the other hand, the main problem of thermal spraying is the relatively poor adhesion of bioactive glass coatings to metal substrate [5]. In order to solve this problem, various strategies may be employed. Goller [10], e.g., used a bond coat layer to increase the bioglass coating adhesion. A three times increase in bonding strength was achieved. However, this result was obtained at the cost of an additional step on an actually complex process and introducing a new substance that is normally harmful to bioactive response. Alternatively, many other coating techniques have been studied aiming the production of a bioactive glass coating [5]. However, no attention has been given to the anodic bonding technique as a method to bond bioactive glasses and titanium to produce a coating or to modify the metal surface.

Anodic bonding is a technique widely used to bond glasses to metals or semiconductor materials. It is recognized as a reliable and simple way to achieve glass to metal bonding, mainly on micro electromechanical devices where silicon is bonded to Pyrex. A comprehensive review of this technique is provided elsewhere [11]. Anodic bonding was first developed by Wallis and Pomerantz in the 1960s [12] and its basic procedures had almost not changed since there. The anodic bonding is

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achieved by applying a dc potential (100 to 1500 V) through the glass-metal pair in temperatures ranging from 200 to 500 °C in a simple experimental setup with no need of complex and expensive equipment as used in plasma spray coating techniques.

The main mechanism attributed to anodic bonding process is related with the formation of a negatively charged region, which can be due to formation of a Na^+ depleted layer by migration of this ion under the electric field established due the dc applied potential. On the glass side of the interface with the metal substrate a negative charge is formed and an electrostatic force pulls the surfaces together bringing them into intimate contact. Non bridging oxygen from glass reacted to anode and permanent bonds are then formed via oxidation at the interface [11]. Although this explanation has been developed primarily within the context of silicon anode substrates, it has been shown to be applicable to a number of metals as well (e.g., Kovar, Al, and Fe) [11,13].

A high strength bonding between metal and glass materials can be achieved with anodic bonding technique [11]. In general, failure of bonded materials is not along the bonded interface. Instead, it occurs at the glass indicating that strong bonding has been achieved, so that the bond is not the weakest part of the system. Usually the failure mode reported is the glass fracture indicated by the residual glass that remains on the bonded interface [11,14,15].

The aim of this paper is to report the use of the anodic bonding technique to bond titanium alloy and two different bioactive glasses aiming the medical application of these biomaterials. The effects of anodic bonding parameters over the total charge transferred and the bonding time were evaluated. The adhesion of Ti alloy and bioactive glasses was measured by shear test. A theoretical model was used in order to clarify the relation between the parameters applied.

2. Materials and methods

2.1. Substrates

Titanium alloy (medical grade Ti-6Al-4 V ELI) and two bioactive glasses close to 45S5 and 52S4.6 Bioglass® in chemical composition were used. Bioglass samples were prepared by mixing and melting oxide reagents to lead to the glass composition 45 - SiO_2; 6 - P_2O_5; 24.5 - Na_2O; 24.5 – CaO named 45S5 and 52 - SiO_2; 6 - P_2O_5; 21 - Na_2O; 21 - CaO (weight percentage) named 52S4.6. The obtained rod bars were cut to obtain face parallel discs that were after sectioned in four pieces each. These particular bioactive glasses were chosen for the present study due to their very high bioactivity [16].

Ti alloy and bioglass were successively graded with SiC papers and polished using 3 μm diamond paste and colloidal silica suspension to obtain a mirror-like finish and then cleaned in ultrasonic bath with acetone, isopropanol and distilled water prior the bonding. The surface roughness (root mean square values - Rq) of Ti alloy and bioglass samples were obtained using a profilometer (Taylor Hobson – TalySurf 2) after the surface preparation.

2.2. Anodic bonding

To achieve the bonding a programmable dc power supply (Chroma 62012P-600-8) and a furnace (Qimis Q317M) were used. The bond was achieved applying the potential at temperatures shown in Table 1. A factorial experimental planning 2^2 with four blocks was chosen in order to evaluate the effects of anodic bonding parameters over the total charge transferred and the bonding time, as well as over the bonding strength. Each experiment was performed with three replicates. For this purpose a multi-variable variance analysis was employed with a confidence level of 95%. The blocks are described by the bioglass used and by the control method of the bonding process (total charge transferred or bonding time).

Table 1
Parameters used in the factorial experiment design.

Levels	Factors	
	Temperature (°C)	Potential (V)
1	300	600–500
2	250	500–400

Preliminary tests shown that relatively long bonding times (close to 12 h) were necessary to obtain a good bonding using a constant applied dc potential. In order to reduce this bonding time, a pulsed dc potential as a square waveform was applied as described by Lee et al. [17]. The difference between base and peak potential and their time period duration were 100 V and 30 s, respectively. These parameters were chosen since they show the greatest bonding time reduction according results from Lee et al. [17].

Raman spectra were used to assess the bioglass structure after the anodic bonding (Confocal Raman Microscopy Witec Alpha 300R). The spectra were obtained using a laser with wavelength of 532 nm. Integration of 10 expositions adding up to a total accumulation period of 30 s was used. The spectra were collected on the glass surface that was in contact with the anode during the anodic bonding. X-ray diffraction technique (XRD – Shimadzu XRD 7000) was used to investigate the crystalline structure of bioactive glass after the anodic bonding. The XRD measurements were collected in the Bragg–Brentano geometry with Cu Kα radiation (λ = 1.54 Å), running at 40 kV and 20 mA in a range between 20° and 60° and scan speed of 1.0°/min.

Cross sections of bonded region were prepared by mounting the bonded samples with phenolic resin and cutting them in slices with thickness of about 2 mm. Scanning electron microscopy (SEM – FEI Quanta 450 FEG) and energy dispersive spectroscopy (EDS - Apollo X SDD) were used to assess the relative quantities of the elements present on close to the interface of bonded samples. EDS profiles of the interface region were then analyzed in order to evaluate the modification in composition in the interface layer The layer is formed by cation migration towards the cathode due to the applied electrical field and a negatively charged layer is formed that enhances the anodic bonding.

2.3. Bonding strength

The bonding strength was evaluated using a shear test. For this purpose a universal testing machine (Instron 8872) was used. Bonded samples with total transferred charge of 0.45C were positioned in a specially designed device in order to hold the metal electrode while a shear load was applied over one of the sides of the bioglass. A clamp was used to hold the device over the test machine table while the shear force was applied under constant actuator speed of 5 mm/min. This test procedure was adopted to avoid the use of epoxy adhesives between the sample and holding device and thus simplify specimen preparation and eliminate variation due to curing of the glue. The bonding strength was obtained from the peak load and the electrode area (28.3 mm^2). Optical microscopy (Olympus BX-51) was used to investigate the failure mode due to shear test.

2.4. Theoretical model

Albaugh [18] proposed a model of variable capacitor in series with constant resistance to predict current–time characteristics for anodic bonding. The layer depleted of cations beside the anode material is modeled as a capacitor which varies as a function of the positive charge moved away from the depletion layer. A schematic representation of this model is shown in Fig. 1. The resistance is simply the resistance of the bulk glass. The charge flowing in the circuit proposed by Albaugh [18] can be expressed as.