Preparation and microstructrure of bi-phase ZrO2 ceramic coating on biomedical NiTi alloy prepared by plasma electrolytic oxidation

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Abstract

ZrO_2 coating was prepared on biomedical NiTi alloy by plasma electrolytic oxidation in $(ZrO_3)_3\cdot 9H_2O$ electrolyte with the sample as cathode. The microstructure and composition were studied by scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. The results show that the coating was composed of bi-phase ZrO2, namely t-ZrO_2 and m-ZrO_2. The coating surface was porous and coarse. The thickness of the coating was 30 μm and the bonding strength of coating was 18MPa.

Keywords

ZrO2 coating, microstructure, plasma electrolytic oxidation, NiTi alloy.

1. Introduction

Nickel titanium is a near-equiatomic intermetallic that possesses attractive properties such as superelasticity, shape memory effect and biocompatibility [1-4] and has been widely used in biomedical fields. It is usually used as cardiovascular stents and staples of broken bones for its superelasticity properties and shape memory effect. However, NiTi has always been facing the problem of leakage of nickel ions in vivo which may cause cytotoxic reactions. The leakage of nickel ions are usually caused by corrosion. Therefore, it is necessary to improve the corrosion resistance of the NiTi alloy and suppress the leakage of nickel ions. Surface treatments have been proved to be an effective method to prevent the leakage of nickel ions [5-6].

Plasma electrolytic oxidation (PEO) is a plasma-assisted electrochemical technique for surface treatment of metals, especially these so called valve metals such as Ti, Al, Mg, Nb, etc[7-9]. It can be used to fabricate ceramic coatings with high corrosion resistance on metal surface. PEO coatings for biomedical application with desirable properties have been obtained on some biomedical metal such as Ti and its alloy, Mg and its alloy. The coatings usually showed high bonding strength to the substrate and the micrometer-scale porous surface is suitable for implant fixation [10].However, due to the limitation of the technique itself, most PEO studies are concentrated on biomedical Ti and Mg and very few PEO studies have been focus on NiTi alloy. PEO is usually suitable for treatment of valve metals such as Ti, Al, Mg and metals possessing much other metal elements such as Fe, Cr, Ni are thought to be difficult to be subjected to PEO. Formation of oxide layers by PEO on NiTi is relatively difficult compared to Ti, Al, Mg. PEO process on non-valve metals usually need pretreatment to first deposit valve metal coating on their surface and then subjected to common PEO treatment. Recently, our group developed a derivative process called cathodic plasma electrolytic oxidation to directly prepare coatings on metals. Experiments proved that many kinds of metals such as stainless steel, iron, Ti, Al, Mg, etc and their alloys could be subjected to PEO with the sample fixed in cathode. This article deal with the PEO process on NiTi alloy and ZrO_2 coating was obtained on its surface. The microstructure of the coating was studied.

2. Experimental details

2.1 Preparation of PEO coating

NiTi alloy (50.8 at.% Ni) sample with a dimension of 20 mm×20 mm× 2 mm were first polished using SiC paper from 200# to 1000# and then thoroughly cleaned. NiTi sample was used as cathode and the stainless steels as the anode. The ethanol solution of $Al(NO_3)_3$ (19 g/l) was used as the electrolyte in experiment. A home-made single-polar power source was used whose pulse frequency and duty cycle were fixed at 1000 Hz and 30%, respectively. The samples were treated for 2 h at the voltage of 550 V.

2.2 Characterization and properties testing of coating T

The morphology and phase composition of the ceramic coatings were investigated by scanning electron microscope (SEM; Hitachi S-570) and X-ray diffractometer (XRD, D/max-rB, Japan, Cu target, Kα radial). The thickness of sample was measured using an eddy current based thickness gauge (TT260, Time Company, China).

3. Results and discussion

3.1 Phase composition of coatings

The XRD spectra of the coating fabricated on NiTi biomedical alloy is shown in Fig.1. It can be noticed that feature peaks of two kinds of ZrO_2 crystal are presented on the spectra. There are tetragonal (t-ZrO_2) and monoclinic (m-ZrO_2). This reveals that the composition of coating is bi-phase of t-ZrO_2 and m-ZrO_2 crystals.

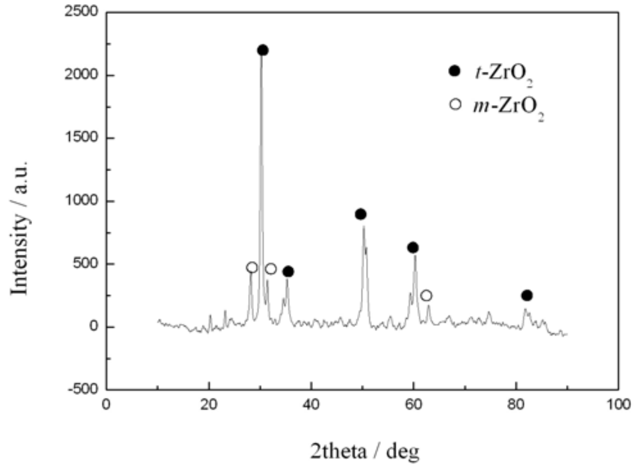

Fig. 1 XRD pattern of coating obatined on NiTi biomedical alloy

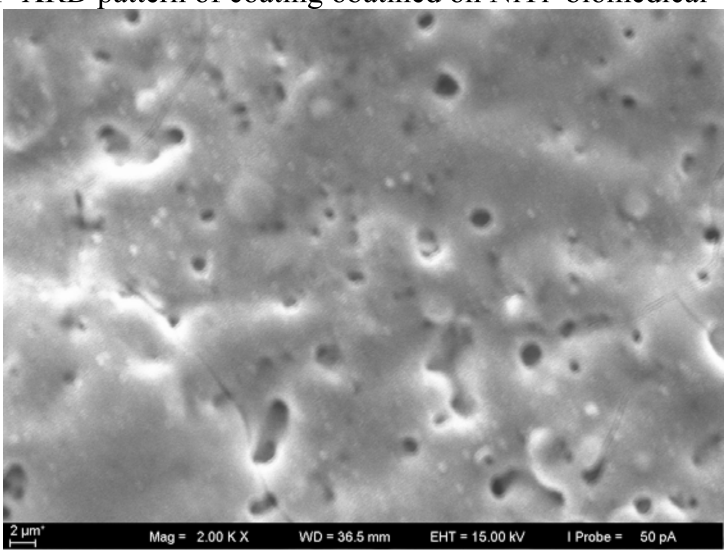

Figure 2. Surface morphology of coating on NiTi alloy

3.2 Surface morphology

Figure 2 shows the surface and cross section morphology of the coatings on biomedical NiTi alloy. Figure 2 tells that the coating surface covered by many micro-pores with different diameters, which range in the size of about 2-5μm. These micro pores were actually the rudimental discharge channels during discharge reaction. Compared to the pores obtained by anodic discharge, the pores here are not like the volcano. There is not a mouth shape around the pore [7-9].

3.3 Thickness and bonding strength

The thickness of the coating tested by the gauge is about 30μm.The force-displacement curve of the pull experiment is illustrated in figure 3, during which the test area is $50mm^2$. It states that the bonding strength of the coating to the NiTi substrate is 18MPa. This value is not very high compared to that of coating obtained by anodic discharge oxidation [9].

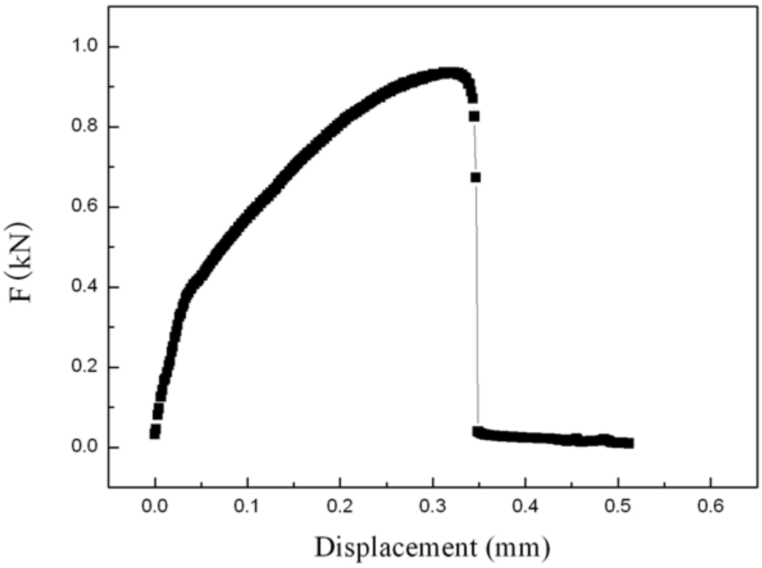

Figure 3 Force-displacement curve during pull experiment

4. Conclusions

ZrO_2 coating containing bi-phase of t-ZrO_2 and m-ZrO_2 was fabricated on NiTi biomedical alloy by plasma electrolytic deposition technique. The coating surface was coarse and porous. The thickness of the coating was 30 μm and the bonding strength of coating to the NiTi substrate was 18MPa.

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