Surface & Coatings Technology 325 (2017) 75–80

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

# Growth of oxide layers on NiTi alloy surfaces through anodization in nitric acid electrolyte

Naofumi Ohtsu *, Yuma Hirano

*School of Earth, Energy and Environmental Engineering, Kitami Institute of Technology, 165 Koen-cho, Kitami, Hokkaido 090-8507, Japan*

ARTICLE INFO

*Article history:*
Received 31 January 2017
Revised 1 June 2017
Accepted in revised form 10 June 2017
Available online 11 June 2017

*Keywords:*
NiTi alloy
Anodic oxidation
Ni-free oxide layer
Pitting corrosion
XPS
SPM

ABSTRACT

The present study demonstrates the formation of an almost Ni-free oxide layer ~180 nm in thickness on a NiTi surface through anodization in 0.1 M $HNO_3$ electrolyte. The anodic oxidation of Ti and release of Ni occurred simultaneously during anodization, resulting in the homogeneous growth of the Ti oxide layer on the alloy surface. However, the release of Ni induced the generation of small pits ~10 nm in size on the surface, which enlarged over time due to a process similar to pitting corrosion. Since the layer growth and pit development were competing reactions that occurred simultaneously, an oxide layer without pits could not be formed through anodization in the $HNO_3$ electrolyte.

## 1. Introduction

Anodic treatment of titanium-based alloys forms titanium dioxide ($TiO_2$) layers that adhere strongly to the surface and impart properties such as decorative color [1–2], photocatalytic ability [3–6], and biocompatibility [7–10] to the alloy surface. Anodization leads to formation of a homogeneous layer, whose thickness can be controlled by varying the applied treatment voltage. In addition, the process is low-cost, as it can be conducted without using special equipment. However, only the so-called valve metals, such as Al, Ta, Nb, and Ti, are able to form an oxide layer through anodic treatment. Accordingly, the addition of an alloying element other than the valve metals inhibits the growth of the oxide layer when the additive concentration is relatively high.

Among the Ti-based alloys, a nearly equiatomic nickel-titanium (NiTi) alloy exhibits the attractive properties of shape memory and superelasticity [11–12]. It has therefore been used in medical devices in the cardiology and dentistry fields in recent years [13–14]. However, medical doctors often hesitate to use a NiTi device because of the risks of cytotoxicity and allergic reactions induced by Ni that constitutes ~50% of the alloy [15–16]. Forming a chemically stable $TiO_2$ layer on a NiTi alloy not only generates a Ni-free surface, but also a corrosion resistant layer, which improves the alloy's biocompatibility [17–22]. Thus, researchers have considered employing anodic treatment as a $TiO_2$-layer forming process. Unfortunately, since Ni is a known non-valve metal, growth of an oxide layer on a NiTi alloy does not proceed as well as it does in the case of pure Ti. Therefore, literature regarding the anodic treatment of NiTi alloys is rare [23–26]. Among the few reports available, Shi et al. demonstrated that galvanostatic anodization in an aqueous acetic acid solution led to the formation of an oxide layer. However, the layer achieved a thickness of only 20–25 nm, notwithstanding the application of high voltages [23–24]. Cheng et al. demonstrated the formation of a thick oxide layer of ~17 μm on a NiTi surface through anodization in a methanol solution containing 10% $NaNO_3$ as an electrolyte [25]. However, the resultant layer contained ~35 at.% Ni, and was thus not considered a $TiO_2$ layer. The results reported by Chu et al. seem to represent one successful case [26]. They demonstrated that an oxide layer ~80 nm in thickness was formed by anodizing in 0.02 M $Na_2SO_4$ using a constant current of 150 $mA\cdot cm^{-2}$. The oxide layer did not contain a significant amount of Ni, and was therefore expected to reduce Ni release from the surface. Based on these reports, it can be concluded that the choice of electrolyte is an important factor in forming a thick, Ni-free $TiO_2$ layer on a NiTi surface, even though the predominant factor determining the oxide layer growth remains to be clarified.

We assumed that the Ni incorporated into the anodic layer becomes an obstacle for the growth of the oxide layer. In other words, a Ni-free $TiO_2$ layer might form if the Ni in the surface layer could be dissolved selectively during the anodic treatment [27]. Nitric acid ($HNO_3$), being a powerful oxidizing agent, is able to dissolve Ni metal effectively. In contrast, Ti metal is not dissolved by $HNO_3$ since its reaction with $HNO_3$ leads to the formation of $TiO_2$. Based on these properties, we considered an aqueous $HNO_3$ solution to be the ideal electrolyte for enabling oxide

---

* Corresponding author.
*E-mail address:* nohtsu@mail.kitami-it.ac.jp (N. Ohtsu).

http://dx.doi.org/10.1016/j.surfcoat.2017.06.021

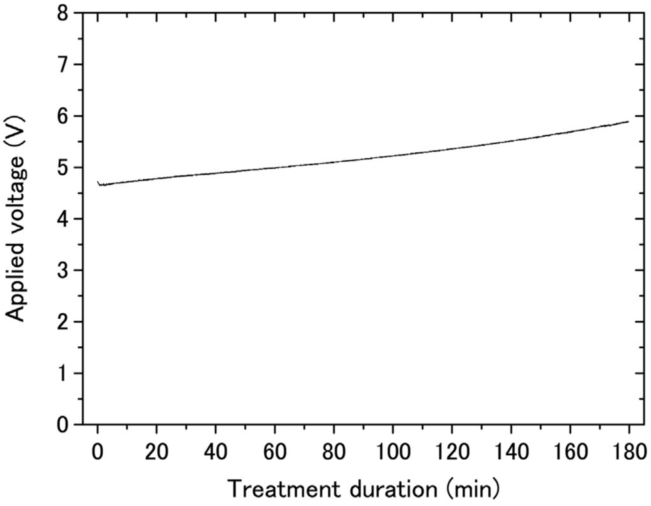

**Fig. 1.** Variation of voltage applied between the cathode and anode during anodization as a function of time.

layer growth on a NiTi surface. Therefore, in the present study, a NiTi substrate was anodized in an electrolyte of 0.1 M aqueous $HNO_3$ solution for various durations. Thereafter, the variation of surface morphology, layer composition, and surface potential distribution were investigated in detail, based on the duration of the treatment. In this article, together with the above results, we discuss the layer growth behavior and the chemical reactions occurring during anodization.

## 2. Materials and methods

The NiTi alloy (55.07 at.% Ni), used as a substrate, was purchased from NEC Tokin, Japan. NiTi disks with 17 mm diameter and 2 mm thickness were chemically polished using a colloidal silica suspension with an average particle size of 40 nm. The electrolyte used for the anodic treatment was an aqueous 0.1 M $HNO_3$ solution with a pH value of 1.5. The substrate and a 20 × 20 × 1 mm Ti electrode were connected to the anode and cathode, respectively, after which a galvanostatic direct current (DC) was applied at a constant value of 50 $mA \cdot cm^{-2}$ [5–6]. The temperature of the electrolyte was kept at 293 K using a water bath. The DC voltage varied with time, and its change during anodization was monitored using a digital voltmeter. After the oxidation process, each specimen was rinsed in distilled water with ultrasonic agitation.

The surface morphologies of the specimens were observed using scanning electron microscopy (SEM; JSM-6701, JEOL, Japan) in the secondary electron imaging mode with an acceleration voltage of 5 kV. Scanning probe microscopy (SPM; SPM-9700, Shimadzu, Japan) was used for obtaining information regarding the topology and surface potential distribution. Topographic measurements were performed using an atomic force microscopy (AFM) mode analogous to the tapping mode, while the potential distribution was analyzed using the Kelvin force microscopy (KFM) mode. The chemical states and compositions of the surfaces at various depths were analyzed by X-ray photoelectron spectroscopy (XPS; PHI 5000 VersaProbe, Ulvac-Phi, Japan) using monochromatic Al $K_\alpha$ radiation ($h\nu = 1486.6$ eV), with a photoelectron take-off angle of 45° and pass energy of 58.7 eV. An Ar ion gun with an acceleration voltage of 3 kV was used to obtain elemental depth profiles, with an etching rate of approximately 7.5 $nm \cdot min^{-1}$, as estimated from a $SiO_2$ layer. All experiments were repeated at least two different times to confirm the reproducibility.

## 3. Results

### 3.1. Appearance of NiTi surfaces anodized in $HNO_3$ electrolyte

The variation of voltage applied between the cathode and anode during anodization is shown in Fig. 1. The initial voltage of ~4.7 V is presumed to be due to the electrical resistance of the electrolyte. A gradual increase in voltage was expected with the growth of the oxide layer, as its main component, $TiO_2$, has semiconducting properties. However, such a change was not observed; instead, a slight increase in voltage with time was seen, which is much lower than the expected value due to the formation of the $TiO_2$ layer.

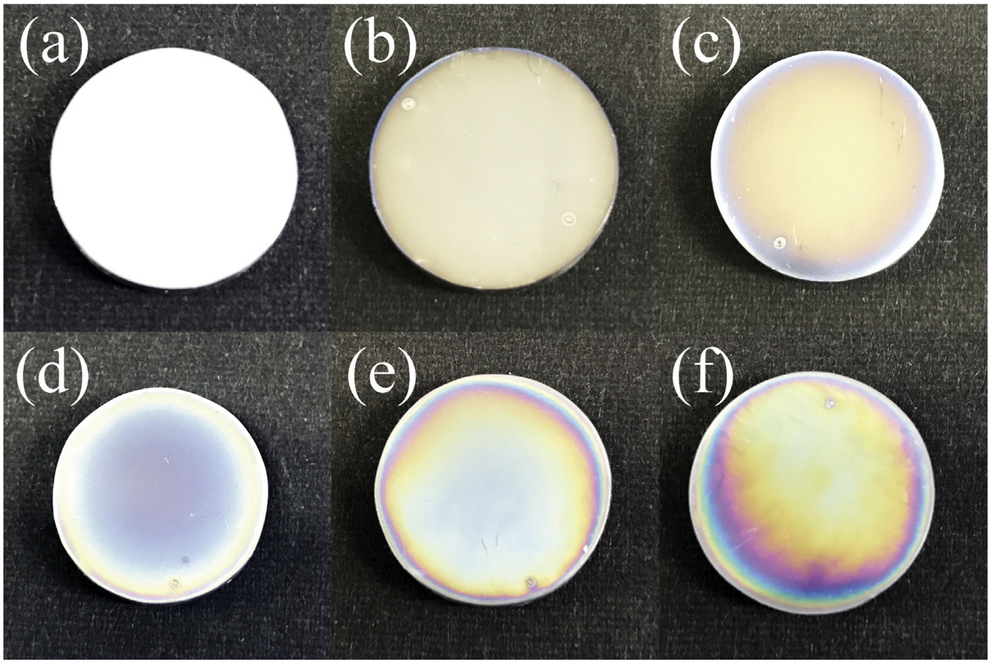

**Fig. 2.** Appearance of NiTi surfaces after being anodized in 0.1 M $HNO_3$ electrolyte for various durations. (a) Untreated surface, (b) 3 min, (c) 10 min, (d) 30 min, (e) 60 min, and (d) 180 min.