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Active metal brazing for joining glass-ceramic to titanium – a study on silver enrichment

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A hermetic encapsulation system for implantable telemetric electronic devices has been developed. It is based on the combination of a glass-ceramic material transparent to radio-frequency signals with commercially pure titanium. The materials were joined by active metal brazing, resulting in a multi-layer structure. The *in vivo* and *in vitro* behaviour of this metal-ceramic interface was studied. *In vivo* experiments consisted of subcutaneous implantation of capsules in piglets and pigs with different weights, while the *in vitro* tests consisted of electrochemical techniques aimed at characterizing the degradation behaviour of the interface. Electrochemical experiments were conducted at 37 °C in a simulated physiological solution (Hank's Balanced Salt Solution; HBSS).

Results show that a silver-rich phase was formed at the interface, both in living tissue and in HBSS. Chloride seems to have an important role in the reaction mechanism. The mechanical integrity of the capsules was not affected by this reaction under *in vivo* conditions.

1. Introduction

The development of implantable electronic devices capable of monitoring and/or controlling health parameters has increased in recent years. Despite this development, little attention has been paid to the problem of device encapsulation. It is still more or less common to see reference in the literature to failures due to the encapsulation system [1]. Most of the failures are related to polymeric [1–8] or glass [9, 10] encapsulants.

With the aim of producing a hermetic and mechanically resistant packaging system for implantable telemetric electronic devices, to be used in animal monitoring and identification, a hard-shell encapsulation system based on the combination of a radio-frequency signal transparent ceramic material with a metallic material was developed [11]. The sealing of this capsule is achieved in two stages: first by high temperature active metal brazing, to obtain a hermetic seal between the metallic and ceramic components, and finally by metal-to-metal laser welding, to assure the final sealing of the capsule. Laser welding is a technique that involves localized heating of the material in a restricted area, thus avoiding damage to the electronic components inside the package.

The active metal brazing process leads to formation of a hermetic multi-layer interface that presents a complex chemical composition. The presence of this multi-layer interface, in which galvanic couples may be formed, necessitates careful consideration of the possibility of adverse degradation processes taking place.

In this paper results concerning the *in vivo* and *in vitro* degradation behaviour of the multi-layer metal-ceramic interface are presented. The work focuses on the characterization of the products resulting from the reaction of the interface layers with a physiological simulated medium and with living soft tissue.

2. Materials and methods

Capsules were 39.4 mm long, with an external diameter of 6.5 mm and an internal diameter of 4.5 mm. Fluorosilicate machinable glass-ceramic (Macor^{TM} from Corning Glass Works, USA) and commercially pure titanium tubes were obtained by machining. They were hermetically joined together by high temperature active metal brazing. The active metal braze foil (71% Ag, 27% Cu, 2% Ti wt%, from Elephant Holding BV, The Netherlands) was 0.1 mm thick. Details of the experimental procedure related to the active metal brazing process have been described elsewhere [11]. The hermetic sealing of the capsule was confirmed by a method based on the MIL-STD-833 (1968) Standard Test condition A – tracer gas (He) fine leak [12].

TABLE I Chemical composition of Hank's Balanced Salt Solution

Substance	Concentration (g l^{-1})
$CaCl_2 \cdot 2H_2O$	0.185
$MgCl_2 \cdot 6H_2O$	0.10
KCl	0.40
NaCl	8.00
KH_2PO_4	0.06
$MgSO_4 \cdot 7H_2O$	0.10
$NaHCO_3$	0.35
Na_2HPO_4	0.48
D-Glucose	1.00

The *in vitro* tests consisted of direct current (d.c.) potentiodynamic and potentiostatic electrochemical techniques. Prior to being tested, cross-sections of the samples were wet-ground down to 4000 mesh with SiC grit paper, cleaned in ethanol and dried. Tests were performed in a simulated physiological solution, Hank's Balanced Salt Solution (HBSS) from GIBCO, at 37 °C; the composition of the solution is given in Table I. The volume of solution was 150 cm^3.

Capsules were implanted in the base of the ear of piglets of 25 kg for 2 weeks and in pigs of 65 kg for 1 month. Implants were not subjected to any passivation treatment. Prior to implantation they were stored in an antiseptic solution (Hibitane from ICI Pharma). Animals were anaesthetized with an intramuscular injection of 2 mg kg^{-1} of azoperone (Stresnil, Janssen Pharmaceutica), followed by an intraperitoneal injection of 10 mg kg^{-1} of medomidate hydrochloride (Hypnodil, Janssen Pharmaceutica). This combination of drugs caused a general anaesthesia of the animals. A hole was opened at the base of the ear by a needle with an external diameter of 6 mm. Subcutaneous implantation of the capsules was then done manually by pressing the capsule into the hole. Retrieval of the capsules was done by anaesthetizing the animals as described above. A stainless steel blade was used to open the wound. Cleaning of the capsules was carried out in acetone for 15 min in an ultrasonic bath.

3. Results and discussion

Fig. 1 shows the microstructure of a cross-section of the interface between the titanium and the glass-ceramic. The interface consists of several reaction layers identified in the micrograph from a to e_n. No pores or fissures were found.

The concentrations of Ag, Cu, Ti and Si were measured by energy dispersive spectroscopy (EDS), using an excitation voltage of 10 keV. A complex reaction process occurred on both the titanium and the glass-ceramic sides of the interface. No signs of the original brazing alloy were found [11]. On the glass-ceramic side (layer e_n, with a thickness of about 4–5 μm), accumulation of titanium (ca. 80 wt %) and the presence of Si (ca. 15 wt %) was detected, indicating a chemical reaction between the materials. On the titanium side (layer a) diffusion of Cu into the titanium was observed. This diffusion is likely to be responsible for the joining process. The intermediate layer d is composed of two phases, the lighter one containing 96 wt % Ag.

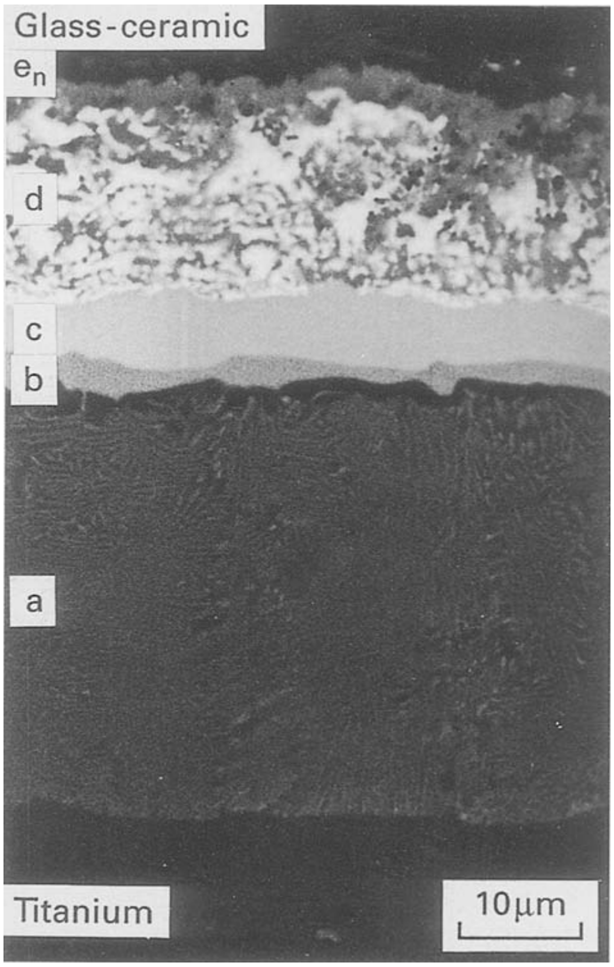
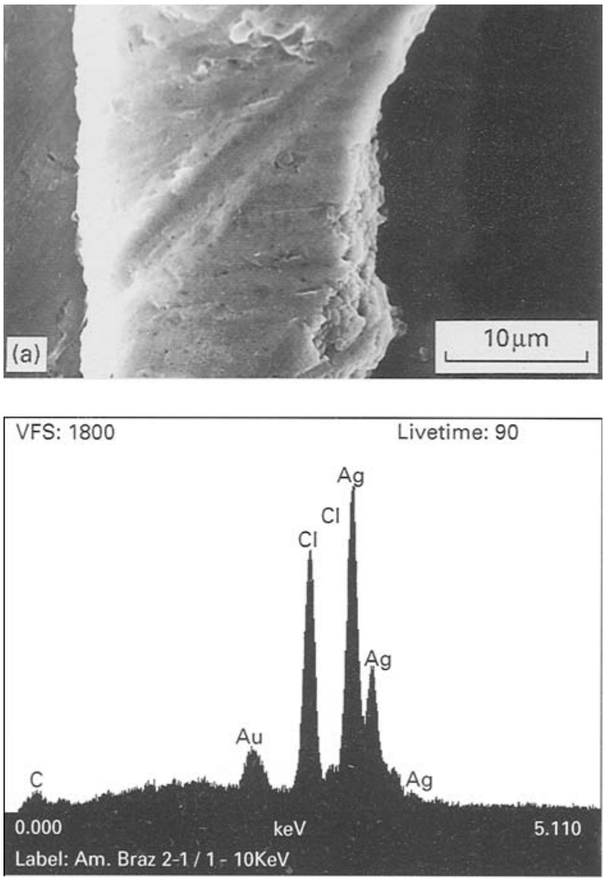


Figure 1 Micrograph of the cross-section of a brazed sample.

A scanning electron micrograph of the metal/ceramic interface of a sample that was subjected to a potentiodynamic polarization between − 900 and 2000 mV is presented in Fig. 2a. After being tested the sample was ultrasonically cleaned in distilled water for 5 min. As it can be seen, a continuous film (ca. 24 μm in width) is present. This film completely covers the layers existing at the interface, except layer a. Probably due to the ultrasonic cleaning procedure, the film was locally destroyed in some spots. As it can be seen in the micrograph presented in Fig. 3, the film observed in these spots has a granular structure.

The EDS analysis (Fig. 2b) of a polished cross-section after potentiodynamic polarization shows that the film consists of only Ag and Cl, with a Ag:Cl atomic ratio of 1.5:1. It is suggested that a preferential reaction occurs in the Ag-rich layer d with the chloride existing in the solution. This reaction is likely to be responsible for the formation of a partially insoluble silver chloride surface film.

From the electrochemical point of view, silver is considered a noble metal (standard electrode potential $E^{\circ}_{Ag^{+}/Ag} = 0.79$ V). It is also known for its aptitude to originate passive protective films and its tendency to form complex ions in solution [13]. As it can be seen in the Ag/H_2O potential-pH diagram in Fig. 4, at low potentials (lower than ca. 0.4 V) silver remains



(b)

Figure 2 (a) Morphology and (b) EDS analysis of the titanium/glass-ceramic interface of a polished cross-section of a sample after being potentiodynamically polarized between − 900 and 2000 mV.

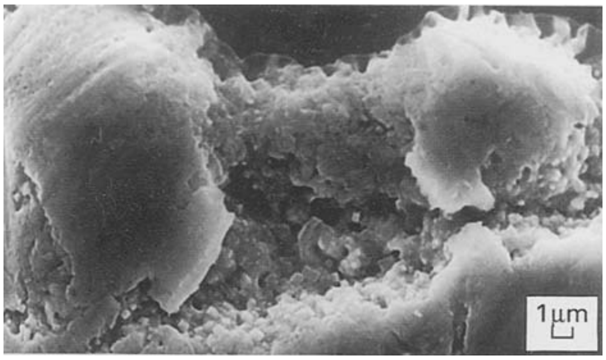


Figure 3 Magnification of the surface film presented in Fig. 2 in a spot where it was partially damaged.

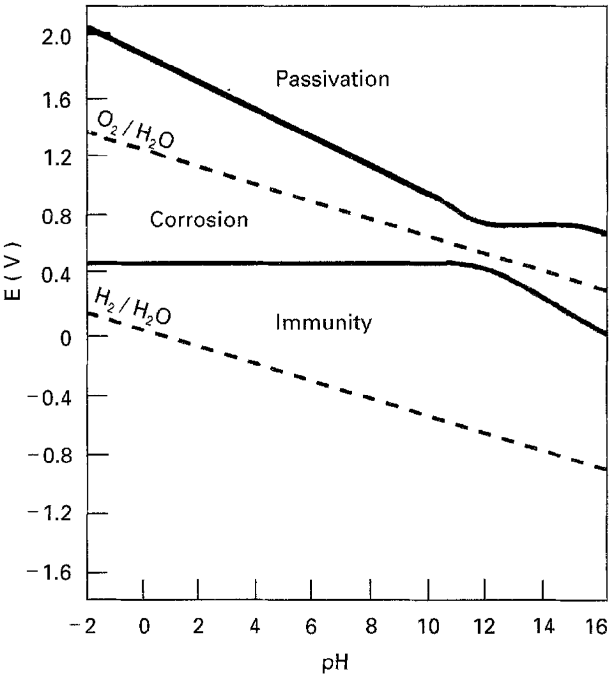
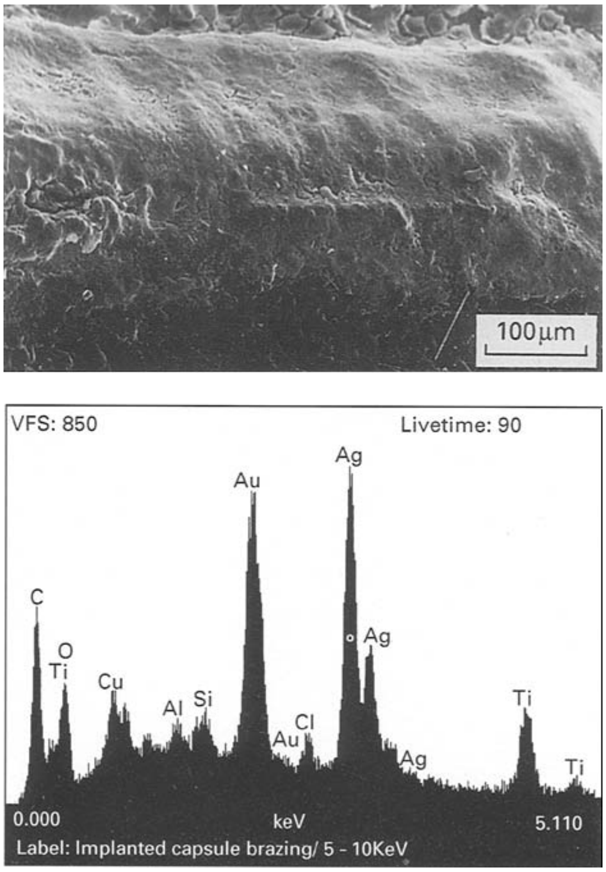


Figure 4 Ag/H_2O potential-pH diagram [13].



(b)

Figure 5 (a) Morphology and (b) EDS analysis of the titanium/glass-ceramic interface of retrieved capsules.

immune to attack over almost the whole pH range. The Ag/H_2O diagram is considerably modified by the presence of ions such CN^- and Cl^- [13]. In particular, in the presence of halides (with the exception of fluoride), the zone of passivity is substantially increased. This behaviour is attributed to the low solubility products of silver halides ($[Ag][Cl] = 1.7 \times 10^{-10}$) [13]. When silver is passivated by a halide, the film is in general adherent, self-healing and highly insoluble.

As can be observed in Fig. 5a, a continuous, relatively adherent, and apparently voluminous film (ca. 100 µm in width), present all around the metal-ceramic interface, was found on the retrieved capsules. The EDS analysis presented in Fig. 5b reveals that this film contained 25–77 wt% of Ag and 1–8 wt% of Cl. The increase in Ag content was always associated with an increase in Cl content.

4. Conclusions

An Ag-rich phase was formed at the metal/ceramic interface, both in living tissue and in a simulated physiological solution. Cl seems to have an important role in the reaction mechanism, by combining with Ag and thus forming an adherent layer. The mechanical integrity of the capsules *in vivo* was not affected by this reaction. It is also apparent that galvanic reactions between the layered interface and the metallic part of the capsule may not be deleterious to the performance of the capsules, mainly due to the presence of a Ag-rich barrier.

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