Corrosion behaviour of the NiTiX (X = Si, Mg, Al) alloy prepared by self-propagating high-temperature synthesis

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The NiTi alloys are used in the biomaterial field, because of their shape memory, superelasticity, and good corrosion resistance. The influence of alloying elements on the corrosion behaviour of NiTi was studied in this research. Samples were made by the self-propagating high-temperature synthesis method, milled, and then sintered by the spark plasma sintering method. Si, Mg, and Al were used as alloying elements always in 5 wt.%. Studied materials were compared with reference cast NiTi. Polarization resistance was measured after 1 and 12 hours of stabilization in phosphate-buffered saline. It was found out that alloying elements do not have a clear effect on polarization resistance. Si increased R_p and on the other hand, Al decreased it. Measurement of cyclic potentiodynamic polarization in PBS was conducted, too. All studied samples showed signs of localized corrosion. Corrosion was probably initiated in pores, which are presented on the surface due to used manufacturing technology.

INTRODUCTION

NiTi alloy is used as a biomaterial due to specific mechanical properties such as shape memory, superelasticity, and pseudoplasticity. The superelasticity phenomenon is used the most in stent manufacturing. NiTi alloy has good corrosion resistance. Mechanical properties and corrosion resistance depend on phase composition. It is crucial to suppress Ti_2Ni phase formation. Ti_2Ni phase harms mechanical properties (brittleness) and corrosion resistance [1-5]. Alloying elements with a high oxygen affinity can eliminate the formation of this phase [6]. Alloying elements used in this work should improve the corrosion resistance. The corrosion resistance of NiTi alloy is inferior to the corrosion resistance of pure titanium and Ti-6Al-4V, which are rich in titanium [7, 8]. The NiTi is often thermally treated. The thickness of the oxide layer depends on temperature. The surface layer is formed by TiO_2 . Different phases such as Ni_3Ti , Ni_4Ti and Ni can be formed under the oxide layer. Chemical composition depends on oxygen access, the duration and

the temperature of the heat treatment [9]. The oxide layer is thicker when electropolishing or chemical polishing is applied. Due to this passive layer, the NiTi alloy is resistant to the most types of corrosion attacks. NiTi is susceptible to localised corrosion which is dependent on certain chloride concentrations and potential [10]. Corrosion resistance depends on phase composition. Ti_2Ni phase impairs the resistance to localized corrosion and is more resistant to general corrosion. On the other hand, the Ni_3Ti phase shows worse corrosion resistance against both types of corrosion [11]. Corrosion resistance also depends on the porosity of the sample. Porous samples show no passivity region and lower values of breakdown potential [12-14]. Alloying of NiTi may be used to change mechanical properties. When other alloying elements are presented the corrosion resistance is changed. Cu addition improving the repassivation capability in the crevice, due to Cu redeposition [15, 16]. Co was used as an alloying element too. This element has no significant effect on corrosion resistance [17]. Other studies assess the influence of Pd, Fe, Cr and Co. It was found out that Cr and Co have a detrimental effect on repassivation in comparison to binary NiTi [18]. Fe and Pd increase the corrosion resistance in comparison to binary alloy. In the case of alloying by Pd, the passive layer contains TiO_2 and metallic Pd [16]. The corrosion resistance depends on the composition of the environment. It includes the pH and presence of inorganic and organic compounds. Based on the Pourbaix diagram, it was found out that nitinol corrodes in acid solution when the dissolution of titanium takes place, and it is followed by nickel dissolution. Nitinol shows passivity in a neutral and alkaline environment [11]. When only inorganic compounds are presented (e.g.: SBF, Hank's solution) the passivating film is composed primarily of TiO_2 [7, 8, 19]. When the organic compounds are presented the oxide layer is very similar to the one which forms in purely inorganic solutions.

The film has a smaller thickness and is more porous. Also, the biofilm is formed on the surface [20]. Another factor that influences corrosion resistance is mechanical stress. During mechanical stress, nitinol can be associated with rupture of the passive film and the metal can be exposed to the corrosion environment. The material shows stable passivity under constant strain [18, 21]. The breakdowns occur during the dynamic strain when the rupture of the passive layer occurs. That uncovers the new surface of metal exposed to the environment [18]. Failure of the passive layer can lead to the leaching of nickel ions into the human body. Several studies have shown that nickel concentrations decrease with increasing exposure time [22]. The following methods can be used to produce NiTi alloy using powder metallurgy: hot isostatic pressing (HIP), self-propagating high-temperature synthesis (SHS) and spark plasma sintering (SPS). The specific method is chosen according to whether it is necessary to obtain a compact or porous material [23]. In the case of the SHS method, pure titanium and pure nickel powders are mixed first. Subsequently, the whole mixture is exposed to increased pressure [24, 25]. Then either the ignition mode or the thermal explosion is continued. During ignition, only one side of the sample is heated and due to the heat released during the reaction between the titanium powder and nickel, the reaction moves through the whole sample. Using this mode, a porous pattern is created. There are no pure titanium and nickel phases in the sample [24]. In the thermal explosion mode, the whole sample is heated at once and the reaction is again kept running by the heat generated by the reaction between titanium and nickel, the whole reaction taking place in an inert atmosphere. Using this mode, titanium-rich phases and nickel-rich phases appear in the alloy [25]. Spark plasma sintering is a method that uses electric current to sinter already pre-melted powders under high pressure in a graphite crucible. This method is very fast and requires relatively lower temperatures compared to SHS methods [23]. The sintering takes place in an inert atmosphere of argon. The porosity of the alloy decreases with increasing temperature [26]. Using this method, Ni₃Ti and Ti₂Ni phases also appear in alloy [27].

This study aims to determine the influence of alloying elements on the corrosion behaviour of NiTi alloy prepared by powder metallurgy.

EXPERIMENTAL

Samples

Experiments were conducted on NiTi, NiTiSi, NiTiMg, and NiTiAl samples. Alloying elements were present in 5 wt.%. All samples were prepared by the SHS method at 900 °C, then grounded and sintered by SPS at 1100 °C. The cast NiTi manufactured in UJP Praha was used as reference material.

Samples had a cylindrical shape with a diameter of 3 cm and thickness of 0.21 cm. The exposure area of the samples was 2.5 cm². Before the exposition samples were always ground by sandpaper of roughness P1200. The specimens were washed with distilled water and degreased in ethanol.

Surface characterisation

The microstructure of all samples was described. The samples were ground by sandpaper of roughness P2500 then polished by diamond paste and etched by Kroll's reagent. The microstructure was studied by scanning electron microscope (SEM) Tescan Vega3 LMU and by EDS analysis by OXFORD INCA 350 analyser. EDS analysis provided information about chemical composition in atomic percentages. The microstructure was also studied by metallographic microscope Olympus PME 3.

Corrosion behaviour

The phosphate-buffered saline (PBS) was chosen as a corrosion environment. Table 1 shows the composition of PBS. Before the measurement, the solution was bubbled by nitrogen for 30 minutes to minimize the effect of oxygen. All measurements were conducted at 37 °C.

Tab. 1. Composition of PBS

Component:	Concentration [g/l]:
NaCl	8
KCl	0.2
KH ₂ PO ₄	0.2
Na ₂ HPO ₄	1.15

Open circuit potential (OCP) was monitored for 12 hours followed by the polarization resistance measurement. Polarisation resistance was also measured after 1 hour of OCP stabilisation to minimize polarization resistance data distortion by localized forms of corrosion. The polarization was measured in an interval of ±20 mV/OCP with a polarization sweep rate of 0.125 mV/s.

Tests were performed in a 3-electrode setup with a graphite counter electrode. Silver-silverchloride electrode (SSCE) with a concentration of inner electrolyte KCl 3 mol/l was used as a referent electrode. All measurements were performed at 37 °C using the potentiostat Gamry Instrument model Reference 600.

Susceptibility to localised corrosion attack was tested according to ASTM F2129-08. The measurement setup consists of one-hour stabilization of the open

a) NiTi

b) NiTiSi

circuit potential and cyclic polarization. Polarization started at -0.1 V/OCP and continued to 0.850 V/SSCE and back to the original value. Polarization sweep rate was set to 1 mV/s. The samples were analysed by SEM after every measurement.

RESULTS AND DISCUSSION

Microstructure

Figure 1 shows the microstructure of all studied samples. The microstructure of the NiTi contains 2 phases. The brighter part is formed by the NiTi phase and the darker part is formed by the Ti₂Ni phase. The picture shows that the surface of the sample is not completely compact, and pores are presented on the surface.

d) NiTiAl

c) NiTiMg

e) NiTi ref

Fig. 1. Microstructure of samples studied by BSE (SEM): a) NiTi, b) NiTiSi, c) NiTiMg, d) NiTiAl, e) NiTi ref

By adding the alloying elements, the microstructure is getting complicated. NiTiSi alloy consists of two phases. The NiTi phase with 1 % of Si is presented. The next recognized phase was Ti₂ (Ni, 16 % Si). The microstructure of NiTiMg contains two phases, too. NiTi with 1 % of Mg and Ti₂ (Ni, 4 % Mg) are presented in the material. The phase composition of NiTiAl alloy was as follows. The material contained 3 phases. Two mixed phases with composition Ti (Ni, 8 % Al) and Ti (Ni, 20 % Al) were observed. The third identified phase was Ti₂ (Ni, 8 % Al).

Pores were present on the surface of all studied samples. The presence of the Ti₂Ni phase in NiTiSi and NiTiAl alloys have been found in other studies [28, 29]. The reference sample contains the NiTi phase only. The pores were caused by etching during the preparation of the sample.

Corrosion behaviour

Corrosion behaviour in PBS was investigated because PBS simulates an aggressiveness of the human body environment and also it is an environment recommended by ASTM standards. The open circuit potential of NiTi, NiTiAl and NiTiSi samples did not stabilize even after 12 hours (see Fig. 2). It was caused by pores and by the heterogeneity of the alloys' surface. The open circuit potential of NiTiMg and reference NiTi stabilized after a few hours.

There was no significant difference in values of OCP. The lowest value was measured on the NiTiMg alloy, and the NiTiAl alloy showed the highest value. Compared to the E-pH diagrams of titanium and nickel, values of open circuit potential correspond to the area of TiO₂ and the active dissolution of Ni stability respectively [11]. It can be assumed that TiO₂ is therefore responsible for the

corrosion behaviour of the alloy. A similar composition of the surface layer was also found in other experiments [30, 31]. The phase heterogeneity can significantly impair the resistance to localized corrosion. It is important to mention that the presence of alloying elements can affect the composition of the surface layer.

The highest polarization resistance was measured on NiTiSi alloy (Tab. 2). The R_p of NiTiSi was an order of magnitude higher than the R_p of other alloys. The lowest R_p was recorded on the NiTiAl. The polarization resistance of the reference sample was comparable with a sample of NiTi prepared by powder metallurgy.

Tab. 2. The polarization resistance after 1 hour and 12 hours immersion in PBS

Material	R_p (1 h) [kΩ·cm ²]	R_p (12 h) [kΩ·cm ²]
NiTi ref	20	30
NiTi	36	50
NiTiSi	145	435
NiTiMg	23	20
NiTiAl	3	0.6

The localized corrosion was initiated during 12 hours of immersion on all studied samples (see Fig. 3). The NiTiAl alloy was the most corroded, which correlates with the lowest measured polarization resistance. The NiTiMg sample showed the lowest susceptibility to localised corrosion attack. The microstructure of NiTiAl contained three different phases, for that reason this sample had the highest susceptibility to localised corrosion attack. Also, the corrosion of NiTiSi and

Fig. 2. Time dependence of the open circuit potential in PBS

a) NiTi

Fig. 3. Surface after 12 hours immersion in PBS: a) NiTi (Continue on next page)

Fig. 3. Surface after 12 hours immersion in PBS: b) NiTiSi, c) NiTiMg, d) NiTiAl, e) NiTi ref

NiTiAl samples was initiated under the O-ring, where the crevice was formed. These two samples contained phases that had lower crevice corrosion resistance than other alloys. In the case of NiTi and NiTiMg alloys, less noble phases are preferentially corroded. Reference NiTi showed no visible corrosion at all, due to homogeneous microstructure.

The instability of the OCP was caused by surface heterogeneity and pores on the surface. The influence of alloying elements is not clear. Silicon increased the polarization resistance, aluminium decreased it. The magnesium had an insignificant effect on polarization resistance in comparison with reference NiTi. The high polarization resistance of NiTiSi alloy is probably related to the presence of Si in the surface layer.

The NiTiAl alloy contained multiple phases which were all relatively rich in the alloying element. Another factor that affected the polarization resistance was the porosity of the sample, where a crevice corrosion attack should take place. Since the corrosion attack was also present on the unalloyed sample, it can be stated that the corrosion process takes place preferentially in the pores.

Due to the development of localized corrosion during 12 hours immersion, polarization resistances were also measured after one hour of exposure. The highest R_p was measured on NiTiSi and the NiTiAl showed the lowest R_p (see Tab. 2).

NiTiMg and NiTiAl samples showed higher polarization resistance than after 12 hours exposure because the localized corrosion has not been fully developed yet. NiTi, NiTiSi, and ref. NiTi showed lower R_p in comparison with 12-hour measurement, which may be caused by insufficient stabilization of the passive layer on the surface.

Based on this measurement, it is possible to get a better idea of the effect of alloying elements on the corrosion resistance, because the influence of porosity was suppressed. Silicon improved the corrosion resistance and aluminium impaired it. Deterioration in the corrosion resistance of aluminium-alloyed nitinol may be associated with the presence of multiple phases.

The cyclic potentiodynamic polarization was done to determine susceptibility to crevice corrosion. Figure 4 shows the polarization curves. The breakdown potential

Fig. 4. Cyclic potentiodynamic curves of studied materials in PBS

was presented in all samples. In that region of potentials, the phase Ti_2Ni and other less noble phases were preferably dissolved [32].

In the case of NiTiSi and NiTiMg alloys, the local increases in current densities were presented in the passivity region. This behaviour indicates a higher susceptibility to localized corrosion of phases containing Si or Mg.

The high current density of NiTi was due to the higher content of the Ti_2Ni phase. Ti_2Ni is less noble, so it dissolves preferentially [32]. The homogeneity of the reference sample caused the lowest measured

current densities. Susceptibility to crevice corrosion was also affected by the porosity of the samples. So the susceptibility to crevice corrosion is affected by both the chemical composition and the porosity of the material.

Figure 5 shows post-exposure images taken by SEM. Corrosion of all samples was initiated in the pores, there was a preferential dissolution of less noble phases (Fig. 5e). The initiation of corrosion attack also occurred on the surface in the presence of less noble phases. Images show a significant effect of porosity, which has a negative effect on corrosion resistance.

a) NiTi

b) NiTiSi

Fig. 5. Surface after cyclic potentiodynamic polarization: a) NiTi, b) NiTiSi – corroded Ti_2Ni phase (Continue on next page)

c) NiTiMg

d) NiTiAl

Fig. 5. Surface after cyclic potentiodynamic polarization: c) NiTiMg, d) NiTiAl, e) NiTi – corroded Ti_2Ni phase

CONCLUSION

The study shows the influence of the alloying elements on the microstructure and corrosion behaviour of NiTi alloys. It has been found that no alloying element suppresses the formation of the Ti_2Ni phase. The microstructure of all studied samples contained at least two phases. Immersion in PBS was performed for 12 hours showed the instability of open circuit potential which was caused by phase heterogeneity of the samples. The polarization resistance measuring showed the ambiguous influence of alloying elements. Silicone increased the polarization resistance, while aluminium decreased it. The low value of polarization resistance of NiTiAl alloy may be caused by heterogeneous microstructure and by a non-compact surface caused by the used manufacturing technology. It was found that the corrosion behaviour is influenced by two factors, heterogeneous microstructure and porosity of the material. Heterogeneity is related to the chemical composition of the materials and porosity is related to manufacturing technology. Alloying of Nitinol with Si and Mg can lead to better corrosion properties, but the manufacturing technology needs to be optimized. Above all, it is necessary to reduce the porosity of the material, to improve the resistance to localized corrosion.

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e) NiTi

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