



Comparison of NiTi alloy surfaces formed by anodization in nitric, phosphoric, and sulfuric acid electrolytes

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ABSTRACT

The present study discusses the effect of the electrolyte on the growth of an oxide layer on NiTi alloy via anodic treatment with the aim of understanding the surface reactions that occur during the anodization process. For this purpose, anodic treatments of NiTi substrates were conducted using H_3PO_4 , H_2SO_4 , and HNO_3 electrolytes in concentrations ranging from 1 to 100 mM. Surface analysis using XPS revealed that for all the three electrolytes, a TiO_2 layer containing a small amount of Ni was formed on the anodized surface; however, the type of electrolyte influenced the thickness of the oxide layer formed. Using 100 mM HNO_3 as the electrolyte was the most advantageous condition to obtain a thick oxide layer (thickness ~ 180 nm), whereas, the thickness abruptly decreased for concentrations of HNO_3 above or below 100 mM. In the cases of H_3PO_4 and H_2SO_4 , the thickness did not exceed ~ 60 nm irrespective of concentration. Clear differences in microstructure were observed depending on the electrolyte used: H_3PO_4 electrolytes formed nanometer-sized pores covering the whole area, H_2SO_4 electrolytes generated flake-like precipitates on the surface, and HNO_3 formed both types of surfaces depending on the concentration. The oxide layer growth and its surface microstructure are dominated by two processes, namely, electrochemical reaction and chemical dissolution. The most important condition for obtaining a thick oxide layer is that a balance between the electrochemical reaction and chemical dissolution should be achieved. In H_3PO_4 , the electrochemical reaction was relatively weak, while in H_2SO_4 , chemical dissolution was too high, indicating that a thick oxide layer cannot be formed in these electrolytes. The balance of the two effects is found to be optimal in the case of HNO_3 , where the thickest oxide layer was obtained.

1. Introduction

In recent years, nearly equiatomic nickel-titanium (NiTi) alloys with interesting shape memory and super elasticity properties [1–2] have been used in medical devices [3–4]. Surface modification of these alloys has been investigated with the aim of increasing corrosion resistance in view of the fact that even very small amounts of Ni ions, if released at the surface, can lead to toxic and allergic reactions [5–6]. Forming an additional titanium dioxide (TiO_2) layer through the preferential oxidation of Ti is considered to be an effective solution to this problem [7–12]. Hence, researchers have devoted efforts to develop a surface modification process to preferentially oxidize Ti in NiTi alloys.

Anodic treatment is an electrochemical process, which leads to the formation of an oxide layer on so-called valve metal substrates. Complete anodization can be achieved without heating the substrate, thereby minimizing changes to the structure and phase of the underlying metal substrate. It is well-known that the anodization of a pure Ti substrate results in the formation of a homogeneous TiO_2 layer and

hence, this process is used in industry for functionalizing a Ti substrate to render it more biocompatible [13–16] and to improve its photocatalytic properties [17–22]. Based on these results, it was speculated that a surface layer of TiO_2 can also be obtained on a NiTi surface [23–27]. However, the growth of an oxide layer did not proceed as well on the NiTi alloy as on pure Ti. For instance, Shi et al. reported that galvanostatic anodization in acetic acid led to the formation of an oxide layer, but the layer did not attain a thickness greater than 20–25 nm even after increasing the applied voltage [23]. This is because Ni from the alloy is simultaneously incorporated into the anodic layer, which hinders the growth of the oxide layer. Several reports have shown that a thicker oxide layer with thickness on the order of several tens of micrometers could be formed when a high voltage of several hundred volts was applied [28–29]. However, oxide layer formation using the high voltage process takes place by a micro-arc plasma process occurring on the surface, which raises the substrate temperature during the reaction. Moreover, the oxide layer formed was found to be heavily cracked owing to residual stress caused by the temperature increase; in

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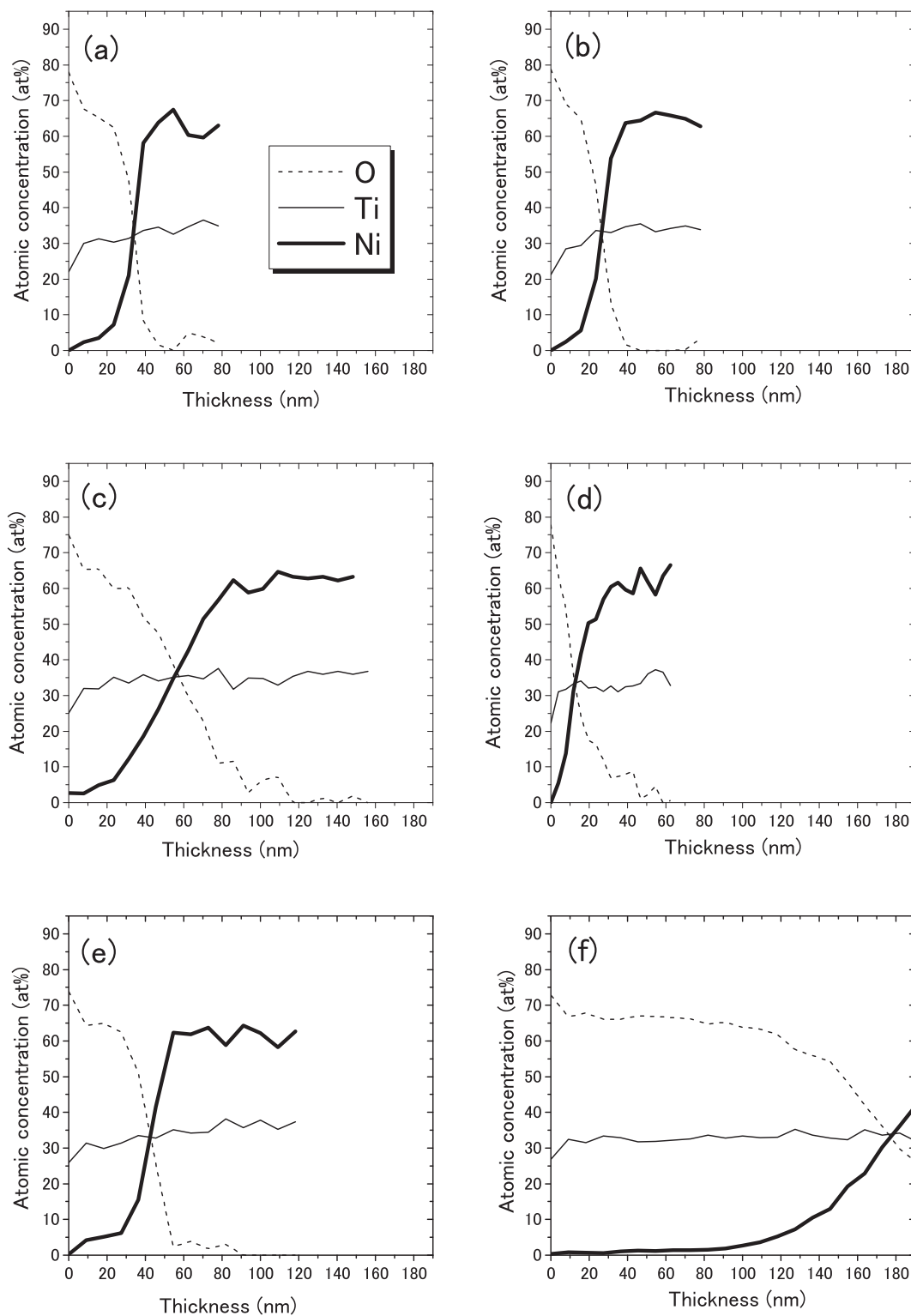


Fig. 1. Typical elemental depth profiles of NiTi surfaces anodized in various electrolytes: (a) 10 mM H₃PO₄, (b) 100 mM H₃PO₄, (c) 10 mM H₂SO₄, (d) 100 mM H₂SO₄, (e) 10 mM HNO₃, and (f) 100 mM HNO₃.

addition, the oxide layer contained around 5–7 at% of Ni [28].

We believe that the growth of an oxide layer on NiTi alloy can progress even at a low voltage if Ni can be selectively dissolved during the anodic treatment. In our previous study, we selected an aqueous nitric acid (HNO₃) solution as the electrolyte, which is a powerful oxidizing agent, and we demonstrated that an almost Ni-free oxide layer could be formed on the NiTi surface [30]. Based on the

experimental results, we concluded that Ni dissolution from the layer is likely to be due to a chemical reaction of the anodized surface with ions present in the nitric acid electrolyte. The influence of the ions in the electrolyte on oxide layer growth can be elucidated by comparing oxide growth in different electrolytes containing various types of ions. Therefore, in the present study, the anodization of NiTi alloy was conducted using HNO₃, phosphoric acid (H₃PO₄), and sulfuric acid

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