

CORROSION RESISTANCE OF Ti13Zr13Nb ALLOY WITH POLYMER AND COMPOSITE SOL-GEL BIOACTIVE GLASS/POLYMER COATINGS IN RINGER'S SOLUTION

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Abstract - The corrosion resistance of an uncoated near- β Ti13Zr13Nb titanium alloy as well as the alloy coated by a polymer (chitosan CHIT or polyetheretherketone PEEK), composite sol-gel bioactive glass/CHIT or porous sol-gel bioactive glass/PEEK coatings was investigated in Ringer's solution at 37°C. The microstructure of the alloy and the coatings was characterized by Scanning Electron Microscopy (SEM). The corrosion measurements were performed by electrochemical techniques like linear sweep voltamperometry and Electrochemical Impedance Spectroscopy (EIS). The corrosion tests showed that the porous sol-gel bioactive glass/PEEK and polymer CHIT coatings had a similar corrosion resistance to the substrate's one. The results indicated also that the deposition of PEEK and sol-gel bioactive glass/CHIT coatings significantly protect the Ti13Zr13Nb alloy from corrosion in a Ringer's solution.

Résumé – Résistance à la corrosion d'un alliage de titane Ti13Zr13Nb revêtu d'un composite bioactif de type sol-gel dans une solution de Ringer. La résistance à la corrosion d'un alliage de titane quasi- β Ti13Zr13Nb non revêtu, d'un alliage de Ti revêtu d'un polymère (chitosan CHIT ou polyétheréthercétone PEEK), d'un composite bioactif verre/CHIT et de couches poreuses bioactives de verre/CHIT obtenues par sol-gel a été étudiée dans une solution de Ringer à 37 °C. La microstructure de l'alliage et des couches a été caractérisée par Microscopie Electronique à Balayage (MEB). Les tests de corrosion ont été faits en utilisant des techniques électrochimiques comme la voltampérométrie à potentiel linéaire et la Spectroscopie d'Impédance Electrochimique (SIE). Les tests de corrosion ont montré que les couches poreuses bioactives de verre/CHIT obtenues par sol-gel et celles de CHIT ont une résistance à la corrosion similaire à celle du substrat. Les résultats obtenus indiquent également que le dépôt de PEEK et les couches poreuses bioactives de verre/CHIT obtenues par sol-gel protègent significativement l'alliage de Ti13Zr13Nb de la corrosion dans la solution de Ringer.

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1. INTRODUCTION

The clinical acceptance of titanium implants is accredited to their ability of Osseo integration which is a direct and stable anchorage of the implant by the formation of bony tissue at the bone implant interface. β -titanium alloys are often described as second generation titanium biomaterials. Their wide application is determined by their mechanical properties. Generally β -titanium alloys have a Young's modulus close to that of human bone [1-5]. The principle advantages of β -alloys include also their good corrosion resistance and biocompatibility compared to Ti6Al4V or other two $\alpha+\beta$ phase alloys. These alloys are vanadium free, with the principal alloying elements being niobium, zirconium, molybdenum, tantalum, and iron, all of which exhibit good biocompatibility and no toxic effects [6, 7]. Prevention of acute inflammation around the implant and its susceptibility to biocorrosion in physiological conditions are also major issues when designing such implants. Therefore, considerable research has been carried out to address these problems and to improve the performance of titanium implants. Despite of many advantages of β -titanium alloys, the inflammation phenomena around implants can occur in long time [8]. Hence, the improvement of the surface properties is a main challenge.

Therefore, an effective technique like electrophoretic deposition (EPD) for deposition of protective coatings on biomedical implants can be used. EPD technique is based on the movement of the colloidal particles in a suspension under the influence of an electric field and the deposition of particles on the oppositely charged electrode [9]. This technique can be used to perform the deposition of ceramics, polymers or composites coatings. In the literature different polymers have been studied as potential materials, which improved the corrosion resistance and biocompatibility of different alloys. The polymers like polyetheretherketone (PEEK) and chitosan (CHIT) are widely used in the biomedical sector. PEEK is a polymer which exhibits good mechanical properties, including low coefficient of friction and non-toxicity [10]. CHIT is a linear polyamine that possesses unique physicochemical properties like biocompatibility, non-toxicity, biodegradability, excellent film forming ability and antibacterial activity [11]. Further, by products of degraded chitosan are also non-toxic, since they are simple sugars and are processed as part of normal cellular metabolism [12]. Bioactive glass particles are added to PEEK and chitosan, in order to increase the coatings bioactivity.

The aim of this study is to develop a polymer and composite sol-gel bioactive glass/polymer coating in order to increase the corrosion resistance of near- β titanium alloy. The morphology, corrosion resistance and adhesion of the coatings on the underlying substrate were examined. The corrosion stability of the uncoated and coated Ti13Zr13Nb alloy in the Ringer's solution was investigated by electrochemical polarization and impedance spectroscopy.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

CHIT, PEEK as well as composite sol-gel bioactive glass/CHIT and sol-gel bioactive glass/PEEK coatings were electrophoretically deposited onto near- β Ti13Zr13Nb alloy. Samples of the substrate material were in the shape of discs with diameter of 27mm and height of 2mm. A calcium-rich glass with a composition (in mol %) of 54 CaO, 40 SiO₂, 6 P₂O₅ produced by a sol-gel method was applied as a composite coatings component [13].

2.2. Electrophoretic deposition of coatings

EPD was carried out in a two-electrode cell under constant voltage conditions. The counter electrode was austenitic stainless steel plate. Electrophoretic mobility, zeta potential and conductivity of the colloidal solutions and suspensions were measured by Zetasizer Nano ZS90 of Malvern Instruments Ltd. pH values were measured using pH-meter EL20 of Mettler Toledo. Current density during EPD was investigated by Tektronix DMM 4040 multimeter.

For EPD of CHIT coatings a dilute solution of medium molecular weight chitosan (0.5g/l, 1g/l, 2g/l) in a mixture of distilled water, different vol. % of acetic acid (0.5%, 1% and 2%) and 50 vol. % of ethanol were prepared by magnetic stirring at room temperature for 72 hours. Degree of deacetylation was in the range of 75-85%. For EPD of composite sol-gel bioactive glass/CHIT coatings, three dilute solutions with different concentrations of sol-gel bioactive glass (1g/l, 1.5g/l, 2g/l) and chitosan (2g/l) in a mixture of distilled water and 0.5 vol. % of acetic acid and 50 vol. % of ethanol were prepared by magnetic stirring at room temperature for 72 hours. EPD of both CHIT and sol-gel glass/CHIT coatings was carried out under constant voltage conditions in the range of 8-30V. The deposition time of coatings varied in the range of 1-5 minutes and the distance between the electrodes was 10mm.

The PEEK coatings were deposited from suspension with the composition of 1.5g of PEEK powder in 50ml of ethanol. The EPD was performed at a constant voltage in the range of 70-90V and deposition time equal from 30 to 120s. A suspension composed of 0.5g of PEEK powder and 1.6g sol-gel bioactive glass as well as 2.5g citric acid in the 25ml of ethanol was used for deposition of sol-gel bioactive glass/PEEK coatings. The suspension was sonicated in an ultrasonic bath for 30 minutes in order to disperse the particles. Before deposition the suspension was mixed for 10 minutes using magnetic stirrer. The EPD was performed at a constant voltage in a range of 30-80V. Deposition time was 2 minutes. As-deposited PEEK and bioactive glass/PEEK coatings were dried at room temperature and next heat treated at temperature of 355°C for 20 minutes in air (heating rate 4.5°C/min, cooling with furnace).

2.3. Characterization of coatings

The as-deposited coatings quality was evaluated by visual inspection, Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) observations. The SEM investigation was carried out using a FEI Nova NanoSEM 450 and JEOL JCM-6000 NeoScope II. TEM investigation was carried out using a JEOL JEM-2010 ARP microscope. Adhesion of the coatings to the Ti13Zr13Nb alloy substrate was evaluated using a Micro-Combi Tester (MCT) by the micro-scratch technique using a Rockwell C spherical diamond stylus. Tests were done under continuously increasing load from 0 to 30N. The scratch distance was 5mm. The critical loads L_{c1} (cohesive cracks) and L_{c2} (adhesive cracks) were obtained from LM observations, acoustic emission and friction force signals.

2.4. Electrochemical studies

The open circuit potential, linear sweep voltamperometry and Electrochemical Impedance Spectroscopy (EIS) studies of the samples were carried out using a potentiostat Autolab PGSTAT302N. The measurements were performed using a classical three-electrode cell, where the working electrode was a titanium alloy. Potentials were measured vs. saturated calomel electrode (SCE) and the counter electrode was made of platinum wire. Ringer's solution was used as the electrolyte for the corrosion study. Ringer's solution was used as the electrolyte for the corrosion study. The chemical composition of the Ringer's solution was: 8.6g/l NaCl, 0.3g/l KCl, 0.25g/l CaCl₂. Measurements were performed for pH equal 7.4 and in deaerated solutions at temperature of

37°C. The linear sweep voltamperometry curves were performed at a scan rate of 1mV/s in the potential range from -1.3V to +1.5V. Electrochemical impedance spectra were carried out at the open circuit potential. The amplitude of the perturbation signal was 10mV and EIS spectra were plotted in the frequency range from 10^5 to 10^{-3} Hz. The EIS data were fitted using the ZView software.

3. RESULTS AND DISCUSSION

3.1. Electrophoretic deposition of coatings

Electrophoretic mobility of suspended molecules in colloidal solution or suspension is one of the main driving forces of EPD and significantly affects the uniformity of as-deposited coatings. Therefore, in our work, electrophoretic mobility of chitosan and sol-gel bioactive glass/CHIT solution used for coatings deposition was measured. The most homogeneous and continuous coatings were deposited at the constant voltage of 10V and deposition time of 4 minutes. The voltage values higher than 10V led to very intensive H₂ bubbles evolution. On the other hand, if the voltage value was lower than 10V, the coating was only partially deposited on the substrate surface.

In the case of PEEK and sol-gel bioactive glass/PEEK coatings, the zeta potential and the conductivity of the suspension were measured as a function of pH. The conductivity for PEEK suspension varied between 0.11 to 0.42mS/cm. It was found in this work that conductivity of suspension increased when pH decreased. PEEK particles in ethanol exhibited negative zeta potential between pH 7 and 14 as well as positive below pH 7. The sol-gel bioactive glass in the same conditions exhibited positive zeta potential. The isoelectric point of PEEK suspension was around pH 7. The anodic deposition of PEEK particles confirmed that the carried charge on the PEEK particle surface is negative for pH values up to 7. The best deposition conditions for PEEK coatings on titanium alloy were obtained applying a constant voltage of 92V and a deposition time of 60 seconds. The best quality, homogeneous sol-gel bioactive glass/PEEK coatings were achieved for suspension containing PEEK, bioactive glass and citric acid in ethanol at 50V during 2 minutes.

3.2. Microstructure and adhesion of the coatings on the Ti13Zr13Nb alloy

During SEM investigation it was revealed that chitosan coating was homogenous and continuous (*figure 1a*). The coating thickness measured on TEM images taken from cross-section specimens was about 350nm. Composite sol-gel bioactive glass/CHIT coatings microstructure consisted of bioactive glass particles (diameter up to 4.5µm) and were homogeneously embedded in the chitosan matrix (*figure 1b*).

SEM investigation revealed that the as-deposited and subsequently annealed PEEK coating was homogeneous (*figure 1c*). The coating thickness was about 70µm. In contrast to the above-described coating the sol-gel bioactive glass/PEEK coating was highly porous with pores diameter up to 35µm (*figure 1d*). The coating had a uniform thickness of approximately 35µm. SEM-EDS microanalysis confirmed the presence of glass particles embedded in the PEEK matrix. The diameter of sol-gel bioactive glass particles was evaluated as up to 20µm.

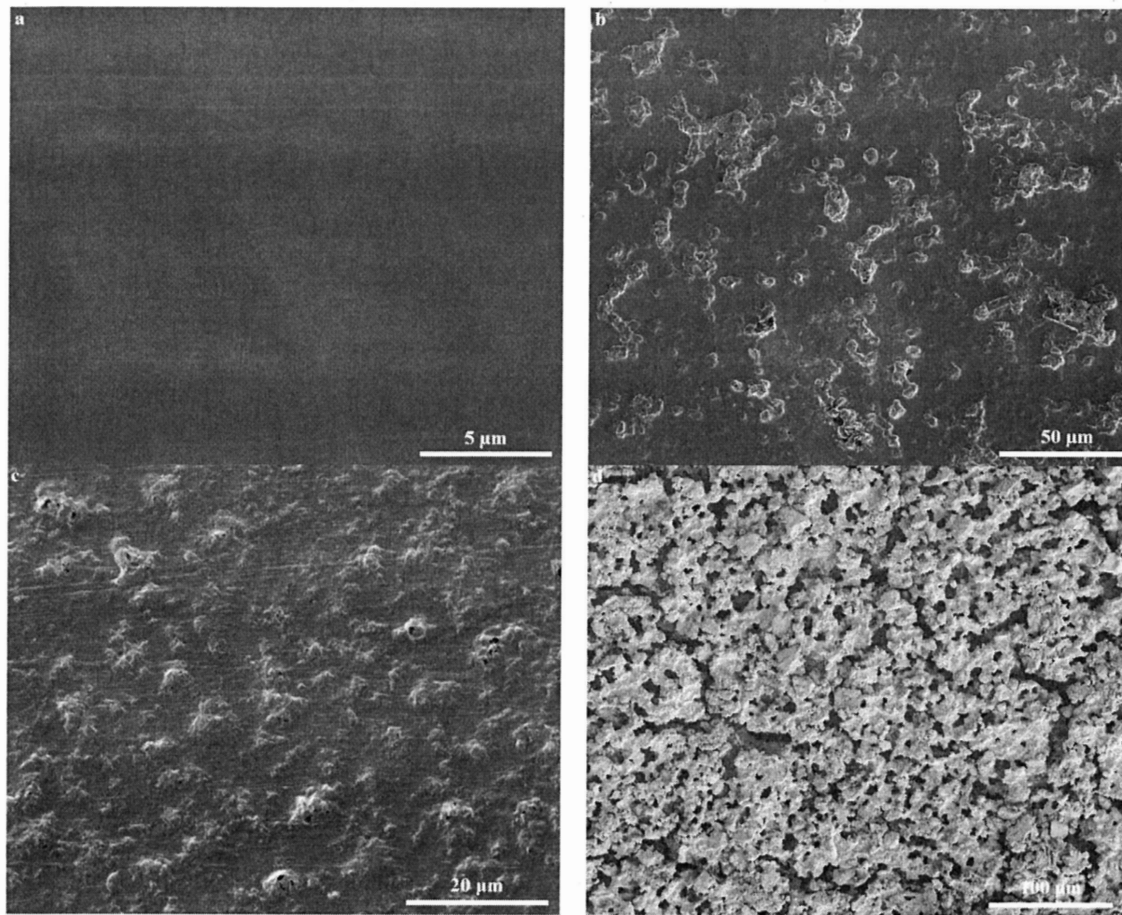


Figure 1. Microstructure of (a) chitosan, (b) sol-gel bioactive glass/CHIT, (c) PEEK and (d) sol-gel bioactive glass/PEEK coatings on Ti13Zr13Nb alloy (SEM plan-view).

Micro-scratch tests revealed relatively poor adhesion of chitosan coatings to Ti13Zr13Nb alloy substrate, but also a lack of cohesive cracks. The measured critical load L_{c2} was 3.2N. The increase of load up to 5N led to the removal of large area chitosan coatings around scratches. It is believed, that such relatively poor adhesion is a result of chitosan properties such as polysaccharide and biodegradable nature. On the other hand, composite sol-gel bioactive glass/CHIT coating was indicated to have much better adhesion to the Ti13Zr13Nb alloy than the chitosan one. The loss of adhesion, cohesive cracks and coating delamination were observed for a load of 7N. The annealed PEEK coating exhibited very good adhesion to the substrate material in comparison with other investigated coatings. The critical load L_{c2} equals to about 25N. The sol-gel bioactive glass /PEEK coating is characterized by a lower adhesion to the substrate in comparison to PEEK coating. No cohesive cracks were observed during scratch test. The critical load L_{c2} was equal to about 8N.

3.3. Electrochemical studies

Figure 2a shows the evolution of the open circuit potential (OCP) for the uncoated- and the coated-(Ti13Zr13Nb) alloy with PEEK, sol-gel bioactive glass/PEEK, CHIT, sol-gel bioactive glass/CHIT. OCP for PEEK coated specimen obtained the highest value of 0.15V. The observed shift in OCP to positive values for PEEK coated alloy may indicate reduction of the driving force

for the corrosion process [14]. Thus, the obtained results suggest that the PEEK coating has improved its corrosion behavior in comparison to the other coatings.

Potentiodynamic polarization curves (*figure 2b*) exhibit a passive range from the potential of the cathodic-anodic transition (-0.59V) for sol-gel bioactive/PEEK, -0.51V for CHIT coatings and -0.43V for uncoated Ti13Zr13Nb alloy. The passive state for corrosion resistance and reasonably small variations in the passive current density are not significant. Significant differences can be seen in the case of PEEK, sol-gel bioactive glass/CHIT coatings and uncoated alloy: distinct differences in current densities of coated-Ti13Zr13Nb alloy compared to uncoated one. In such cases, the corrosion rate can be defined by the limiting current density which passes through the passivating film, thus becoming a measure of the film protective performance [15]. The passive current density (i_p) was reduced from $20\mu\text{A}/\text{cm}^2$ for the uncoated sample to 9 and $2\mu\text{A}/\text{cm}^2$ for the sol-gel bioactive glass/CHIT and PEEK coatings, respectively. This shift in the polarization curve indicates a high improvement of corrosion resistance thanks to these coatings that act as protective layers against corrosion.

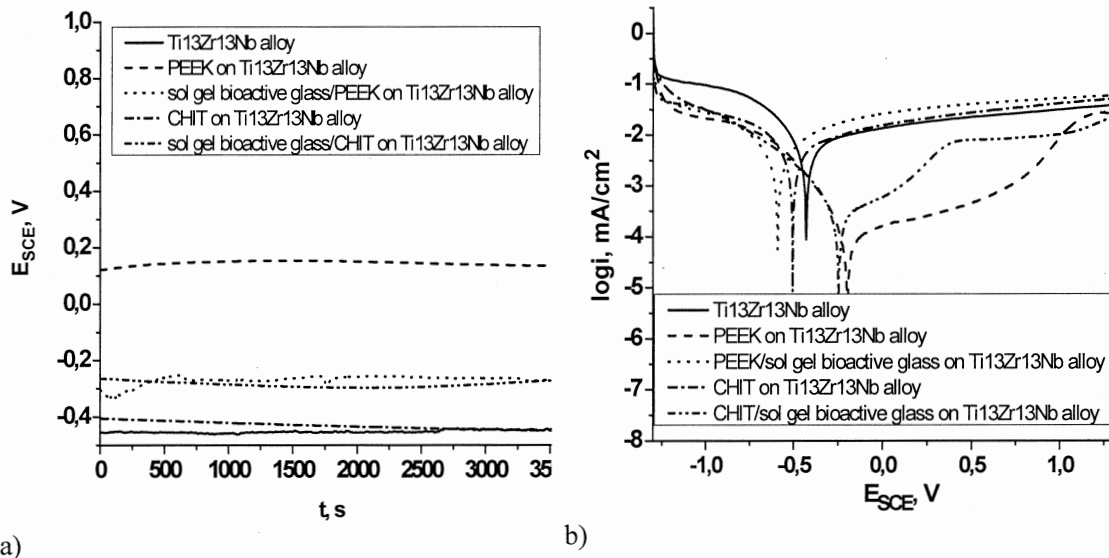


Figure 2. Electrochemical measurements of uncoated and coated Ti13Zr13Nb alloy in Ringer's solution at 37°C : (a) evolution of the corrosion potential vs. time and (b) polarization curves at $1\text{mV}/\text{s}$.

Figure 3 (a-c) show the EIS spectra presented as a Nyquist plot (*figure 3a*) and a Bode plot (*figure 3b-c*) of the uncoated- and coated alloy in the Ringer's solution. From *figure 3b*, higher Z modulus at lower frequency in the Bode impedance plot indicated a better corrosion resistance of the entire coated alloy. The equivalent circuit as shown in *figure 3d* was used to fit the EIS data. According to the double-layer character for the surface coating, the equivalent circuit consisted of the electrolyte resistance (R_1), the coating resistance (R_2) and the constant phase elements (CPE). A good fitting between the experimental and simulated results was achieved and the parameters are listed in *table I*.

Table I. EIS fitting results obtained from EIS data.

Samples	OCP (V)	R ₁ ($\Omega \cdot \text{cm}^2$)	CPE-T ($\text{Fs}^{n-1} \text{cm}^{-2}$)	CPE-P	R ₂ ($\Omega \cdot \text{cm}^2$)
Ti13Zr13Nb alloy	-0.45	20.41	$3.8235 \cdot 10^{-5}$	0.8142	296660
PEEK on Ti13Zr13Nb alloy	-0.45	86.37	$1.0838 \cdot 10^{-5}$	0.9525	$9.900 \cdot 10^{20}$
sol-gel bioactive glass/PEEK on Ti13Zr13Nb alloy	-0.30	34.84	$6.5334 \cdot 10^{-6}$	0.8893	334130
CHIT on Ti13Zr13Nb alloy	-0.27	81.77	$6.1685 \cdot 10^{-5}$	0.7691	37766
sol-gel bioactive glass/CHIT on Ti13Zr13Nb alloy	0.15	16.08	$3.2936 \cdot 10^{-5}$	0.9185	$1.634 \cdot 10^8$

The CHIT coating had a lower CPE-P, R₂ and CPE-T compared to the Ti13Zr13Nb alloy. These results of EIS investigation indicated that this coating had a worse corrosion resistance than the uncoated alloy.

The PEEK and sol-gel bioactive glass/CHIT coatings had a higher CPE-P value which was the closest to the capacitance (typical of passive coatings). The coating resistance (R₂) of PEEK and sol-gel bioactive glass/CHIT coatings was also significantly higher than that of Ti13Zr13Nb alloy, which suggested that these coatings had a better corrosion resistance than the uncoated alloy. Moreover, the PEEK coating had the highest CPE-T value. However, in the case of sol-gel bioactive glass/PEEK coating, the R₂, CPE-P and CPE-T parameters were also slightly higher than that of the uncoated alloy. These results are consistent with the OCP and polarization investigations.

4. CONCLUSIONS

- 1) The results presented in this work demonstrate that the electrophoretic deposition is a very efficient technique used for the production of PEEK, CHIT as well as sol-gel bioactive glass/CHIT and sol-gel bioactive glass/PEEK coatings on near- β Ti13Zr13Nb titanium alloy.
- 2) The CHIT coating had the worst corrosion resistance parameters compared to the other coatings and also the uncoated alloy. This result can be connected with the relatively poor adhesion of the chitosan coatings to the Ti13Zr13Nb alloy substrate, the coating thickness and the biodegradable nature of chitosan.
- 3) The sol-gel bioactive glass/PEEK and sol-gel bioactive glass/CHIT coatings exhibited a better corrosion resistance compared to the uncoated alloy.
- 4) The best corrosion resistance was shown by the PEEK coating. This result is probably an effect of its thickness, its homogeneous microstructure and its very good adhesion to the substrate material.

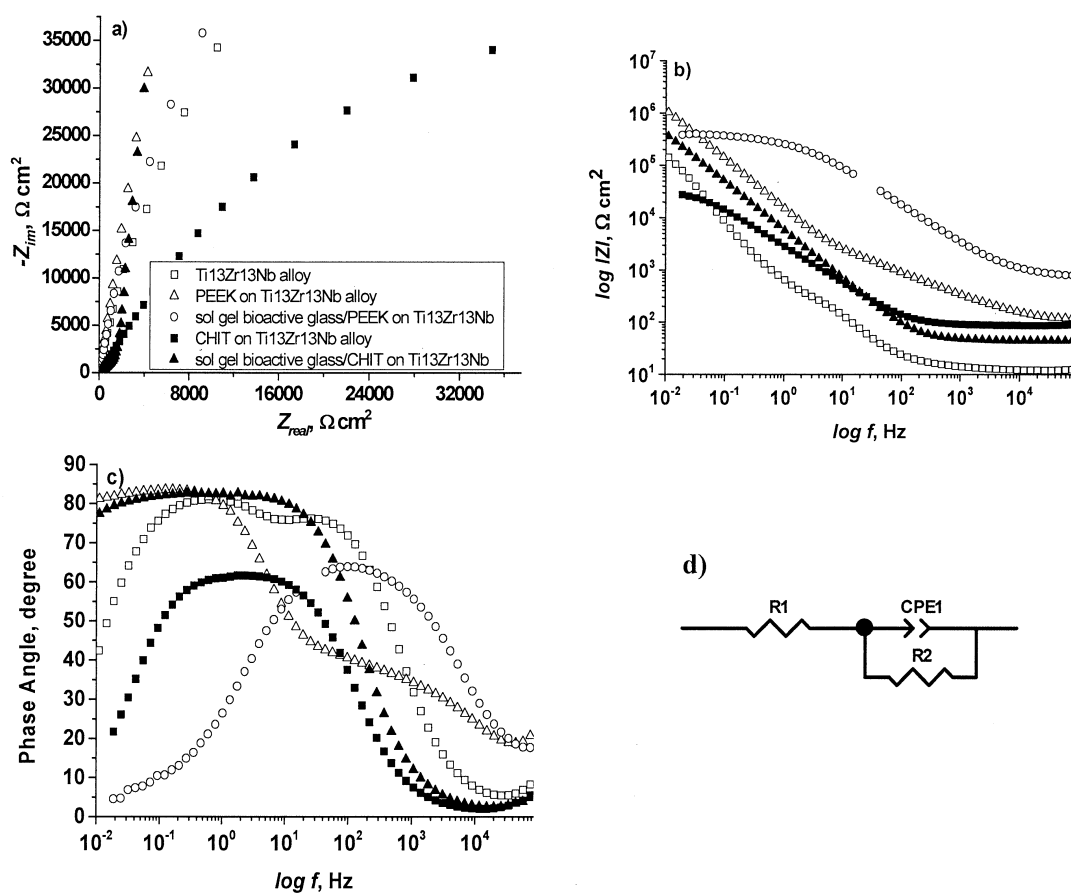


Figure 3. Electrochemical impedance curves of the uncoated- and coated alloy in Ringer's solution: (a) Nyquist impedance plot, (b) Bode impedance plot, (c) Bode phase angle plot, (d) Equivalent circuit used for fitting EIS data of investigated samples.

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