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Biocompatibility and corrosion behavior of the shape memory NiTi alloy in the physiological environments simulated with body fluids for medical applications

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ABSTRACT

Due to unique properties of NiTi shape memory alloys such as high corrosion resistance, biocompatibility, super elasticity and shape memory behavior, NiTi shape memory alloys are suitable materials for medical applications. Although TiO_2 passive layer in these alloys can prevent releasing of nickel to the environment, high nickel content and stability of passive layer in these alloys are very debatable subjects. In this study a NiTi shape memory alloy with nominal composition of 50.7 atom% Ni was investigated by corrosion tests. Electrochemical tests were performed in two physiological environments of Ringer solution and NaCl 0.9% solution. Results indicate that the breakdown potential of the NiTi alloy in NaCl 0.9% solution is higher than that in Ringer solution. The results of Scanning Electron Microscope (SEM) reveal that low pitting corrosion occurred in Ringer solution compared with NaCl solution at potentiostatic tests. The pH value of the solutions increases after the electrochemical tests. The existence of hydride products in the X-ray diffraction analysis confirms the decrease of the concentration of hydrogen ion in solutions. Topographical evaluations show that corrosion products are nearly same in all samples. The biocompatibility tests were performed by reaction of mouse fibroblast cells (L929). The growth and development of cells for different times were measured by numbering the cells or statistics investigations. The figures of cells for different times showed natural growth of cells. The different of the cell numbers between the test specimen and control specimen was negligible; therefore it may be concluded that the NiTi shape memory alloy is not toxic in the physiological environments simulated with body fluids.

1. Introduction

The NiTi binary shape memory alloys are suitable materials for medical applications. This is due to unique characteristics of shape memory NiTi alloys such as high corrosion resistance, biocompatibility, super elastic and shape memory behavior. One of the significant factors of biomaterials for medical application is the elastic modulus compared with body tissues and bone. It is well known that biomaterials such as titanium alloys and stainless steels have high elastic modulus compared with NiTi shape memory alloys. Besides, NiTi shape memory alloys have super elastic behavior (up to 10% reversible strain). These excellent properties have made NiTi alloys a good candidate for medical applications. Formation of Titanium oxide (TiO_2) layer on the surface of the alloy enhances good biocompatibility with regard to high Ni content (above 50%) of NiTi shape memory alloys. Corrosion and release of Ni ion into the body environment lead to the decrease of biocompatibility in NiTi alloys; but many investigations approve long performance of NiTi implants [1–6], so NiTi alloys should present good corrosion resistance in contact with body fluids. Many factors affect corrosion resistance and biocompatibility of NiTi alloys such as quality of finished surface, remained elements on the surface and homogeneity of microstructure [7]; therefore corrosion investigation of NiTi alloys in the body environment can determine the biocompatibility of NiTi alloys. The body fluid consists of 1% sodium chloride and scarce value of different salts and organic components at 37 °C. Thus corrosion in the body environment is similar to warm sea water which leads to many types of corrosions such as galvanic, pitting and grooving corrosion. Many studies have been performed by researchers related to the corrosion behavior of NiTi alloys in physiological environments. Many researchers presented the corrosion resistance of Nitinol alloys is excellent and others reported the poor corrosion resistance of NiTi shape memory alloys in the literature [7]. Good corrosion resistance is due to formation of titanium dioxide on the alloy surface at natural conditions. TiO_2 has low free energy formation in comparison with TiO and NiO [8], thus titanium dioxide forms thermodynamically on the surface of NiTi alloys. Self healing of titanium dioxide in scratch test is low. It is due to existence of Ni in oxide composition. Heat treatment and surface composition of NiTi alloys affect the stability of titanium oxides.

In the present research work biocompatibility and corrosion behavior of NiTi shape memory alloys at simulated body aqueous fluids have been investigated.

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Table 1
The composition of Ringer solution.

NaCl	KCl	$CaCl_2$, $2H_2O$	Na^+	Ca^{++}	K^+	Cl^-
0.86 g/100 ml	0.03 g/100 ml	0.03 g/100 ml	147 mEq/l	4.5 mEq/l	4.0 mEq/l	156.0 mEq/l

2. Materials and methods

NiTi shape memory alloy with 50.7 atomic percent Nickel was produced by VIM (vacuum induction melting) method [9]. Pure titanium slab (99.5%) and pure Nickel plates (99.9%) were used to produce $Ni_{50.7}Ti$ shape memory alloy. The produced slab (15 × 10 × 5 cm) was rolled up to 1.5 mm thickness. The rolled sample was homogenized at 1050 °C for 24 h. This composition of NiTi alloy was chosen since it shows super elastic behavior at room temperature. In the other words the austenite finish temperature (A_f) is below 25 °C. In order to investigate the microstructure and evaluate the grain size number using the optical microscope (Olympus PMB3), the samples after grinding and polishing were etched in $2H_2O$, $2HNO_3$, and 1HF solution. Grain size number of samples was determined according to ASTM E112 standard.

2.1. DSC experiments

DSC experiments were performed (type 822e Mettler Toledo) according to ASTM F2004 standard in the air in order to determine the transformation temperatures. DSC specimen (48.2 mg) was heated up to 125 °C, where they were held for 5 min. Then the DSC measurements started by cooling the specimens down to −100 °C with a cooling rate of 10 °C min^{-1}. At −100 °C the specimens were again held for 5 min and then heated up to 125 °C with a heating rate of 10 °C min^{-1}.

2.2. Corrosion experiments

Electrochemical tests at physiological environment simulated with body fluids were done according to ISO 10993-15 standard. The electrochemical behavior was investigated in different solutions, such as Ringer solution and NaCl (0.9 weight percent) solution. The composition of Ringer solution has been presented in Table 1. The reference electrode was an Ag/AgCl electrode. The PGSTAT instrument of Autolab Company was used for electrochemical tests. General Purpose of Electrochemical Software (GPES) was used to data analysis and plotting the corrosion curves. Electrolyte solution was degasified by nitrogen for 10 min with 0.3 l/min intensity and then it was poured into the cells. Samples (2 × 1.5 × 0.15 cm) were polished and all of their surfaces except the area of 1 cm^2 were covered to preserve from contacting with electrolyte solution. The surface of the samples was degreased by acetone. The electrochemical cells were calibrated

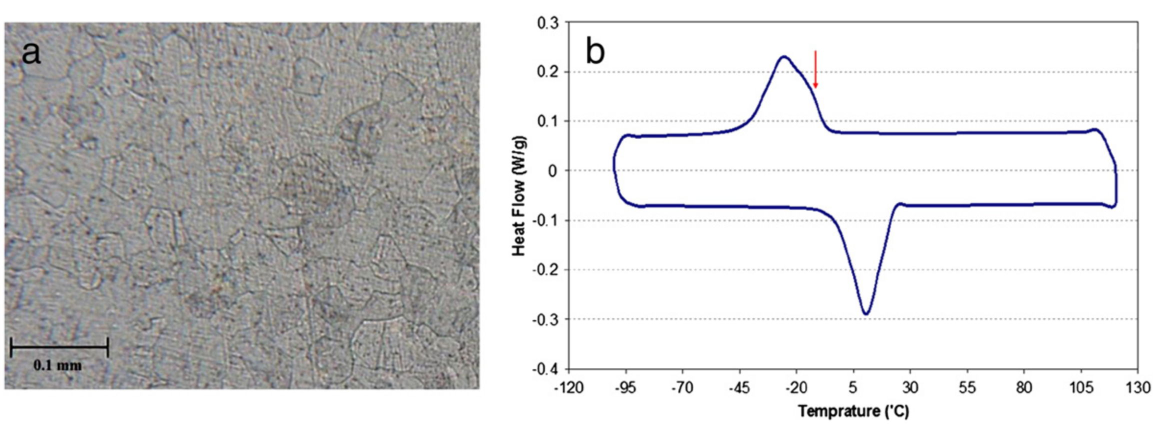

Fig. 1. a) Optical micrograph and b) DSC curve of NiTi shape memory alloy with 50.7 at.% homogenized at 1050 °C for 24 h.

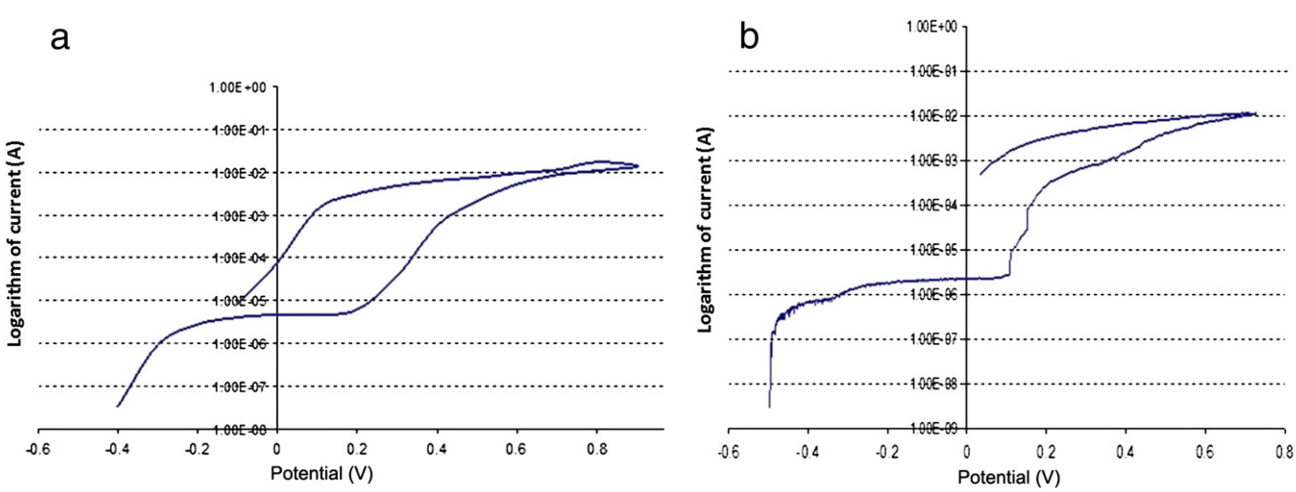

Fig. 2. Potentiodynamic polarization curves of NiTi samples in the a) 0.9% NaCl and b) Ringer solutions.