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Experimental Research on Biomedical Titanium Coating Corrosion Effects

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The NiTi shape memory alloy sample is subjected to a plasma spraying technique to form a layer of 400 um thick titanium coating on its surface. The corrosion resistance of the samples can be compared by the electrochemical measurement in the simulated body fluid environment. Thus, the presence of galvanic corrosion between the titanium coating and the nickel-titanium shape memory alloy substrate can be measured. The anodic polarization curves show that the NiTi shape memory alloy after titanium coating has a decrease in the current density of the dopant, while the polarization resistance increases with the corrosion potential and the passivation potential. In addition, the galvanic current time curve shows that the tantalum coating and nickel-titanium alloy between the galvanic current density is minimal. The experiments demonstrate that the surface modification of nickel titanium shape memory alloy surface coating can effectively improve the corrosion resistance of the matrix metal and there is no galvanic corrosion between the coating and the base metal.

1. Introduction

In recent years, with the development of orthopaedic and interventional medicine, nickel-titanium alloys, which have many advantages, such as its unique shape memory effect, super-elasticity and good biocompatibility, become one of the important biomedical metal materials. It has been used in the motor system injury, oral orthodontic and cardiovascular and cerebrovascular intervention and other medical fields in order to improve the quality of human life (Franks et al., 2005). Although the nickel-titanium alloy is an excellent implanted alloy material, its corrosion resistance and abrasion resistance have not yet reached the ideal standard. Corrosion and wear will not only reduce the mechanical and mechanical properties of metal materials, but also the alloy in the high nickel, the surrounding tissue will produce some side effects, such as sensitization, carcinogenic reactions (Beltrán-Partida et al., 2017). Therefore, as a biomedical metal material widely used in the human body, the research on the corrosion resistance of NiTi (NiTiSMA) is of great practical significance to ensure its safe use in the human body (Leng et al., 2003). In recent years, the surface coating technology has developed rapidly, and it has achieved the purpose of preventing metal corrosion and improving biocompatibility by forming a protective coating on the metal surface (Ye et al., 2014). In this experiment, the titanium (Ti) coating was formed on the NiTiSMA surface by plasma spraying technique. The electrochemical test method of NiTiSMA before and after coating is used to simulate the anodic polarization curve and characteristic parameters (Campanelli et al., 2017). In addition, the corrosion resistance of NiTiSMA before and after the coating is also investigated. The galvanic corrosion is investigated between the titanium coating and the NiTi alloy substrate according to the measurement of the galvanic current-time curve (Cui et al., 2013). The method of effectively enhancing the corrosion resistance of NiTiSMA is discussed in this paper (Novoa et al., 2017).

Biomedical metal materials are present in the environment for a long time, such as in contact with the body fluids and on the one hand body metal, will produce corrosion of metal materials, which will lead to the precipitation of metal ions and their derivatives and reduce the mechanical strength of the implanted material (Zhang et al., 2016). On the other hand, the metal ions will be generated during the corrosion process long-term exposure to body tissue, which produce a variety of damage in the body, such as cytotoxicity, allergies,

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carcinogenic. Therefore, the improvement of biocompatibility of medical titanium alloys is largely dependent on its improved corrosion resistance.

Test methods of corrosion resistance of metal materials are divided into two kinds which are in vivo and in vitro. Metal corrosion resistance in vivo is extremely difficult for measurement, and the results are difficult to summarize (Shah et al., 2014). Thus, vitro method is generally used, which can mainly be divided into two categories: one for the soaking test can directly detect the amount of precipitation of ions, but the test cycle is long (De Gopegui, 2010). The other is electrochemical measurement, which has fast, sensitive and accurate advantages. The electrodynamic polarization method is a kind of electrochemical measurement method. The linear relationship between the applied potential and the current reflects the potential range of the metal to keep the passivation, the pitting tendency and the ability of the metal or alloy to reach the steady state in the medium (Huang et al., 2016). Especially it is suitable for low corrosion rate of a variety of materials measurement, screening cited. When the potential polarization is scanned, the change in the positive direction through the anode current electrode is called as the anodic polarization (Liu et al., 2006). The curve of the anode current or current density is the abscissa, and the curve plotted with the anode potential as the ordinate is called the anodic polarization curve (Çelik, 2016).

In recent years, the titanium with its stable biological characteristics, good biocompatibility and unique structural properties of biomedical industry has attracted more and more attentions. Titanium in the physiological or other environment, even in the state of hypoxia, the surface can immediately generate a layer of chemical stability of the passivation film, thus the titanium has excellent chemical stability and resistance to physiological corrosion, and has a good biocompatibility (Zhang et al., 2009). In 1940, pure metal titanium was first used in medical care. So far, most cases have reported that there is no adverse reaction of metal titanium as a human implant, except that there are 1 case of chronic urticarial after implantation of titanium nails. Titanium research and deepening of clinical research and achieved satisfactory results. Titanium is expected to become a new generation of biomedical metal materials. If the corresponding coating technology will be sprayed on the surface of nickel-titanium alloy and made of medical materials, the theory of this material not only has a good comprehensive mechanical properties, such as nickel-titanium alloy matrix, natural bone close to the elastic modulus with the increase of titanium coating surface modification treatment, but also make up the nickel-titanium alloy corrosion resistance, wear resistance. The shortcomings of the difference will greatly improve the biocompatibility of the material (Burnat et al., 2015). In this study, Ti / NiTiSMA composite samples are prepared by Ni-ray coating on NiTiSMA matrix and tested for corrosion resistance.

2. Materials and Method

2.1 Sample matrix material and sample preparation

The base material used in this experiment is NiTiSMA (supplied by Baoji Tianrui Nonferrous Metal Material Co., Ltd.), and the composition is Ti: 49.3%, Ni: 51.7%.

The samples are cut into 20mm x 20mmX1.5mm square pieces, 24 samples of which are randomly divided into a coating group and a control group, each group of 12 samples. And the test surface by gold phase sandpaper is step by step grinding (from W40 sandpaper polished to W10 sandpaper) into the anhydrous ethanol to save stand-by. Spray coating tantalum coating, the coating group of samples in the vacuum plasma spraying equipment prepared tantalum coating, spraying parameters for the spray distance of 150mm, coating thickness of 400 pull m, vacuum chamber pressure 100mm, current 600A, voltage 7V. When the copper wire is welded on the non-test surface of the specimen, it is cured with epoxy resin and exposed only to the test surface. The test area is 1cm2, and all samples are ultrasonically cleaned with absolute ethanol for 10min before the experiment with dry spare.

2.2 Laboratory equipment and experimental medium

DH2080 plasma spraying equipment (Shanghai Ruifa spraying Machinery Co., Ltd.); 351 type electrochemical corrosion test system (the United States EC & GPrinceton Applied Research company); CS501-3C constant temperature water bath box (Chongqing four of the Experimental Instrument Co., Ltd.); Scanning Electron Microscope (JEOM, Japan).

800ml simulated body fluid electrolytic cell will be filled with into the 370C constant temperature water bath box. Simulated body fluids using Troyde'S type, and its composition is: NaCl8.0g/L, KCl 0.35/L, NaHCO3 0.006g/L, KH2PO4, 0.0475 g/L, Na2HP4 1g/L, Glucose 3.57g / L. The electrolyte is not degassed.

2.3 Experimental method and data processing

Galvanic corrosion is called contact corrosion, which is different metal by different parts of the contact and resulting in galvanic current caused by corrosion. The cause of the galvanic current is that the corrosion potential of the dissimilar metal is different, which results in an increase or in corrosion of the metal with lower corrosion potential. In vivo environment, metal or alloy implants inevitably produce varying degrees of wear with body tissue such as bone tissue, teeth, etc., which can lead to loss of metal or alloy surface coating. So that the coating metal and the base metal at the same time are exposed to the internal environment, such as in the tissue fluid, saliva and other electrolytes under the action of the formation of the original battery and produce galvanic current. The size of the galvanic current is mainly determined by the self-corrosion potential difference of the pair of metals, that is, the greater the difference between the values of the two metals is, the faster the galvanic corrosion rate is. Thus it can affect the quality of the implant. In order to scientifically evaluate the galvanic corrosion situation, the necessary galvanic experiments are only carried out in the simulation of the body environment in order to obtain reliable conclusions.

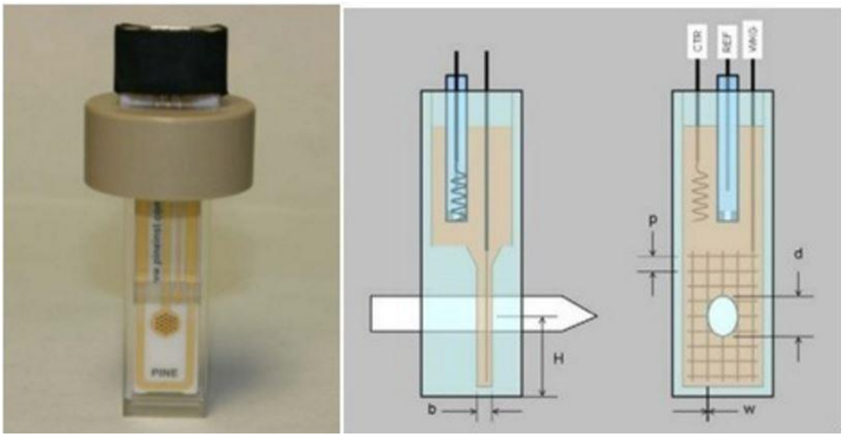

Figure 1: Schematic plan of three electrode

As seen in Fig.1, the classic three-electrode system is used in corrosion test system to saturation calomel electrode (saturated calomel electrode, SCE) as the reference electrode, and platinum (Pt) electrode is seen as the auxiliary electrode. The working electrode is studied, and measured temperature is controlled at 37 ℃. The results of corrosion measurement: 1) Anodic polarization curve test: NiTiSMA sample and Ta/NiTiSMA composite specimen are immersed in 37 ° C Troyde'S simulated body fluid (pH=7.0) in 351 electrochemical corrosion test system, so that the surface tends to be stable. After 30 minutes, the electrochemical test software will be opened. Firstly, the entire initial delay period of the open-circuit potential value is shown on the screen, and the value changes with time is very small, and then it will be around a relative set of ups and downs with the potential fluctuation of not more than 2mV effective. This indicates that the surface condition of the test specimen has been stabilized, and the potential value at this time is the self-corrosion potential. After the initial delay, the anodic polarization curve is plotted with an initial potential of 100 mV (relative to the self-etching potential) and a final potential of 2000 mV (relative to the reference electrode) with a scanning speed of 1 mV / s. each of the coating group and the control group should repeat six samples with 6 polarization curves. One of the six polarization curves is selected by software analysis, and the experimental group and the control group are superimposed to compare the polarization curve shape of the samples before and after the tantalum coating. The current density tests the same electrode system, the auxiliary electrode platinum electrode is replaced with Ti/NiTiSMA composite sample, the working electrode for the NiTiSMA sample, wire lead H, and then access the same electrode test side, the second is composed of pairs of pairs.

Since the data are affected by environmental and operational errors, all data are expressed as mean ± standard deviation (z±s). Using SPSS11 the statistical software for completely randomized design data variance analysis and t test with significance level a = 0.05. For the galvanic current time curve, the scan time is set to 400s, and then we can measure the even current density value. Coating group and the control group of 6 samples are completely random combined to 6 pairs.

Average value:

$$\bar{x} = \frac{\sum_{i}^{N} x_i}{N} \qquad (1)$$

Standard deviation:

$$s = \frac{\sum_{i}\left(x_i - \bar{x}\right)^2}{N} \tag{2}$$

3. Experimental results

The Ti coating is successfully prepared on the surface of NiTiSMA sample by plasma spraying method, and the Ti / NiTiSMA composite sample can be obtained with the visual inspection of titanium coating for the silver-gray, no skin, bubbling phenomenon. SEM micrograph of NiTi SMA after coating titanium is shown in Fig. 2. Titanium coating and the matrix in close contact with the surface are the microcrystalline. And the polarization curve is a graph which shows the relationship between the electrode potential and the polarization current or the polarization current density.

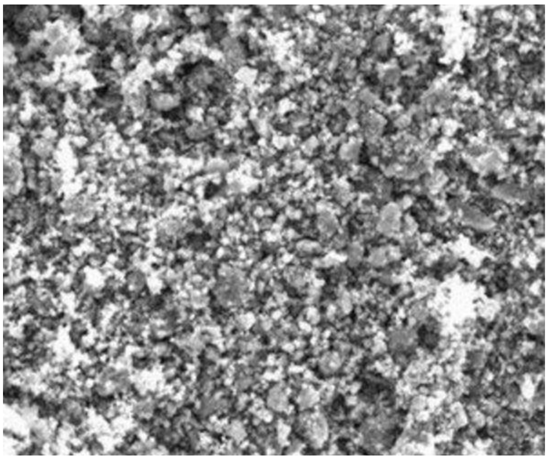

Figure 2: SEM micrograph of NiTi SMA after coating titanium

From the shape of the polarization curve, we can see the degree of electrode polarization to determine the electrode reaction process.As shown in Fig.3, the anodic polarization curve of the NiTiSMA sample before and after spraying the Ti coating are given. And the average value of the corrosion potential, the dummy current density (Ip), the polarization resistance (Rp), and the passivation potential (Etp) are also considered in this paper. The results show that the corrosion potential of NiTiSMA is increased after the Ti coating treatment, and the polarization resistance and the passivation potential are increased. It can also be seen from Fig. 3 that the passivation interval of Ti / NiTiSMA complex is obviously longer than that of NiTiSMA.

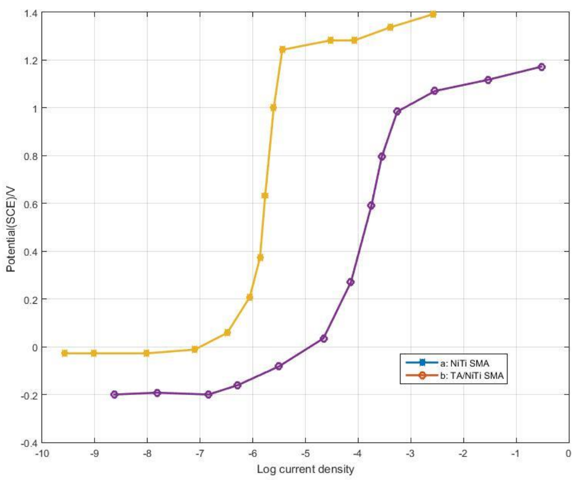

Figure 3: Anodic polarization curve of NiTi SMA before and after coating titanium

Statistical analysis shows that the values of Ip and Rp of NiTiSMA samples before and after Ti coating are statistically significant (P<0.01), and Etp is also different. The time curve of the galvanic current between the metal coating and the NiTi SMA base metal is shown in Fig. 4. The electric current density is (1.37±0.14) uA/cm2 (n=6). It can be seen that the galvanic current density between the tantalum metal coating and the base nickel-titanium alloy is stabilized at uA (10^{-6}A/cm^2).

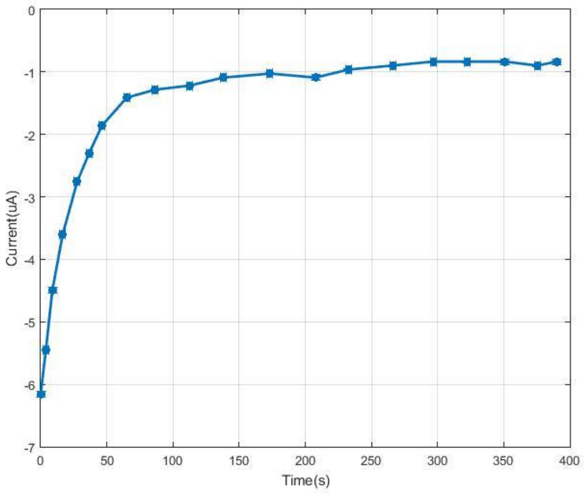

Figure 4: Galvanic current-time curve of Ti-NiTi SMA

In this experiment, the anodic polarization curves and several important electrochemical parameters of NiTiSMA coated Ti coating are obtained by this method: self-corrosion potential, dimensional current density, polarization resistance, over-passivation potential. Ti / NiTiSMA is used to replace the auxiliary electrode platinum sheet, and the pair of NiTiSMA is formed. The galvanic current flowing through the alloy electrode is measured under the condition of no voltage applied to the system. It can be seen from Fig.3, even on the current decreases with time, the most obvious performance is appeared in the first 50s, then the current decreases slowly and gradually to be stabilized. And then we measure the current, which is then divided by the electrode test area, so you can get the even current density value. Ti metal coating and NiTiSMA stable after the galvanic current density value can be maintained in the uA (10^{-6}A/cm^2) class, whose value is minimal and no galvanic corrosion is occurred. Therefore, this experiment shows that metal titanium is safe to use as a coating material and nickel-titanium alloy, meanwhile it can improve the corrosion resistance of nickel-titanium alloy at the same time, between which there is no galvanic corrosion.

4. Conclusion

The surface of the NiTi shape memory alloy can be coated with a layer of titanium, which has a thickness of about 400 um by a plasma spray method. The surface modification treatment can effectively improve the corrosion resistance of nickel-titanium shape memory alloy by electrochemical measurement, and there is no galvanic corrosion between them. It is optimized for Ni-Ti shape memory alloy implant, which provides a direction for development. However, electrochemical measurement is a short-term, rapid method on the Ti / NiTiSMA composite long-term corrosion resistance, which still need a variety of experimental methods of comprehensive evaluation. The experiments demonstrate that the surface modification of nickel titanium shape memory alloy surface coating can effectively improve the corrosion resistance of the matrix metal and there is no galvanic corrosion between the coating and the base metal.

Acknowledgments

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