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EIS study of porous NiTi biomedical alloy in simulated body fluid

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The electrochemical impedance spectroscopy was used for monitoring the formation of surface film on a fixtured sintering porous NiTi biomedical alloy in simulated body fluid (SBF) media during 12 days. Effect of NiTi sintering time on the formation of surface film in SBF was investigated. The formed surface film was calcium phosphate hydrate (CPH) with a pillar particulate structure which was developed to a spongy network with increasing the sintering time. Using such electrochemical techniques, it was shown that NiTi samples obtained after 3 h sintering at 950 °C, have higher tendency for the formation of a stable CPH film during the test.

1 Introduction

Nitinol (NiTi) alloys have been used extensively as one of the most famous shape memory materials since they were introduced in the late 1970s. Due to their unique shape memory properties, superelasticity, resistance to fatigue and corrosion, biocompatibility, and bioactivity, they have been utilized in biomedical applications as implants and prostheses [1–6].

Despite the satisfactory clinical applications of NiTi alloys, its nickel content should be concerned as a great challenge with regards to its biocompatibility [7]. Since theoretically Ni may be released from NiTi as a result of corrosion [8] and additionally due to its clinical toxic and allergic influence on human [9–11], it is necessary to modify the surface of NiTi alloys in order to increase their biocompatibility and bioactivity [7].

In this respect, various techniques for surface modification of NiTi alloys have been reported in the literature [12–16], among which electrochemical techniques have been utilized as relevant procedures for the formation and monitoring of surface films on the NiTi alloys [17]. Electrochemical impedance spectroscopy (EIS) as a widely used method for nondestructive characterization of surface films, was used for monitoring the interfacial behavior of the formed layer on the surface of NiTi alloy [18–22].

In this paper, electrochemical techniques were used as powerful tools for monitoring the formation of surface films on the NiTi alloy in the simulated body fluid (SBF). In addition, effect of primary process parameters was investigated on the formation of final coating.

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2 Materials and methods

Nickel and titanium powders with respective particle sizes of 3–5 and 21 μm and equal atomic ratio were blended together for around 1 h in an eccentric shaker under argon. Cylindrical tablets, 15 mm in diameter and 1.9–2.3 mm in thickness, were made by bi-axial cold pressing of the mixture under 600 MPa pressure. Then the samples were sintered at 950 °C in a mold. From sample 1 to 4, sintering time changed from 2, 3, 4 to 5 h. Details of production methods was discussed elsewhere [1].

Sample was polished in ethanolic HNO_3 solution by implying 2 V for 10 min and rinsed with distilled water. Then samples were immersed in Ringer SBF for 12 days at 37 °C. EIS in 1 k–10 mHz frequency range with three electrode setup by Autolab® PGSTAT30 was done in Ringer solution, at 37 °C. EIS was used for interfacial behavior monitoring. Results of EIS were fitted to equivalent circuit which is depicted in Fig. 1 [18–20] and fitted results were presented. Potentiodynamic polarization curve is also gained in Ringer solution after 1 h immersion. X-ray diffraction analysis (XRD, Siemens D500, Cu-Kα irradiation) and scanning electron microscopy (SEM, Philips XL30) were used to investigate the phases and morphologies of the surface layer before and after the immersion.

3 Results and discussion

Through the previously mentioned production method [1], porous NiTi tablets were obtained. In all the samples, B2 and B19′ phases were present and as the sintering time elapsed, the phases were formed better and more homogeneity was achieved (Fig. 2a). The XRD results revealed the formation of calcium phosphate hydrate (CPH) on the surface of NiTi pellets, after the immersion into the Ringer solution (Fig. 2b). As it is obvious, different sintering times culminated in the formation of various amount of CPH on the NiTi samples and as the sintering time went on, more CPH phase was formed subsequently on the

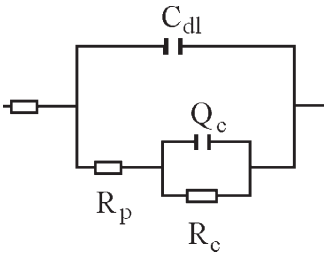

Figure 1. Equivalent circuit which fitted to EIS results

surface. On the NiTi sample which was sintered for 5 h, detectable CPH peaks can be observed. In the case of sample 1, which was sintered for 2 h and immersed for 12 days in Ringer solution, minor CPH peaks were observed in XRD pattern (Fig. 2a).

SEM investigations were used for morphological characterization of the NiTi pellets which were immersed for 12 days in Ringer solution. As shown in Fig. 3, CPH deposits were formed on the surface of the NiTi obtained in all the sintering times. However, some distinctions are clear which could be due to the difference in the sintering phenomenon in the exposed time. Comparing the SEM images of the samples with different sintering time (from 2 to 5 h) reveals that the morphology of CPH phase converts from a particulate structure to a porous spongy

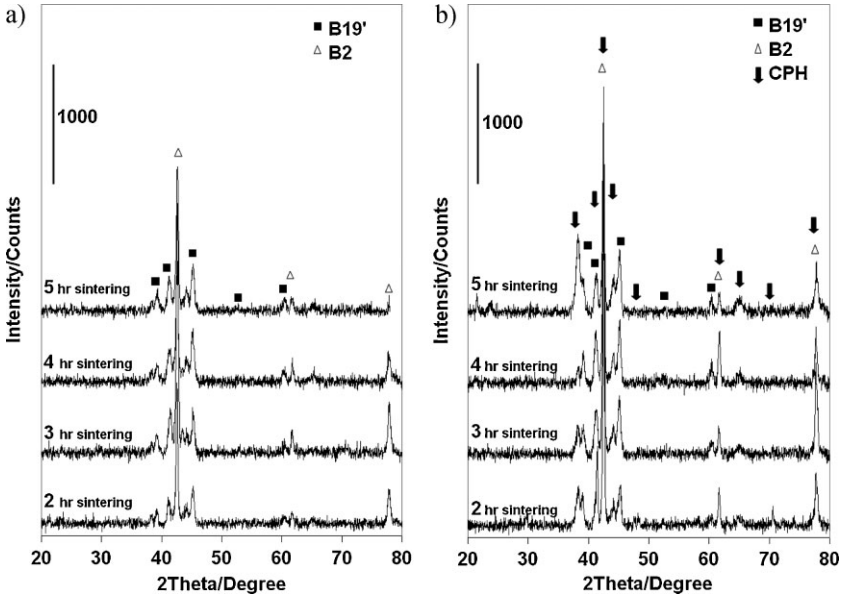

Figure 2. XRD patterns of NiTi samples (a) before and (b) after immersion in Ringer SBF

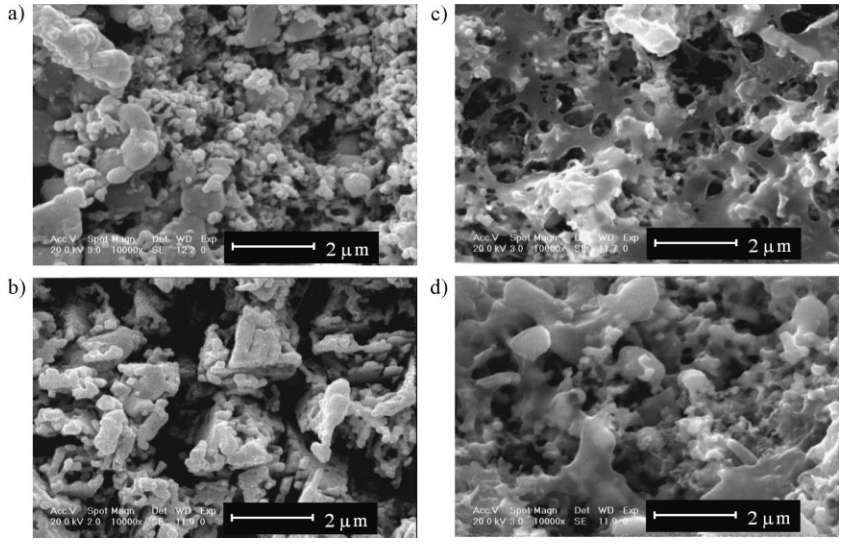

Figure 3. SEM micrographs of films on the sintered NiTi (a) 2 h, (b) 3 h, (c) 4 h, and (d) 5 h after 12 days immersion in Ringer SBF

pattern. Another feature is that the structure transforms from a compact pillar shape to a wide porous network. Such spongy network-like morphology is relevant in tissue engineering applications since it could be used as a suitable substrate for ingrowth of osteoblasts.

Results of EIS were well fitted to an equivalent circuit (Fig. 1) as what was reported previously [18–22]. Double layer capacitance (C_{dl}) was increased as a function of immersion time, as what is shown in Fig. 4a. Generally capacitance is expressed as:

$$C = \frac{\varepsilon\varepsilon_0 S}{d} \quad (1)$$

in which ε, S, and d are relative permeability, surface area, and thickness, respectively. At a constant surface area, capacitance increases due to effect of two parameters, i.e., decreasing the thickness or increasing the relative permeability (ε), through replacing surface-adsorbed molecules by water. In Fig. 4a, the increase in C_{dl} curve is attributed to the formation of CPH layer on the NiTi metallic tablet which can increase capacitances rapidly.

Constant phase element (CPE) diagram which is defined as:

$$Z_{CPE} = (C_c i\omega)^{-n} \quad (2)$$

is illustrated in Fig. 4b. When $n = 1$, C_c is equal to ideal capacitance and with decreasing the value of n, CPE is becoming a nonideal capacitance. The other parameter, i, is an imaginary component and ω is frequency. The values of CPE for the defined equivalent circuit do not show same features (Fig. 4b). During the immersion times relatively below 100 h, an overall decrease is observable in all the capacitance (C_c) curves. However, above the mentioned time, there is no distinguishable similarity in the capacitance deviations. Another important phenomenon which is clear in the C_c–t curves (Fig. 4b), is the hierarchical decrease of capacitance for the samples with 3, 4, and 5 h sintering times. This trend is attributed to the growth of CPH layer on the surface of NiTi samples which is in harmony with the SEM observations (compare Fig. 3b–d). It is noticeable that in the sample which was sintered for 2 h, the coating capacitance curve is clearly below the others (Fig. 4b). Such behavior can be related to the compact pillar structure of the formed layer (as seen in Fig. 3a), which resulted in decreasing the active sites for further nucleation of CPH phase.

As illustrated in Fig. 4d, resistances increased during the immersion times <100 h, followed by decrease in all the samples. This indicates that during the first time periods (lower than 100 h), the CPH film began to grow as was observed in C_c–t curves (Fig. 4b). The subsequent decrease in R_p–t curves for times above 100 h can be attributed to the increase in porous structure of the formed layer as the same feature observed in SEM investigations.

Potentiodynamic polarization has been applied as a relevant tool for characterization of corrosion behavior of surface films. Here, this method was used to determine the stability of the formed layers after 12 days immersion in SBF solution. As it is shown in Fig. 5, there was a potential breakdown in all the samples except for sample 2. The continuous charge transfer for sample 2 is in good agreement with its dense structure in SEM

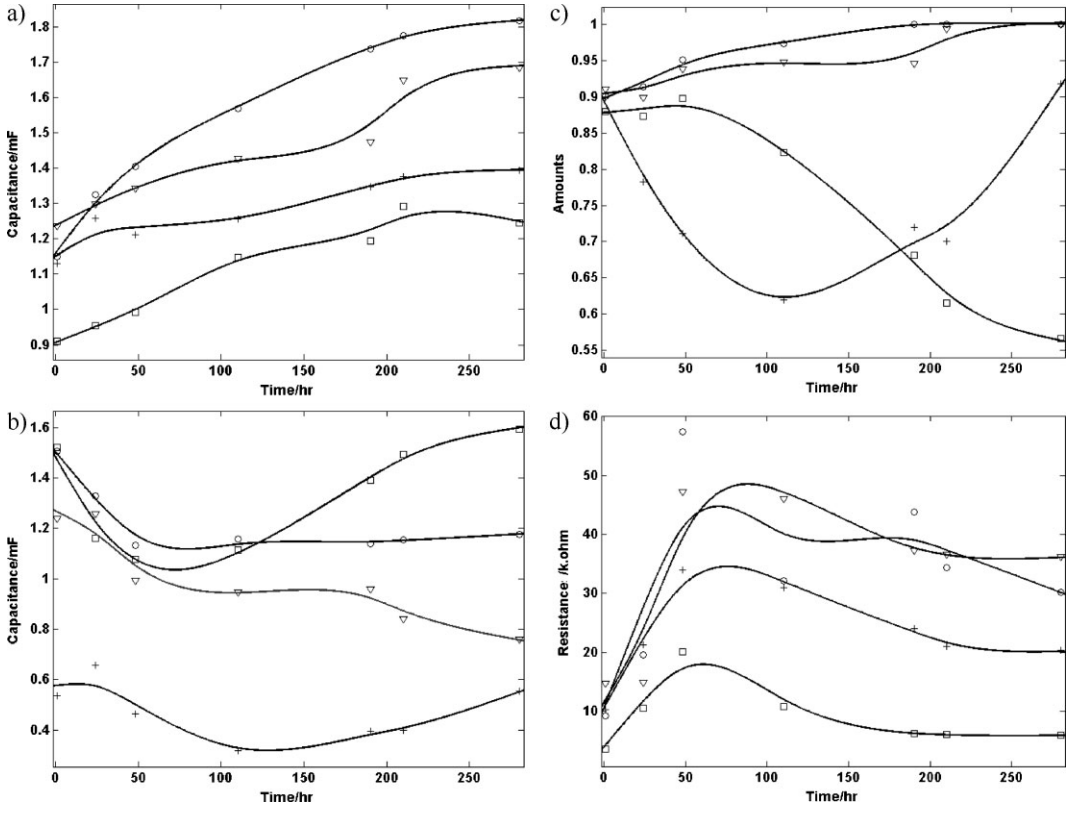

Figure 4. EIS fitted results (a) C_{dl}, (b) Z_{CPE}, (c) n_{CPE}, and (d) R_c for (+) 2 h, (o) 3 h, (□) 4 h, and (▽) 5 h sintered NiTi

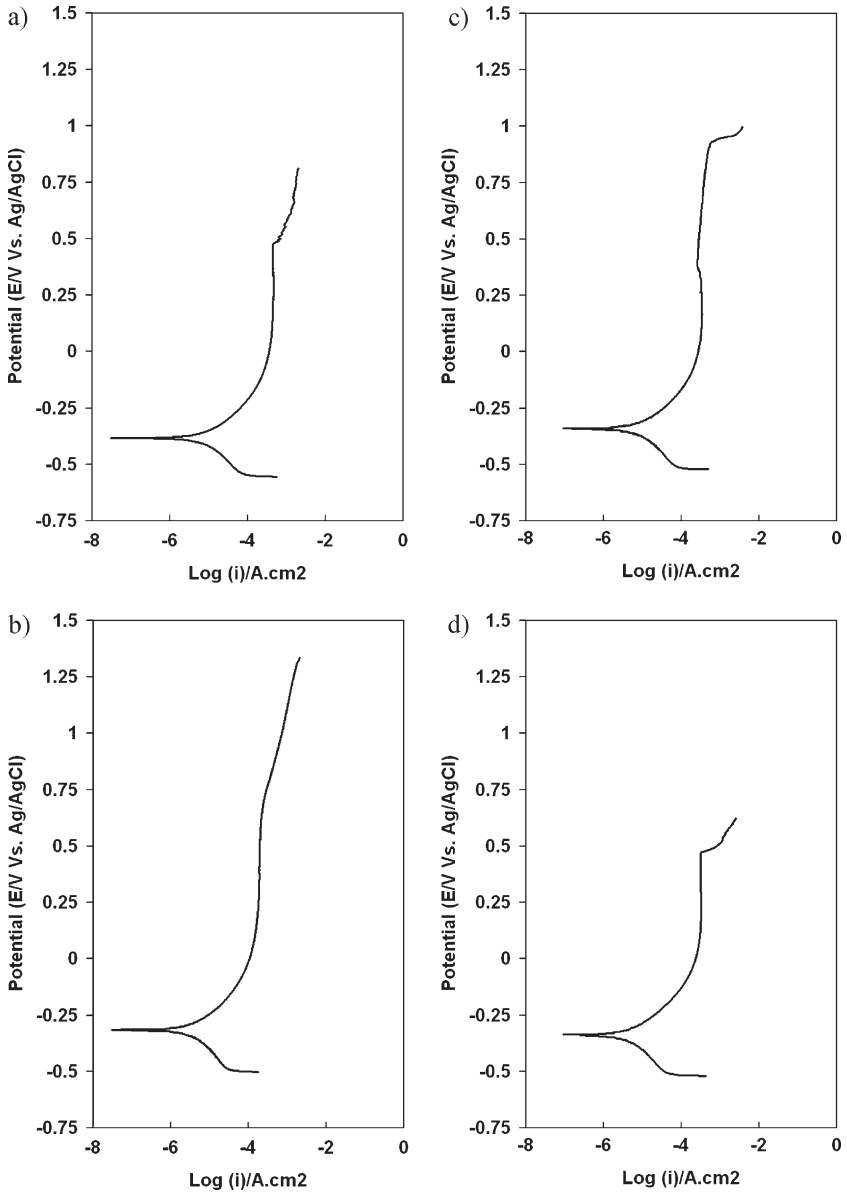

Figure 5. Potentiodynamic polarization of the (a) 2 h, (b) 3 h, (c) 4 h, and (d) 5 h sintered NiTi after 12 days immersion in Ringer SBF

images. Also the potential breakdown in low voltages in samples 1 and 4 confirmed their porous structure (i.e., pillar-like and spongy-like, respectively) as discussed previously. In the potentiodynamic curve of sample 3, a decrease in current density is observed followed by an increase and a final breakdown. Therefore, a change in structure of the surface layer is expectable.

4 Conclusions

The electrochemical behavior of sintered NiTi pellets which were immersed for 12 days in SBF solution, was investigated using EIS analysis and potentiodynamic polarization. It was shown that CPH phase was formed on all the samples while their morphology changed from a pillar particulate structure to a spongy network. The electrochemical results showed that NiTi samples obtained after 3 h sintering at 950 °C, exhibit enhanced tendency for the formation of a stable CPH film during 12 days immersion in SBF solution.

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