



Effects of surface oxidation behavior of NiTi shape memory alloy on adhesion of epoxy resin/polytetrafluoroethylene composite coating



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ABSTRACT

The nickel-titanium (NiTi) shape memory alloy (SMA) substrates were firstly subjected to different high-temperature oxidation treatments. Then they were sprayed by the polymer coating (epoxy resin (EP): polytetrafluoroethylene (PTFE) in a mass ratio of 3:1). Effects of the surface chemical composition, morphology, roughness and oxide thickness on adhesion between the NiTi SMA substrate and the coating were studied. The results demonstrated that the adhesion of the oxidized samples could be improved significantly as compared with that of the untreated sample. A heating temperature of 600 °C was determined to be optimal in the range of 300–700 °C for preparing the composite coating for NiTi SMA substrates. The highest adhesion strength was 6.76 MPa for the oxidized sample with a duration time of 30 min under 600 °C. It has been found that the adhesion was strongly depended on the high surface oxygen content, uniform morphology, appropriate roughness and oxide thickness.

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1. Introduction

NiTi SMA has the characteristics of shape memory effect and superelasticity with excellent corrosion resistance, wear resistance, mechanical properties and good biocompatibility. These properties make it become an ideal biological material, especially in the orthopaedic surgery and orthodontics [1–4]. However, some people have allergic or toxic reactions to the untreated NiTi SMA material due to nickel release [5,6]. In order to solve the problems, the NiTi SMA material surfaces have been modified mainly by the oxide [7,8], calcium phosphate [9,10] and polymer [11,12] materials with different methods. Many studies have already proved that the coatings can effectively decrease the nickel release by exceeding 85% [10,11,13]. However, for the calcium phosphate and polymer coatings, the poor adhesion between the coating and the substrate is still an important issue to be improved. It is reported that the adhesion has been increased by nearly two times after the substrate treated with chemical surface modification using silane coupling agent (SCA) [14,15]. On the other hand, various polymer materials have been used as the coating materials, such as polypyrrole (PPy), polyamide (PA6), polyester (PE) and vinyl ester (VE), etc. [12,15,16].

Specially, the mixed homogeneous EP and PTFE as polymer coating material has been successfully performed with better adhesion strength, mechanical properties and higher biocompatibility [17–19].

In this work, the NiTi SMA substrates have been oxidized at different temperatures (300, 400, 500, 600, 700 °C) for 20, 30, 40, 50 min, respectively. The Ti-O layers on the NiTi SMA substrates surface were formed. Then the SCA modified Ti-O layers have been sprayed by the polymer coating consisting of EP and PTFE. Both the Ti-O layer and the polymer coating can effectively inhibit Ni ions release. Moreover, the method with low material cost and easy operation is suitable for mass production.

2. Experimental

2.1. Sample preparation

The commercially available NiTi SMA plates used in this study contain 50.8 wt% Ni and 49.2 wt% Ti. Each sample was cut into dimensions of 30 mm × 30 mm × 3 mm. Subsequently, they were gradually abraded with 400–1000 waterproof abrasive papers and polished with the colloidal silica suspension to a mirror finish in order to homogenize the topography and remove contamination of the surface. Finally, each sample was ultrasonically cleaned in deionized water and ethanol, respectively.

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2.2. High-temperature oxidation

The samples were divided into two groups for high-temperature oxidation in air atmosphere. A group of samples were heat-treated for 30 min at 300, 400, 500, 600 and 700 °C, respectively. Another group of samples were heat-treated at 600 °C with 20, 30, 40 and 50 min, respectively.

2.3. Surface spraying

The samples were immersed in hydrolyzed KH–560 SCA solution for 5 min and dried in air. The quality of the SCA accounted for 15% of the solution quality. Then, the polymer blend was prepared, which was composed of EP, PTFE, polyamide curing agent and ethanol in a mass ratio of 15: 5: 3: 10. The polymer blend was sprayed using a W–71 spray gun equipped with one OT S–750 air compressor at a base pressure around 7 bar lasting for 9 s. The distance of the spray nozzle and the NiTi SMA substrate was kept constantly at 300 mm. The thickness of the polymer coating was controlled at about 15 µm. Eventually, the sprayed samples were cured in a drying oven at 120 °C for 40 min.

2.4. Surface characterization

The surface morphology of the oxide layer was demonstrated by field emission scanning electron microscopy (SEM) under an applied voltage of 20 kV (FE–SEM, Hitachi SU–8010, Japan). The chemical composition analysis of the surface oxide layer was carried out using an energy dispersive spectrometer (EDS) detector attached to the SEM. X' Pert PRO X-ray diffraction (XRD) was performed at room temperature over the 2θ range of 10–80°. To evaluate the surface roughness, samples were studied by atomic force microscopy (AFM) (Dimension Icon), using tapping mode in air with a non-conductive silicon nitride tip.

2.5. Adhesion characterization

The Pull-off test was performed to determine the critical load between the polymer coating and NiTi substrate. The tensile testing machine was pulled with a constant speed of 1 mm/s. The coating adhesion strength was calculated by the critical load divided by the cross-sectional area of bonding plane. In order to estimate the adhesion strength of the samples more precisely, the error bar at each point was determined by average deviation of the three sample measurements for each processing condition.

3. Results and discussion

3.1. Chemical composition analysis

Fig. 1a shows the EDS analysis results of the samples heat-treated for 30 min at 300, 400, 500, 600 and 700 °C, respectively. It illustrates that the oxygen atom concentration increases and nickel ion concentration decreases obviously with the increase of heating temperature. The oxidation is inadequate when the temperature is lower than 400 °C. The components of the surface layer are mainly oxygen atom, the stable level of Ti and a small quantity of nickel ion when the temperatures are above 500 °C, which indicates that the oxide layers have been formed in the large area.

Fig. 1b shows the XRD analysis results of the samples heat-treated in the range of 300–700 °C for 30 min. When the oxidation temperatures are lower than 500 °C, the surface chemical compositions of the samples have not significantly changed and oxides peaks are hardly observed. The inadequate oxidation takes place in the upper surface layer from the EDS analysis, which

indicates that the oxide may be amorphous. It is consistent with the result reported by Kim et al. [20]. The peak of the rutile–TiO₂ (at 28°) appears at 600 °C and the intensity increases obviously at 700 °C. These changes are corresponding to the previous research [21]. In addition, a little anatase–TiO₂ is observed at 700 °C. These phenomena suggest that the oxide layers have been formed on the sample surface when the oxidation temperatures are higher than 500 °C. This is consistent with the EDS analysis results.

3.2. Micro-structure analysis

Fig. 2 shows the SEM images of the samples heat-treated for 30 min at 300, 400, 500, 600 and 700 °C, respectively. The surface morphology and color of the samples change evidently after the high-temperature oxidation. Ti–O compounds with spots-like structure non-continuously attach to the sample surface at 300 °C, as shown in Fig. 2a. The sample color appears light goldenrod yellow, suggesting the formation of the surface oxide layer. When the temperature is 400 °C, oxide distribution becomes intensive and the average particle size decreases (Fig. 2b). The sample color becomes golden. When the temperature is 500 °C, the oxide layer continuously covers on the sample surface, and the sample color becomes calamine blue (Fig. 2c). The dimension of the oxide particles becomes larger and the surface color is blue-grey at the oxidation temperature up to 600 °C (Fig. 2d). The Ti–O particles grow significantly and the sample color becomes light slate grey by increasing the oxidation temperature to 700 °C (Fig. 2e). It suggests that the average grain size of Ti–O compounds is increased with the increase of the heat treatment temperature, when the temperatures are above 400 °C, corresponding to the previous research [22].

Fig. 3 shows the surface morphologies of the samples heat-treated at 600 °C for 20, 30, 40 and 50 min, respectively. The morphology of the sample surface is more homogeneous and oxide particle size is more uniform at a treatment time of 30 min (Fig. 3b). When the time increases to 40 min, the morphology of oxide is not as uniform as that of the sample at 30 min, accompanied by some little dark spots in local scale (Fig. 3c). When the time increases to 50 min, different sizes of holes appear on the sample surface and a great quantity of the dark spots can be observed (Fig. 3d).

3.3. Oxide roughness analysis

Fig. 4 illustrates two-dimensional (2D) and three-dimensional (3D) AFM images of the samples heat-treated for 30 min at 0, 300, 400, 500, 600 and 700 °C, respectively. The micrograph of the untreated sample shows unidirectional scratches formed during the mechanical polishing process in Fig. 4a. Surface roughness values of the samples, Ra and Rq, are shown in Table 1. The values of Ra change from 0.891 nm (0 °C) to 68.7 nm (700 °C), and Rq change from 1.21 nm to 85.8 nm. It is obvious that the roughness values of the surface oxide layer increase with the increase of heat treatment temperature due to oxides growth, corresponding to the work reported by Ohtsu [23] and Firstov et al. [24].

Fig. 5 exhibits the AFM morphologies of the samples heat-treated at 600 °C for 20, 30, 40 and 50 min, respectively. Surface roughness values of the samples, Ra and Rq, are shown in Table 2. The values of Ra change from 26.3 nm (20 min) to 59.7 nm (50 min). With the increase of time, the surfaces become rougher and rougher due to oxides growth, which also attributed to the non-uniform morphology of oxide layer. This change of surface roughness confirms the results of Fig. 3.

3.4. Oxide thickness analysis

Fig. 6 shows the EDS line scans analysis results of the samples

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