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Effect of temperature on nitinol electropolishing

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Abstract: Electropolishing has been used in TiNi alloy in several fields for its special characteristics, but its essential details and electropolishing mechanism have not been reported yet as a demand from business competition, which, to a great degree, restricts the application and extension of the electropolishing technology. In this paper, effect of temperature on nitinol electropolishing is explored. Studies on the effect of the temperature on the electropolishing process show that the higher the temperature is, the bigger the electropolishing rate is, following a near Gauss law. The relationship between the temperature and surface roughness follows near parabolic law, the relationship between the temperature and surface reflectivity follows near Sigmoidal law.

Key words: shape memory alloy; nitinol; electropolishing; temperature

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1 Introduction

In recent years, the study of surface preparation has attracted considerable attention due to its potentially important effect on properties of NiTi medical components. Among those surface treatment methods, electropolishing has attracted a great attention for its distinctive advantages. Electropolishing removes slag, burrs, scratches, heat affected zones and creates a new, smoother surface. The polishing rate can be carefully adjusted within tight tolerances to meet different requirements. Electropolished NiTi alloy is covered by a thin (about 3 nm) oxide film which is responsible for the outstanding corrosion resistance and biocompatibility. The polishing process results in a protective film consisting of nearly pure Titanium oxide. The entire Nickel free surface is a clear advantage compared to mechanically polished surfaces[1-3].

Thanks to those advantages of electropolishing, it has been applied in NiTi alloy in many fields, especially in medical field. But few literatures report the mechanism and technics of NiTi alloy in details due to the business competition[4,5]. In this paper, effect of temperature on electropolishing of NiTi alloy will be analyzed, and it is expected that our work will be beneficial to optimize the electropolishing parameters of NiTi alloy.

2 Experimental methods

A nearly equiatomic NiTi alloy with an analysed composition of 55.6%Ni was prepared from the raw materials of titanium (purity 99.9%, mass fraction) and nickel (purity 99.97%, mass fraction) with vacuum inductive melting technique being used. The ingot was then forged and drawn to wires 0.88mm in diam-

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eter. The Af temperature of the wires measured by DSC is about 10℃.

In a special solution, samples were electropolished with DP—1 electropolishing instrument at different temperatures by ZL-L-1800 semiconductor refrigeration system. Then they were investigated with a JSM-840 scanning electron microscope. The surface roughness of samples was measured by the MHT-Ⅲ non-contact three-dimensional surface topography measuring instrument and the surface reflectivity by the CS5 computer color matching system.

3 Results and discussions

3.1 Effect of temperature on nitinol electropolishing

The electrolyte should be used in the scope of certain temperature, that is, some should be kept in hot water for keeping higher temperature, such as H_3PO_4-CrO_3 electrolyte, while the electrolyte we have used in this experiment should be cooled during the electropolishing process are that the temperature of electrolyte can be kept lower. The inner-resistance and current of the electrolyte are very large, so there is large amount of energy produced during the electropolishing process, then the temperature of electrolyte and the anode rise rapidly, which causes the electropolishing current to rise remarkably and has a great influence on the electropolishing quality.

Metal has a feasible temperature scope in special electrolyte. Generally, the lower the temperature is, the bigger the viscosity of electrolyte is, then the smaller the ions' diffusion velocity is and the slower the dissolution velocity is. The principle of determining the electrolyte temperature is choosing the higher temperature within the allowable scope, so we can get a smaller electrolyte viscosity, bigger ions' diffusion velocity and limiting current density, then a faster metal dissolution velocity and a better surface. But if the temperature turns too high, the electrolyte viscosity will be smaller and the activity of acid ions be strengthened, so the surface of the metal tends to be over etched. Furthermore, if the electrolyte temperature goes too high, especially when the temperature of the reaction zone increases too fast, it will cause the electrolyte decomposition, and then aggravate ageing process of the electrolyte.

Different kind of metal has different temperature scope in different electrolyte system. The stainless steel has a higher electropolishing temperature, mainly above 50℃; the electroplishing temperature of dental Cr-Co alloy is mainly 50—70℃ while the nickel-base alloy is mainly 80—100℃. We can not determine the ideal electropolishing temperature scope of different metals theoretically now, and we can confirm it only through experiments.

The optimum temperature of NiTi alloy was investigated in detail in this paper by reviewing the effects of the electropolishing temperature on the electropolishing rate, surface roughness and surface reflectivity. The other parameters were: electropolishing time 45 seconds, spacing between anode and cathode 1.8cm, current dentisity 0.7 A/cm^2. All samples were mechanically polished with successive emery papers down to No.400 producing a similar finish with an original surface roughness (R_a: 216 nm) and original surface reflectivity (R_z: 47.68%).

Electropolishing rate=mass of metal removal /(electropolishing time×metal surface area), that is, mass of metal removal per unit of time on per unit of area.

It can be seen from Fig.1 that the higher the electrolyte temperature is, the bigger the electropolishing rate is, following a near-Gauss law, which is in accord with the results of studying the relationship between the electropolishing temperature and electropolishing with surface roughness method by Matlosz[6].

It can be seen from Fig.2 and Fig.3 that the relationship between the temperature and surface rough-

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ness follows near parabolic law, the relationship between the temperature and surface reflectivity follows near Sigmoidal law.

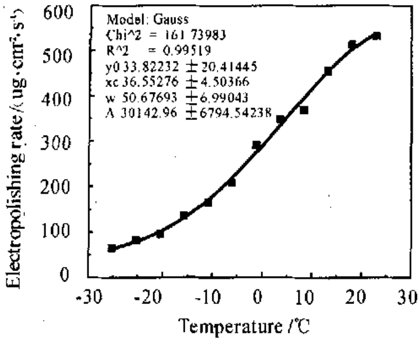

Fig.1 Effect of electropolishing temperature on electropolishing rate

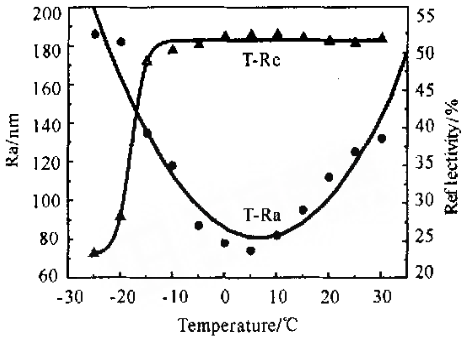

Fig.2 Effect of electropolishing temperature on surface roughness and surface reflectivity

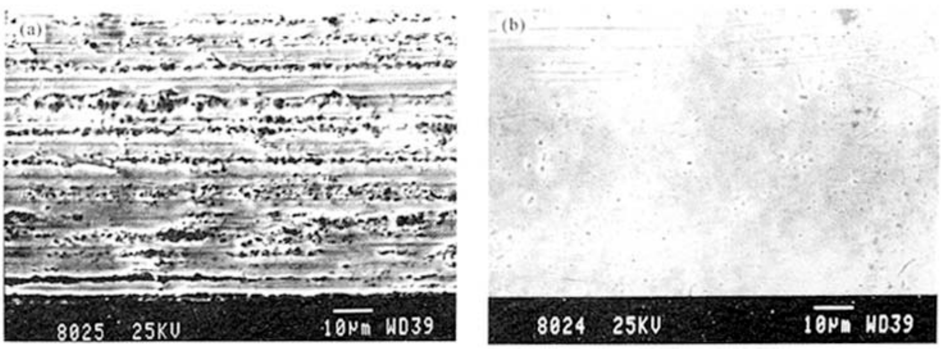

Fig.3 Surface morphologies of TiNi alloy after different surface treatments
(a)—mechanical polishing(1000#); (b)—electropolishing

If the electropolishing temperature is lower than −20℃, namely, not in the appropriate range, the dissolution of the NiTi alloy's surface will be active, so stable film can not form on the surface to electropolish it. Instead of polishing, a type of etching is introduced, so the surface will be coarse and lack of luster, and thus bad.

When the electropolishing temperature rises to a critical point (about −15℃), the speed at which metal dissolves becomes bigger than that at which the dissolving products (metal ions) diffuses to the solution. So, the zone near the anode will form an electrolyte layer (high concentration saline) composed of metal anode ions and negative ions in the electrolyte solution-we call it viscous layer which is a very viscous liquid membrane. If the original surface of the metal is coarse, the membranes on peaks will have more acute diffuse action on electrolyte, so the thickness of membranes on peaks will be thinner than that on valleys. Since the resistance of the membranes is very high, and the thinner the membrane is, the smaller the resistance will be, so the current density rises remarkably. That means the current densities in different parts on the surface are completely different. The anodic current density is highest at the peaks and lowest at the valleys, so metal from the anode dissolves faster and easier at the peaks, and gradually, a level, smooth surface forms. We thus think that the electropolishing speed is controlled by the diffusion speed at which

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the reaction products passing the viscous layer.

With the increase of electropolishing temperature, the current density on NiTi alloy (the anode) reaches a critical value, the oxygen begins to separate out from the anode. If the current is not big enough at this time, only few bladders attach to the surface of the anode. It takes a long time to transgress, so it is apt to cause spots. With the temperature rising ulteriorly (about 0—10℃), the current and the reaction speed will be larger accordingly, so the bladders will no longer stay on the surface and transgress to the liquid. In this condition, we can get nice electropolishing surface. However, the anodic reaction is so hard, the bladders' bubbling break up the original relative balance of the viscous layer, so the electropolishing mechanism is mainly corrosion pits' spreading: under the action of high current density, a large number of corrosion pits are produced on the electropolishing surface in a short duration, the corrosion pits will expand, spread and link up together, so the surface dissolves evenly (see Fig. 3 (b)).

It can be seen from the quantitative analysis on the experimental results that the surface roughness reduces with the temperature goes up. When the temperature goes to 0—10℃, the surface roughness shows the lowest values, the reflectivity tends to be the highest and we can get nice electropolishing surface in this condition.

With the temperature rising ulteriorly, the dissolution of nitinol anode and the surface roughness will be larger accordingly, while the surface reflectivity will be lower. Pitting corrosion will happen acutely during the electropolishing process. Even with naked eye, we can see it is full of corrosion pits on the surface. In addition, there are too many raw materials, including NiTi alloy and electrolyte, are wasted in the process. And the electrolytic heat will remarkably increase accordingly.

3.2 Surface morphologies

One of the excellences of electropolishing is that it can reduce the surface roughness and increase the surface reflectivity, then improve the surface smoothness. Under the appropriate processing parameters, such as temperature, current density, spacing between anode and cathode, electrolyte stirring, we can get a smoother surface. Fig. 3 shows the surface morphologies of TiNi alloy after different surface treatments, mechanical polishing and electropolishing.

There are many irregular crystal planes on the mechanically polished surface, they reflect the rays to all directions, while there are not exit the deformed layer made with broken crystal grains on the electropolished surface, the passivating film belongs to the state between crystalline and amorphous states, it has more regular configuration and uniformity than the mechanical film, so the electropolished metal has a smoother and brighter surface than the mechanical polished one.

4 Conclusion

(1) With the appropriate processing parameters, electropolishing can reduce the surface roughness, increase the surface reflectivity, and then create a new and smoother surface.

(2) Studies on the effect of the temperature on the electropolishing process show that the higher the temperature is, the bigger the electropolishing rate is, following a near Gauss law. The relationship between the temperature and surface roughness follows near parabolic law, the relationship between the temperature and surface reflectivity follows near Sigmoidal law.

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