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Evaluation of NaOH pre-treatment on the corrosion behavior and surface characteristics of hydroxyapatite coated NiTi alloy

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Abstract
Successful short-term implementation of nickel-titanium (NiTi) alloys as implants has been a motivation for the development of long-term applications. However, rendering these as safe implant materials is challenging. The major problem associated with the use of NiTi for in-vivo applications is the potential risk of Ni release from the implant surface due to the corrosive environment of the body. Various methods including surface treatment techniques with acid and alkali solutions and application of biocompatible coatings have been used to overcome these difficulties. In particular, NaOH pre-treatment has been commonly performed for surface activation of the substrate material to enhance the adhesion properties of coatings. The present work investigates the effect of NaOH pre-treatment on the hydroxyapatite (HA) coating and the resulting corrosion behavior of and cell response to HA coated NiTi wires. Microstructural examinations showed that the coating integrity deteriorated with prior NaOH treatment which also increased the corrosion rate as evidenced by potentiodynamic measurements. XPS analysis revealed heightened Ni levels on the sample surfaces and cytotoxicity tests showed decreased cell viability for the samples with pre-treatment. Absence of NaOH pre-treatment led to lower contact angle values pointing to higher biocompatibility.

Keywords NiTi · Coating · Hydroxyapatite · Corrosion · Cell viability · Surface wettability

1 Introduction

Nickel-titanium (NiTi) shape memory alloys are increasingly utilized in biomedical fields such as orthopedic [1–3], dental [4] and cardiovascular [5, 6] applications owing to their superior properties including shape memory effect, super-elasticity and reasonable biocompatibility [7]. Having a large force to size ratio and being easily applicable in small dimensions render NiTi wires a favorable material for particular medical applications that require limited operational area and faster implantation. Although NiTi has been utilized very widely in biomedical applications, Ni release is still arguably the most fundamental concern of using NiTi alloys as an implant material. One promising approach to inhibit or mitigate Ni leaching is to coat the implant surface with hydroxyapatite (HA) since it shows enhanced corrosion resistance and high resemblance to bone tissue and provides a strong interface [8]. This coating approach aims to obtain a synergistic effect combining extraordinary mechanical and functional properties of NiTi alloys with the biocompatibility of HA to meet the strict requirements for biomedical applications. Among various coating techniques [9–12], dip coating method is a common approach that increases the biocompatibility of the metallic implant by depositing a biocompatible coating layer on the substrate creating an interface between the implant surface and the surrounding tissue [13, 14].

In order to improve the stability of the coating layer and to enhance its attachment on the substrate, several researchers have utilized different surface treatment methods on NiTi substrates. With the use of acid and alkali solutions, it is possible to modify the substrate surface for improved coating quality [15]. NaOH treatment is a well-known method that has been applied to various substrate-coating couples. While there are numerous studies focusing on the positive effects of this treatment on the

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biocompatibility and the following deposition characteristics of the apatite layer [16–20], only a few discussed its disadvantages focusing on NiTi especially on Ni release after surface treatment using NaOH [21, 22]. Hence, combining different strategies as NaOH pre-treatment and HA coating to improve the biocompatibility of NiTi samples needs further attention due to the inevitable risk of Ni release.

Despite the inherent challenges, there have been many efforts reporting that sintering may improve the adhesion by enhancing the bonding at the coating-substrate interface [23, 24]. Furthermore, sintering may affect the porosity of the coating layer, which is an important property that needs consideration for implantable materials. Sintering treatments typically take place at high temperatures. However, particularly for NiTi alloy, high-temperature sintering may trigger phase transformations and thus results in recrystallization mechanisms which may cause deterioration of the mechanical properties. In this study, thermal treatments were conducted during the sintering step in order to improve the coating adhesion between the HA layer and the underlying NiTi wire substrate surface.

Biocompatibility is one of the crucial features of a successful implantation process. Medical implant materials usually have direct contact with living tissue in a body environment and their response must be tested before the implementation to ensure safe and long-term usage for humans. The in-vitro cytotoxicity test is a widely utilized method which evaluates toxicity and biocompatibility of the implantable materials. Three types of cytotoxicity experiments, extract, direct and indirect contact tests are mainstream for evaluating cytotoxicity [25]. Among these, the indirect cytotoxicity method is commonly applied being highly sensitive, fast and easy to use.

Surface wettability measurements provide the observational basis for a detailed understanding of material surface and behavior in biological environments by evaluating their biocompatibility. In order to analyze surface wettability, contact angle is one of the most convenient and commonly used methods due to its simplicity [26]. Several studies have reported the consistency between wettability values and biocompatibility and proved that biomaterial surfaces with moderate hydrophilicity possess enhanced cell growth and biocompatibility [27, 28].

Studies recorded in the literature evaluating the formation of HA coatings on NiTi utilized substrates in the form of plate [8, 13]. However, use of wire form metallic implants is inevitable in particular when operational space is limited. NiTi shape memory alloys have been considered efficient implant materials due to their capability of providing high force/mass ratio with small footprint including wire geometry [29, 30]. Nevertheless, there are few studies focusing on the coating of wire shape substrates [10, 31].

To the best knowledge of the authors, the present study demonstrates for the first time that the effect of surface pre-treatment of wire form NiTi with NaOH prior to HA coating is noticeable even for low concentrations and adversely affects the corrosion performance and the ensuing biocompatibility. Hence, results of the present study would be instrumental for filling the knowledge gap in HA coating of NiTi wires using the dip coating method and revealing the resultant corrosion performance, surface wettability characteristics and also affirmative behavior in biological environment.

2 Materials and methods

2.1 Sample preparation

Equiatomic NiTi wire of 0.8 mm diameter was selected as the substrate. NiTi substrates were treated with 0.5 M, 1 M and 4 M NaOH solutions at 60 °C for 24 h, followed by drying at 40 °C for 24 h. Dip coating method was chosen due to favorable outcomes including the provision of a more quantitative coating layer and the non-destructive characteristics and fairly simple procedure of the process. Dip coating suspension was prepared by adding 1 g of HA (Alfa Aesar, Germany) into 140 ml distilled water followed by vigorous stirring on a magnetic stirrer to obtain a homogenous suspension. NiTi samples were immersed into the dip coating suspension, held for 2 h and withdrawn with a constant speed of 6 mm/s which is followed by heat treatment at 520 °C for 30 min in order to accomplish sintering of the HA layer to improve mechanical stability of the coating. Substrates were named according to their NaOH treatment condition as XNaOH-C, where *X* represents the concentration of NaOH solution and *C* indicates the application of the subsequent coating process. For instance, *0.5NaOH-C* refers to the sample which is treated with 0.5 M NaOH solution followed by HA coating and heat treatment. Sample naming is summarized in Table 1.

Table 1 Sample naming convention based on NaOH surface treatment and HA coating conditions

Sample name	Concentration of NaOH treatment solution	HA coating following NaOH treatment
As-received	–	–
C	–	+
0.5NaOH-C	0.5 M	+
1NaOH-C	1.0 M	+
4NaOH-C	4.0 M	+

2.2 Characterization methods

Following the coating process, the structural integrity of the HA layer was investigated via microstructural observations. Surface morphology of the HA coating layers was studied by scanning electron microscopy (SEM, Zeiss Ultra Plus Field Emission). X-ray photoelectron spectroscopy (XPS, Thermo K-Alpha) measurements were carried out to evaluate the chemical composition of the sample surfaces as a function of NaOH treatments with varying concentrations. Contact angle measurements were carried out to evaluate the wettability of selected NiTi samples including as-received, C, 0.5NaOH-C and 1NaOH-C samples. All measurements were achieved using a light microscope system. The average contact angles of the selected NiTi surfaces were examined by using the sessile drop technique at room temperature. Experiments were conducted by dropping distilled water onto the surfaces. Average of four consecutive measurements was calculated for each sample.

Corrosion experiments were designed to simulate the body environment and surface treatment conditions are selected to signify the effect of solution concentration. Electrochemical measurements were obtained utilizing a potentiostat (Gamry Interface) to determine the corrosion resistance of the samples in a simulated body fluid (SBF) at 37 °C with a pH of 7.4 in order to mimic the body environment.

2.3 Evaluation of cytotoxicity

The biological responses of the samples were evaluated via cell culture assessments. In order to determine the cell viability on the NiTi samples, indirect toxicity assessment was conducted using mouse L929 fibroblast cells. As-received, C and 0.5NaOH-C samples were evaluated for their cytotoxicity responses. All samples were eluted in a specific cell culture medium involving DMEM + 10% FBS at 37 °C for 72 h. A routine subculture was used to maintain the cell line. The samples were placed in a multi well tissue plate and L929 fibroblast cells were seeded with 10.000 of cells/ml for each well. The cell attachment process was initiated by keeping all samples in a CO_2 incubator at 37 °C for 24 h. Then, the MTT metabolic activity test was performed and the results were obtained by photometric reading at 570 nm. DMSO solution was used as a positive control while the DMEM medium was used as a negative control. The results were calculated by considering the negative control as 100% alive.

3 Results and discussion

3.1 Surface morphology

Surface morphologies of the as-received and coated (with and without NaOH pre-treatment) samples are shown in Fig. 1a–e. Morphology of the as-received material contains surface irregularities with an initial roughness (Fig. 1a). Formation of a HA layer was observed after dip coating followed by the subsequent heat treatment as evidenced by the disappearance of the grain substructure. The combination of coating and heat treatment resulted in the coalescence of HA particles and the formation of a well-densified layer (Fig. 1b). Previous works report that nanosized HA particles accomplish a dense coating layer even at low sintering temperatures which is in agreement with the observations of the current study [12, 32]. The uniform coating on sample *C* can be observed in view of the lower magnification SEM micrographs (Fig. 1b—inset) while the other surfaces which belong to NaOH pre-treated samples have inhomogeneous surface topography pointing to the reduced coating quality with increasing NaOH concentration. The non-uniform distribution of HA particles is visible as shown in Fig. 1c–e.

3.2 XPS analysis

The Ca/Ni and Ni/Ti coefficients as a function of different surface treatment conditions were obtained using XPS measurements as shown in Fig. 2 to evaluate the effect of NaOH pre-treatment on the surface characteristics of the samples. Results indicated that the Ca/Ni ratio decreased with the increasing concentration of NaOH treatment denoting elevated Ni levels on the surface of the samples. The Ca/Ni ratio was the most favorable (26.56) for sample *C* having no surface treatment. Moreover, increasing the concentration of the NaOH solution intensified the Ni/Ti ratio in the treated samples. These findings are in agreement with Chrzanowski et al. [22] reporting increased nickel content in the surface top layer with NaOH treatment which would pose the potential risk of decreasing the biocompatibility due to the heightened risk of Ni release.

With increasing NaOH concentration Ni/Ti ratio was observed to escalate, indicating that the obtained surfaces are rich in Ni. The increase in the Ni/Ti ratio may be attributed to the formation of a thin film in oxide form rich in Ni on the substrate surface as a result of NaOH treatment [21]. However, Ni was also traced for the sample without NaOH treatment although to a much lesser extent as compared to its counterparts with NaOH treatment. This observation indicates that the increase in Ni/Ti ratio may also be related to another phenomenon in addition to the NaOH treatment.

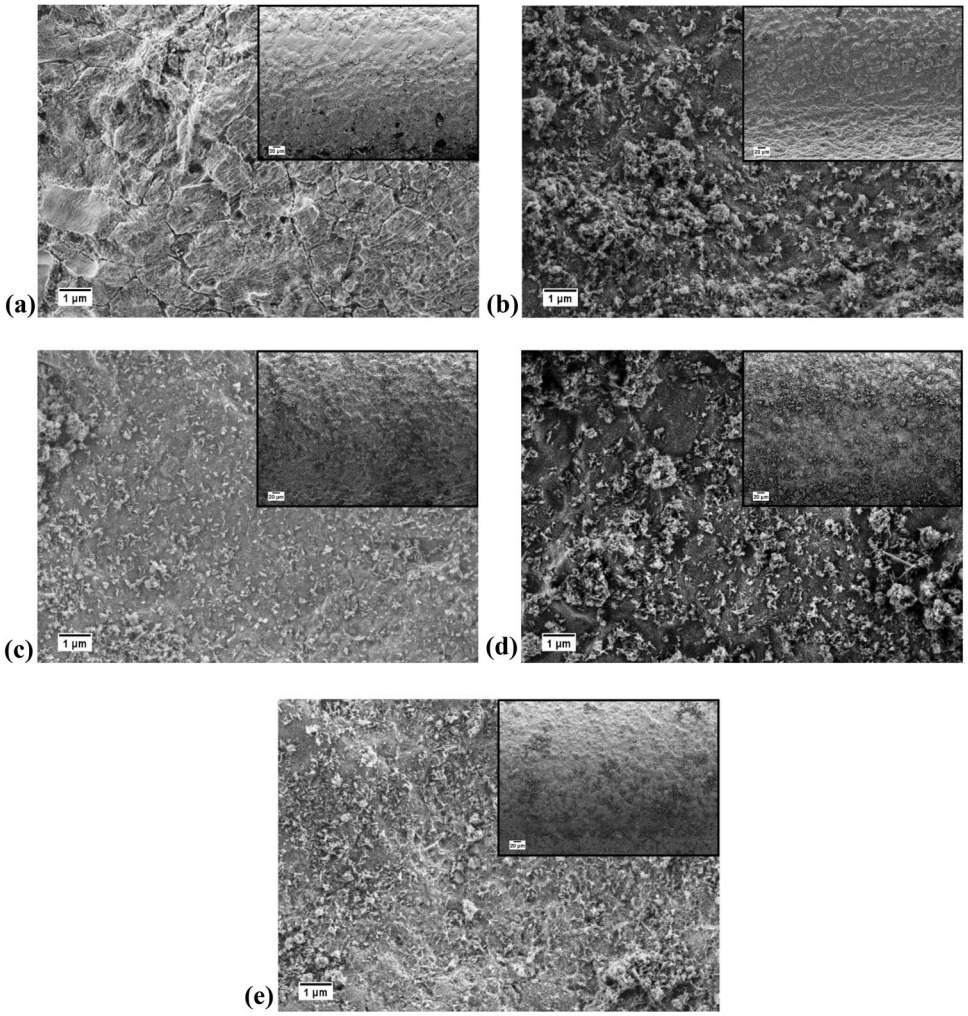

Fig. 1 SEM micrographs of NiTi samples with different surface conditions; **a** as-received, **b** C, **c** 0.5NaOH-C, **d** 1NaOH-C, **e** 4NaOH-C

The increase in Ni/Ti ratio on the sample surfaces may also be associated with the heat treatment applied for sintering purposes. Several research efforts underline similar observations. For instance, a significant increase of Ni concentration was reported after a heat treatment at 500 °C for 15 min [33]. Wu et al. also revealed the effect of heat treatment on the Ni release from NiTi surfaces exhibiting that the released concentration increased significantly between 450 °C and 550 °C [34]. However, sintering is a crucial step which may not be omitted in order to obtain a sufficiently strong bond between the HA coating and the NiTi substrate for real life applications. Results obtained in this study indicate that NaOH treatment and sintering may have a combined effect on the increased Ni/Ti ratio however, the former is the dominating factor as observed by the XPS measurements.

Surface irregularities and cracks occurring on the NaOH treated samples could also affect the Ni/Ti ratio. The *4NaOH-C* has the highest Ni/Ti ratio (9.84) and the lowest Ca/Ni (1.63) which obviously is not suitable for biomedical applications since a Ni/Ti high ratio is undesirable due to the risk of Ni release and its detrimental biological effects [35]. It can be asserted that among the conditions studied, C displays the most suitable characteristics for biomedical applications by displaying the highest Ca/Ni and the lowest Ni/Ti ratios.

3.3 Surface wettability

Contact angle measurements were conducted to assess the wettability characteristics of selected surfaces (Fig. 3), for which the contact angle values are given in Table 2. As-received NiTi was used as a reference having the highest contact angle. HA coating clearly had a positive effect on decreasing the contact angle thus increasing wettability. However, as it can be seen in Table 2, NaOH treatment resulted in a variation of the contact angle where the contact angle increases as the NaOH concentration increases. The contact angle values were significantly higher for both NaOH treated samples when compared with that of the HA coated sample without prior surface treatment.

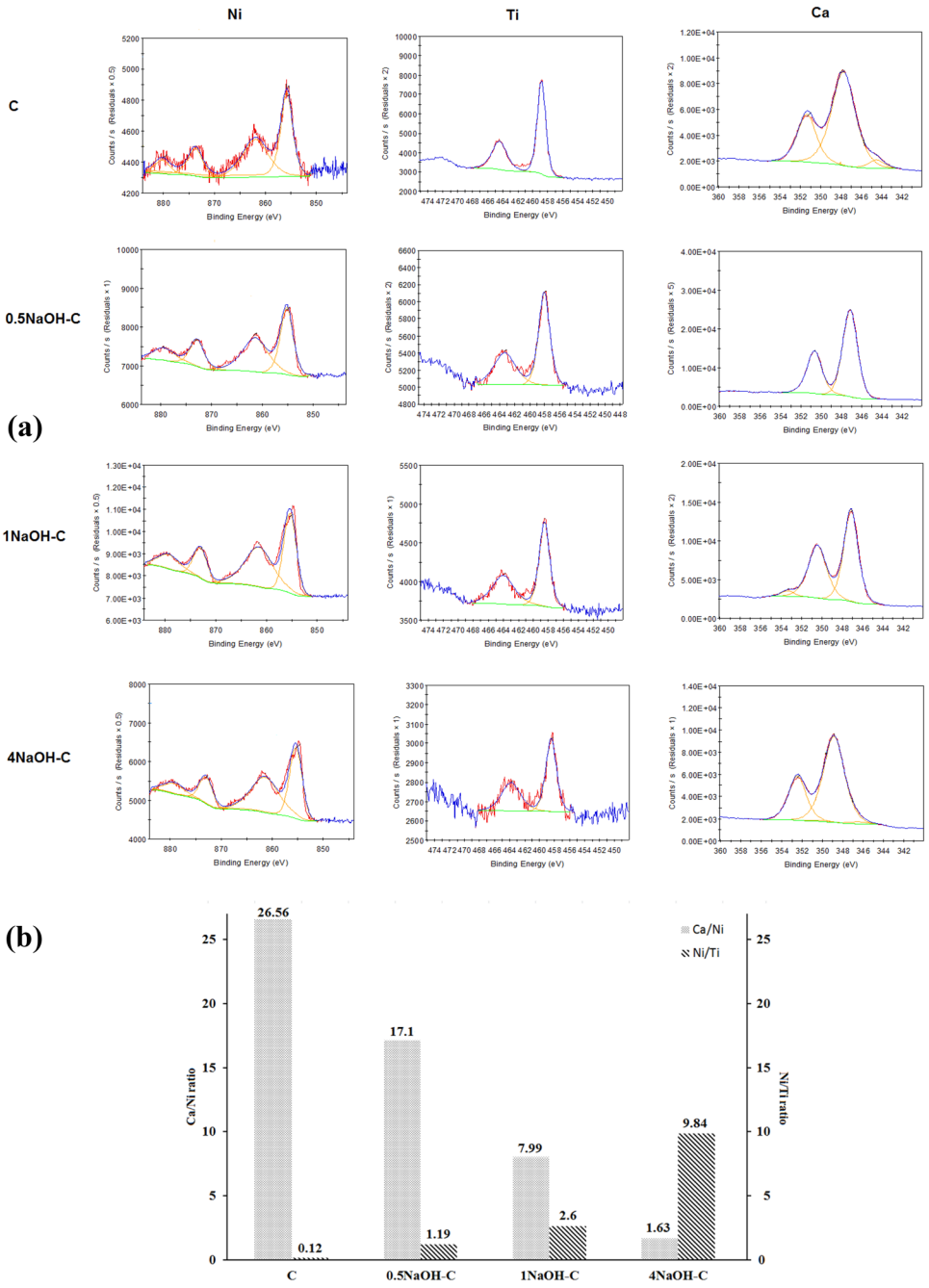

Fig. 2 Results of XPS measurements; **a** curves of selected samples for Ni, Ti and Ca elements, **b** Ca/Ni and Ni/Ti ratios of the samples

Sample C has the lowest contact angle value and the surface shows hydrophilic characteristics. Several studies have confirmed that hydrophilic surfaces which have contact angles smaller than 90° are more suitable for biomedical applications [26]. The low contact angle mostly addresses favorable properties which improve cell attachment onto the surface including good adhesion, high wettability and high surface energy [27]. Results of the contact angle measurements suggest that the surface obtained with HA coating without any prior NaOH treatment has good adhesion properties and thus might have higher biocompatibility which is clearly evidenced by the findings of cell viability tests as elaborated in the following.

3.4 Corrosion rate

Corrosion experiments were performed in SBF solution at 37 °C, according to which the effect of NaOH treatment on corrosion behavior was found significant. It was determined that sample C possessed the best corrosion resistance while 4 NaOH-C has the highest corrosion current density and corrosion rate as given in Table 3. Results of the corrosion

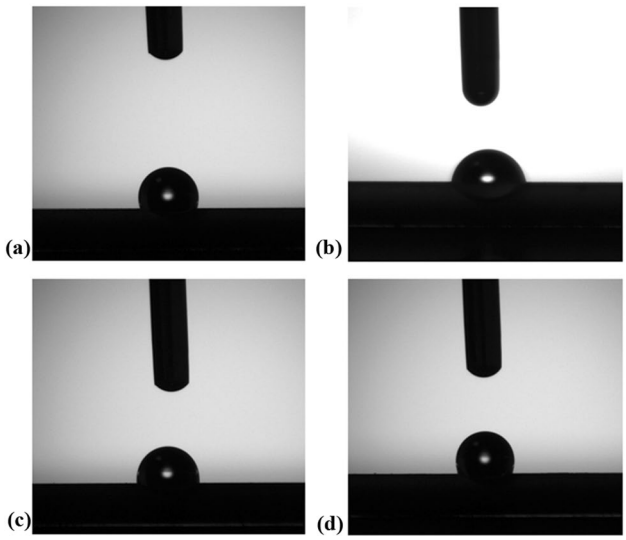

Fig. 3 Images of contact angle measurements; **a** as-received, **b** C, **c** 0.5NaOH-C, **d** 1NaOH-C

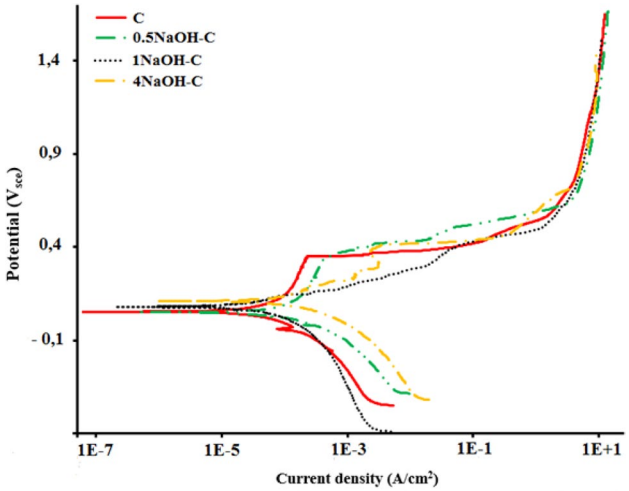

Fig. 4 Polarization curves of NiTi samples with different surface conditions

Table 2 Contact angle measurement results for the as-received, C and 0.5NaOH-C conditions

Sample	Average contact angle (degree)
As-received	111.15
C	75.81
0.5NaOH-C	97.83
1NaOH-C	109.26

Table 3 Potentiodynamic polarization results of samples in simulated body fluid solution

Sample	I_{corr}(A/cm^2)	Corrosion rate (mpy)
C	3.92×10^{-5}	19.97
0.5NaOH-C	8.71×10^{-5}	44.33
1NaOH-C	8.8×10^{-5}	45.04
4NaOH-C	4.49×10^{-4}	228.90

test denote to pitting corrosion of the NaOH treated samples where corrosion rates increase with increasing NaOH concentration. The polarization curves are shown in Fig. 4. The results showed that the corrosion performance degraded with the increased concentration of NaOH solution.

In Fig. 5, the surface morphology of NiTi samples subjected to SBF solution can be traced. It is notable that the application of 0.5 M NaOH treatment reveals cracks on the coating layer (Fig. 5b–d) while sample C has crack-free morphology pointing to a more stable coating structure against corrosion (Fig. 4a–c). The NaOH treated sample had a higher pit density on the surface and the surface pits can easily be discerned at high magnification as observed in Fig. 5b. This observation is in parallel with the potentiodynamic polarization test results and may be attributed to the mismatch of the thermal expansion coefficients of the HA coating layer and the underlying oxide layer rich in Ni which forms due to the NaOH treatment. Moreover, comparison Fig. 5c, d shows that NaOH treatment leads to a variation in the surface morphology of the samples possibly due to an intermediate oxide layer between the NiTi surface and the HA coating.

3.5 Cytotoxicity

Cell culture assessments were obtained using mouse L929 fibroblast cells. After 1-day incubation, the cell viability on the samples was determined via photometric reading. Figure 6 shows that no remarkable toxicity is observed for all samples. The results indicated that L929 fibroblast cells successfully grow on all NiTi surfaces after 24 h following seeding. As-received sample had relatively lower cell viability compared to the negative. A similar result was obtained for 0.5 NaOH-C sample which had a lower cell viability compared to the negative and a similar value compared to the as-received sample indicating that the sample with NaOH pre-treatment followed by HA coating had no significant improvement on the cell viability as compared to the as-received state. On the other hand, sample C without prior NaOH treatment had cell viability almost 10% higher than the sample with NaOH pre-treatment. It can be asserted that this result is promising in favor of the non-treated sample and corroborates the SEM observations (Fig. 1a–c) indicating that the samples

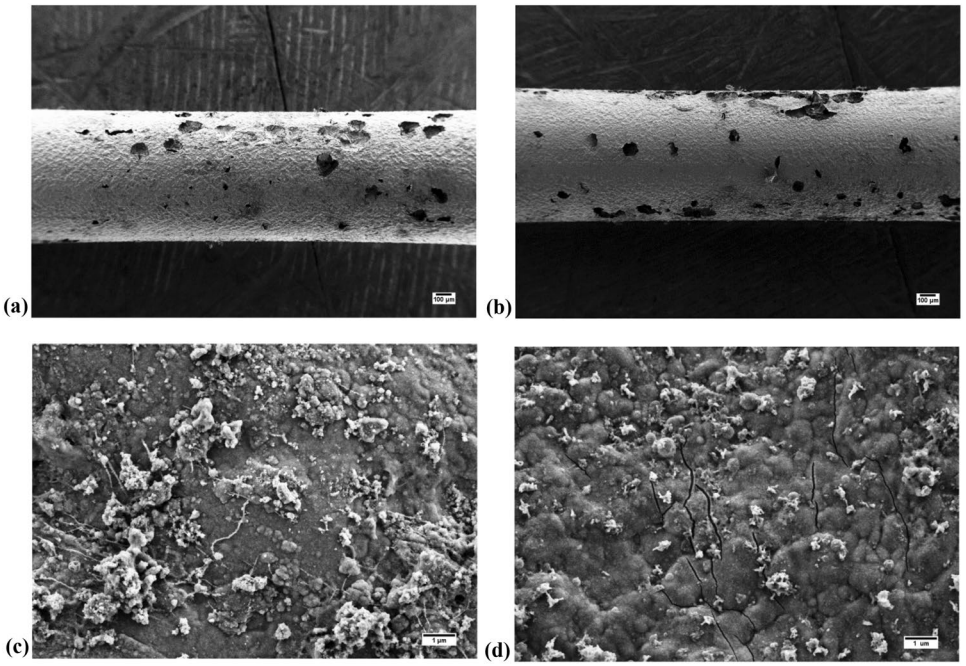

Fig. 5 SEM micrographs of NiTi samples following corrosion experiments; **a** sample C at × 100, **b** sample 0.5 NaOH-C at × 100, **c** sample C at × 20k, **d** sample 0.5 NaOH-C at × 20k

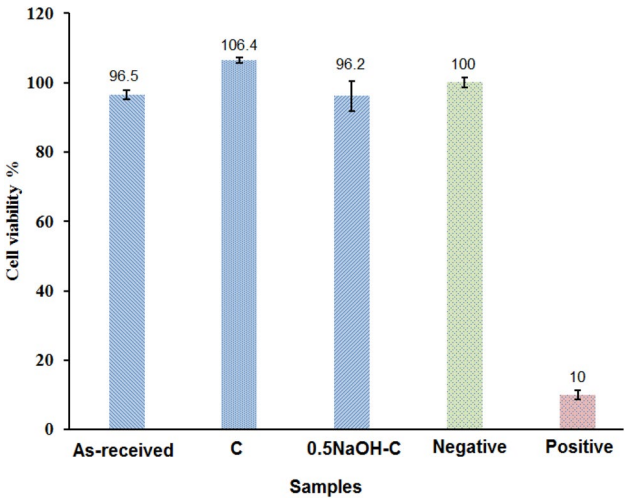

Fig. 6 Cell viability test results of as-received, C and 0.5NaOH-C NiTi samples

without NaOH treatment result in a more successful subsequent HA coating layer. Accordingly, findings obtained in this work via a blend of surface characterizations and biological analysis have the potential to shed light on the utilization of HA coated NiTi as a prospective implant material. Still, further biocompatibility studies based on the target biomedical application are required for detailed insight regarding the specific use.

4 Conclusion

NaOH pre-treatment of substrate materials prior to coating is a widely utilized method to chemically activate the substrate surface in order to achieve better adhesion of coatings. In the present study, the effects of NaOH treatment on the corrosion resistance of HA coated NiTi shape memory alloys were investigated. HA layers were successfully deposited on untreated and surface treated NiTi via dip coating. It was shown that the application of NaOH surface treatment strongly and negatively affects coating quality and corrosion resistance. The coated sample without prior surface treatment showed the best corrosion performance. In contrast, elevation in Ni amount was recorded on the treated sample surfaces with the increase of NaOH concentration, clearly indicating that coating quality and corrosion resistance deteriorate with NaOH modification. NaOH treatment considerably decreased the surface wettability such that the surface without NaOH treatment prior to HA coating has better wettability characteristics. Cytotoxicity experiments demonstrated the absence of significant toxicity for all samples irrespective of the NaOH pre-treatment. However, HA coated samples without prior NaOH treatment resulted in more promising cell viability counts.

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