Corrosion Resistance of Injection-casting Dental Implants

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In this paper the results of corrosion resistance for dentistry implants-commercial and produced by injection casting were presented. The produced and commercial implants were made from the same material (Ti6Al4V ELI). Studies were carried out on six samples: two were input materials (E1, E2), two were commercial implants (C1, C2) and two were produced implants (P1, P2) where P1 was produced from input material E1 and P2 was produced from input material E2. For corrosion resistance potentiodynamic studies were carried out. It was found that produced samples through injection casting have better corrosion resistance than commercial implants. However, produced implants have similar corrosion resistance to input materials. The studies have shown that it is possible to use innovative injection casting to improve corrosion resistance of dental implants.

Keywords: titanium alloys, dentistry implants, Ti6Al4V, injection casting

Modern materials engineering is looking for newer materials that will meet the demands of the latest technologies. The requirements for such materials include mechanical, physicochemical and structural properties. A very good example of that kind of material is titanium and its alloys. These are widely used in industries such as aerospace, chemical, construction. Due to its properties: relatively low density-to-strength proportion and very high corrosion resistance in aggressive environments it can be used practically in all conditions [1-6].

Thanks to the research conducted by Per-Ingvar Brånemark in 1952, it has been shown that titanium possesses properties that allow it to be used within the human body. These properties are osteointegration and biocompatibility. Since this discovery, titanium and its alloys have been used in medicine. Further studies have allowed to conclude that the best alloy for this purpose is the biphasic áâ, which is characterised by all properties that the material should have inertia. Further studies have shown that the best alloy for this purpose is a biphasic áâ which is characterised by all properties that the material should have in vivo [7-21].

Progress in many areas of science and practical research have enabled the ever-widening application of this type of alloys in medicine, including dentistry. The most common titanium alloy used in dentistry is Ti6Al4V.

Thanks to the combination of materials engineering, microsurgical procedures and endodontics, modern dentistry focuses not only on the issues related to the preservation and health of the stomatognathic system but also on the aesthetics of the performed work. The use of said Ti6Al4V alloy allows to fill the defects by means of dental implants after extraction of the teeth.

The use of implants positively affects health - restoring normal functioning of the stomatognathic system. Replenishment of tooth defects allows for the proper distribution of forces that carry teeth in the chewing process, which in turn affects the correct loading of the temporomandibular joint. Incorrect work in this system can cause the degradation of healthy teeth and may also affect other aspects of health. In areas where tooth is missing lowering of the gum line, alveolus vanishing, tooth movement or headaches due to asymmetric temporo-mandibular joint load are observed. The use of implants also has an impact on aesthetic issues that are equally important because they directly affect the patient's quality of life [22-29].

As a part of conducted studies implants were produced using innovative injection casting method and then compared with textured commercial implants. The innovative injection method consists of an inductive melting of the Ti6Al4V alloy ingot in a quartz capillary, after then liquid material is injected to radially cooled copper mould. The method allows to obtain a finished product in a very short, repeatable cycle. Scheme of the machine used in innovative injection method is presented in figure 1 [30, 31].

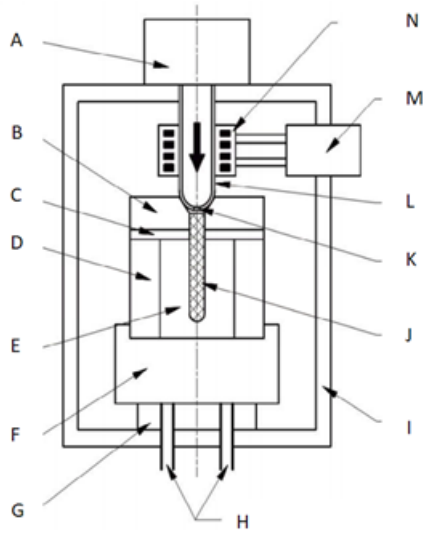

Fig. 1. Scheme of device used to produce dental implants. A - mounting bracket of quartz capillary, B- top plate with funnel, C - thermal isolation, D - copper mould cover, E - copper mould, F - cooling system, G - Teflon isolating ring, H - inlet and outlet of the cooling medium, I - working chamber, J - element after casting process, K - hole in capillary, L - quartz capillary, M - vacuum conduit connecting the coil with the transformer, N - induction furnace coil [32]

Obtained implants as opposed to commercial do not have any threads. This is due to the recent news that textured or CNC-fabricated implants have a higher chance of inducing inflammation after implantation in comparison

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Table 1
CHEMICAL COMPOSITION OF INPUT MATERIALS

Material	Elements, wt. %							
	Ti	Al	V	Fe	O	C	N	H
E1	89.71	6.00	4.00	0.10	0.15	0.03	0.01	0.003
E2	89.46	6.20	4.00	0.18	0.11	0.04	0.01	0.004

to smooth ones, which increases the time of implant acceptance and may even lead to rejection. In addition the use of textured implant can cause soft tissue contraction in the gingiva which is associated with their injury during screwing process into the alveolar [33-36].

Computational details

The samples used in studies were made from the same material – Ti6Al4V ELI-titanium grade 23 which is used for medicine due to its purity. Six samples were studied (E1, E2, C1, C2, P1, P2): two samples were input material before injection process (E1, E2), two samples were implants produced using injection process from input materials (P1, P2) and two samples were commercial implants (C1, C2). Chemical compositions of input materials were shown in Table 1. Produced samples (P1, P2) were made using injection casting where time of melting of ingots - input materials (E1, E2) in quartz capillary was 12 s. After melting, the alloy was injected to copper mould by using argon. The pressure of gas amounted to 2 bars, duration time of injection was 1 s. Copper mould was water-cooled with water flow of 4 L/min. Temperature of water in the coil of cooling system was 12°C (water was taken from the tap) [32].

Electrochemical studies were carried out by using CHI-1130A potentiostat. The tests were carried out in an electrochemical cell with a Luggin capillary in a three-electrode system with a working electrode in the form of a spinning disk. The set parameters during the potentio-dynamic measurements were as follows: range of potentials from -1.5 to +3.0 V, scanning speed from the cathode value in the anodic direction 5 mV·s^{-1}, disk rotation speed was 12 rps, the temperature was 25°C ± 0.1°C. As the reference electrode AgCl / Ag (with an external solution of 1M KCl) was used of which the working potential was +0.222 V and the auxiliary electrode was platinum in the form of a spiral.

Table 2
CHEMICAL COMPOSITION OF RINGER'S SOLUTION USED DURING STUDIES

Substance	Concentration [g·l^{-1}]
Sodium chloride	8.60
Potassium chloride	0.30
Hexachine calcium chloride	0.48

The solution contained ions with the following concentrations expressed in mmol·l^{-1}: Na^+ = 147.16, K^+ = 4.02, Ca^{2+} = 4.38, Cl^- = 155.56.

Results and discussions

According to the theory of corrosion kinetics, the rate of corrosion of a metal passed in corrosive environment is equal to the density of the anode current within the passive range. [37] Therefore, potentials 0.7 V higher than the potentials corresponding to the anodic peaks were chosen as representative for both the primary and secondary passivation range. It means that for the characterisation of the corrosion rate in the area of primary passivation the current density reading at E = +0.5 V was used, and for the corrosion rate characteristics in the secondary passivation region the reading at E = +2.5 V (vs. AgCl / Ag), it means

$$i_{cor.,\ prim.} = i_{a(+0,5\ V)} \text{ and } i_{cor.,\ sec.} = i_{a(+2,5\ V)}$$

As it is known from the equilibrium of the anode electrode, oxidation of hydrogen is possible below the equilibrium potential of this electrode, whereby:

$$E^{eq}_{\frac{H_2O}{H_2}} = 0.00 - 0.0591 \cdot pH \quad (1)$$

where: E - equilibrium potential of hydride electrode, 0.00 - hydride electrode potential, 0.0591 - constant

Bearing in mind that the tests were carried out in an environment of pH = 6 and pH = 3 oxidation of hydrogen is possible below the potentials:
for pH = 6:

$$E^{eq}_{\frac{H_2O}{H_2}} = 0.00 - 0.0591 \cdot 6 = -0.355\ V$$

for pH = 3:

$$E^{eq}_{\frac{H_2O}{H_2}} = 0.00 - 0.0591 \cdot 3 = -0.177\ V$$

In addition, the values of potentials, for which water oxidation occurs, are calculated $2H_2O - 4e \rightarrow O_2 + 4H^+$ which is observed in the form of a characteristic peak nearby E = +1,5 V [38-40] and its presence may be the result of the polymorphic transition of the oxide formed on the surface of the material based on Pourbaix's charts for titanium (fig. 2), it is probably a transition $TiO_2 \cdot H_2O$ do TiO_3H_2O. [41, 42] Knowing that:

$$\mu^0_{H_2O} = -237190 \frac{J}{mol}$$

$$\mu^0_{O_2} = 0 \frac{J}{mol}$$

$$\mu^0_{H^+} = 0 \frac{J}{mol}$$

this:

$$E^0_{\frac{O_2}{H_2O}} = \frac{\mu^0_{O_2} + 4\mu^0_{H^+} - 2\mu^0_{H_2O}}{4F} \quad (2)$$

where: E - equilibrium potential of oxygen electrode, μ - activity factor, F - Faraday constant

$$E^0_{\frac{O_2}{H_2O}} = \frac{-474380 \frac{J}{mol}}{4 \cdot 96500 \frac{C}{mol}}$$

$$E^0_{\frac{O_2}{H_2O}} = 1.228V$$

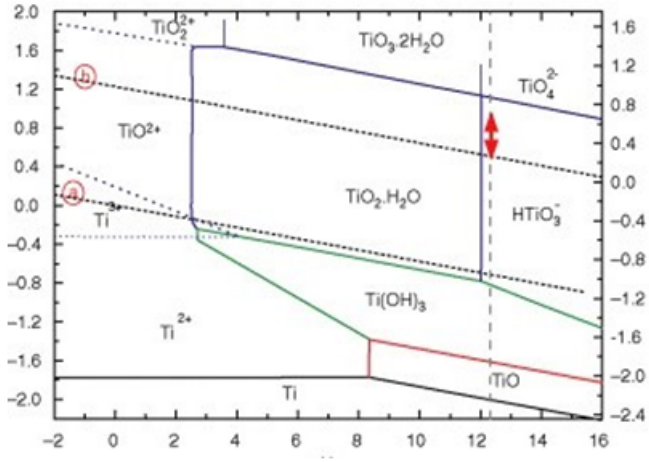

Fig. 2 Potential-*p*H equilibrium graph at temperature 25°C without TiH_2 [42]

Based on the above data, 21% oxygen content in atmospheric air (p_{O_2} = 0.21 bar) and the measurement temperature of 25°C, the values of the potentials, for which the water is oxidised ,are calculated.

$$E^{eq}_{\frac{O_2}{H_2O}} = 1.228 - 0.0591 \cdot pH + 0.0148 \cdot \log p_{O_2} \quad (3)$$

where: 1.228 - calculated potential value of oxygen electrode, p - partial pressure

for *p*H = 6:

$$E^{eq}_{\frac{O_2}{H_2O}} = 1.228 - 0.0591 \cdot 6 + 0.0148 \cdot \log 0.21 = 0,883\ V$$

for *p*H = 3:

$$E^{eq}_{\frac{O_2}{H_2O}} = 1.228 - 0.0591 \cdot 3 + 0.0148 \cdot \log 0.21 = 1.060\ V$$

Bearing in mind that the reference electrode is AgCl/Ag for which $E^{eq}_{\frac{AgCl}{Ag}} = +0.222\ V$ then the values of individual potentials are equal to:

for *p*H = 6:

$$E^{eq}_{\frac{H_2O}{H_2 vs \frac{AgCl}{Ag}}} = (-0.355) - 0.222 = -0.577\ V$$

$$E^{eq}_{\frac{O_2}{H_2O vs \frac{AgCl}{Ag}}} = 0.883 - 0.222 = 0.661\ V$$

for *p*H = 3:

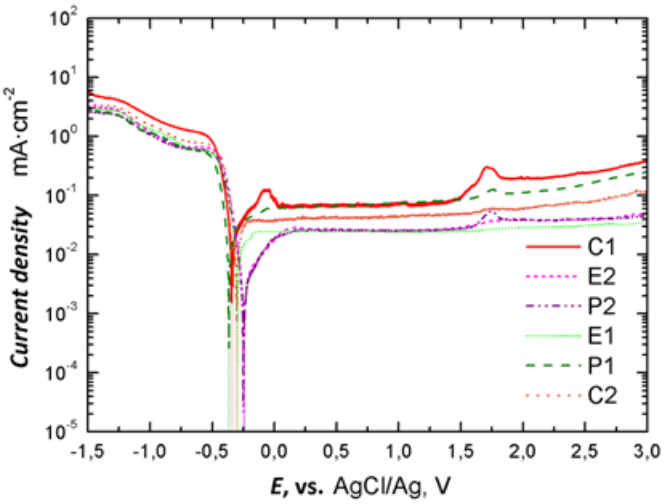

Fig. 3 Polarisation curves for all samples (environment *p*H = 3)

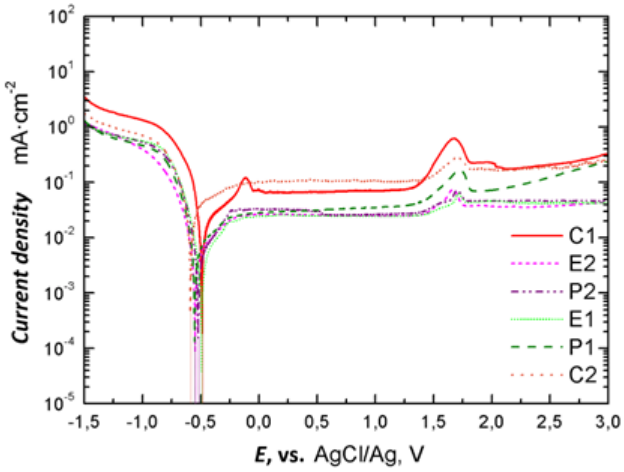

Fig. 4 Polarisation curves for all samples (environment *p*H = 6)

$$E^{eq}_{\frac{H_2O}{H_2 vs \frac{AgCl}{Ag}}} = (-0.177) - 0.222 = -0.399\ V$$

$$E^{eq}_{\frac{O_2}{H_2O vs \frac{AgCl}{Ag}}} = 1.060 - 0.222 = 0.838\ V$$

During the measurement, for the given parameters, the results of corrosion current density for primary and secondary passivation were obtained. To confirm the calculated oxidation values an experiment was carried out. All measurements were burdened with an average of 9%

Table 3

RESULTS OF CORROSION CURRENT DENSITY FOR PRIMARY AND SECONDARY PASSIVATION

($i_{cor.,\ prim.} = i_{a(+0,5\ V)}$ and $i_{cor.,\ sec.} = i_{a(+2,5\ V)}$)

Sample	pH=3		pH=6	
	$i_{(+0,5\ V)}$ [mA·cm^{-2}]	$i_{(+2,5\ V)}$ [mA·cm^{-2}]	$i_{(+0,5\ V)}$ [mA·cm^{-2}]	$i_{(+2,5\ V)}$ [mA·cm^{-2}]
C1	$6,6 \cdot 10^{-2}$	$2,4 \cdot 10^{-1}$	$6,6 \cdot 10^{-2}$	$2,1 \cdot 10^{-1}$
C2	$4,3 \cdot 10^{-2}$	$7,6 \cdot 10^{-2}$	$1,1 \cdot 10^{-1}$	$1,9 \cdot 10^{-1}$
E1	$2,6 \cdot 10^{-2}$	$3,1 \cdot 10^{-2}$	$2,5 \cdot 10^{-2}$	$4,2 \cdot 10^{-2}$
E2	$2,7 \cdot 10^{-2}$	$4,0 \cdot 10^{-2}$	$2,5 \cdot 10^{-2}$	$3,9 \cdot 10^{-2}$
P1	$6,7 \cdot 10^{-2}$	$1,5 \cdot 10^{-1}$	$3,1 \cdot 10^{-2}$	$1,3 \cdot 10^{-1}$
P2	$2,5 \cdot 10^{-2}$	$4,0 \cdot 10^{-2}$	$2,9 \cdot 10^{-2}$	$4,6 \cdot 10^{-2}$

of the measurement error, where five measurements were taken for each of the samples. In order to visualise the differences in the density of corrosion currents for individual environments, polarisation curves for the studied materials were made. The measurement results are presented in graphs (fig. 3, 4) and also summarised in tabular form (table 3).

Based on the obtained results, it was found that the pH of the environment, in which the tests were carried out, has no significant effect on the corrosion current density. A clear difference between the densities of the corrosion current is visible for C2 commercial implant. In the case of secondary passivation a roughly twice the value of the corrosion current density was observed for all samples in relation to primary passivation. For commercial implants C1, C2 and samples of P1 produced these differences were significantly greater.

Conclusions

Based on the conducted tests it was shown that the use of an innovative injection method can affect the improvement of the corrosion resistance of dental implants. A nearly two-fold decrease in the value of corrosion current density was observed in the case of produced implants in comparison to commercial ones. Bearing in mind that the entire cycle of manufacturing the finished implant takes about 5 minutes it can be concluded that the use of an innovative injection method can be an alternative to commercial production of these elements e.g. CNC.

The increase in corrosion resistance may be related to grain refinement within the surface layer of the implant produced. This fragmentation is the result of a very rapid dissipation of heat through the copper mould at the interface layer of the implant - the inner layer of the copper mould which is radially cooled.

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