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Materials

Electrochemical Method for Evaluating the Passivated State of Medical Stainless Steel 317L

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Abstract: The electrochemical behavior of the medical stainless steel 317L which is used as *in vivo* fixation materials has been investigated at different passivated states in several candidate-testing solutions. The potentiodynamic scanning polarization technique was employed to measure the polarization curves of 317L in 0.9%NaCl solution at 37℃. The results showed that the electrochemical behavior in 0.9% NaCl solution at 37℃ and in 2% NaCl solution at 30℃ can be better used to detect and evaluate passivated states and corrosion resistance of 317L. In addition,the pitting potential E_b can be used as a criterion and its lower limit could be 0.85 V(SEC) for this system.

Key words: stainless steel 317L; passivation; pitting potential; electrochemical method

In medical science, the application locations of metallic surgical implanted materials in human body are varied, so the quality of these products directly influences human body health. Stainless steel materials have increasingly extensive usage in the field of medical science. However, some enterprises in China do not comply with the standards in treating technology, the quality and properties of inner fixing pieces of medical stainless steel 317L can cause great differences in corrosion resistance of the products. So far, the testing standard ZBC 35005-86 [1] for passivation technology applied in similar domestic enterprises can not clearly distinguish the passivated and non-passivated surface state of stainless steel. Base on these facts, this paper investigated electrochemical evaluating methods, criteria of passivation state and corrosion resistance of medical stainless steel 317L, and proposed a corresponding method recommended for reference by similar domestic enterprises and concerned department.

1 Experimental

Medical stainless steel 317L sheet was selected as the experiment material. The chemical composition of 317L is Cr, 18.93%; Ni, 13.82%; Mo, 3.17%; S, 0.008%; C, 0.018% and Fe, balance in mass fraction. The steel sheet was cut into squares of 12 mm×12 mm, and then welded with conducting wire and sealed by epoxy resin. The specimens as working electrodes had an area of 12 mm×12 mm exposed. Their surfaces were grounded to 1000# by water-sand paper, mechanically polished and prepassivated according to the requirement of research purpose.

In this study, the technical condition of prepassivation of 317L was: solution, 30% HNO_3 + 2.5% $K_2Cr_2O_7$; temperature, 25℃ and passivated time, 6 h. In order to investigate the electrochemical method for evaluating, four solutions were selected in as the testing media candidates, shown in **table 1**.

With reference to ASTM Standard, *etc.*[2–4] for pitting potential testing methods of implanting metals, we chose the traditional triple-electrode system. Platinum and calomel electrodes were used as the counter electrode and the reference electrode respectively. The potentiodynamic scanning method was employed to mea-

Table 1 Measured pitting potential E_b of prepassivated and non-passivated stainless steel 317L in four selected testing media.

No.	Testing media	Testing temperature / ℃	E_b / V (SCE)	
			Passivated	Non-passivated
01	5% H_2SO_4+2% NaCl	30	974.3	956.0
02	5% NaCl+0.1% H_2O_2	22	965.2 (Reference value)	328.2 (Reference value)
03	2% NaCl	30	911.0	229.0
04	0.9% NaCl	37	893.0	206.0

sure the polarization curves. The starting potential was the free corrosion potential E_{corr} and the scanning rate was 20 mV/min. The potential point at which the current increased drastically was defined as the pitting potential E_b. In this experiment, we used M351-2 corrosion measure system produced by EG&G Corp. and PS-168 electrochemical measurement system manufactured by Beijing Zhongfu Corrosion and Protection Corp..

2 Results and Discussion

2.1 Determination of testing media

The same stainless steel materials in different electrolytes and deferent kinds or under different states in the same electrolytes revealed different electrochemical behaviors and showed different pitting potentials. Therefore, it was possible to choose an appropriate electrolyte solution through measuring pitting potential to evaluate the passivation quality of stainless steel materials or parts. According to the requirement of *in vivo* application, the surface of the medical stainless steel 317L products must undergo passivation treatment. In order to test the passivation quality 317L products, an electrochemical solution as a testing medium should be defined first, which was sensitive to passivated, non passivated states and surface conditions of different passivation qualities. Under this requirement, we selected four representative solutions as candidate testing media, in which we measured the electrochemical polarization curves of the specimens in prepassivated and non-passivated surface states. The measured polarization curves are shown in **figures 1–4**, and the measured pitting potential values are listed in table 1.

From the polarization curves of 317L measured in 5% H_2SO_4+2% NaCl solution, we can find that the pitting potential values of passivated and non-passivated

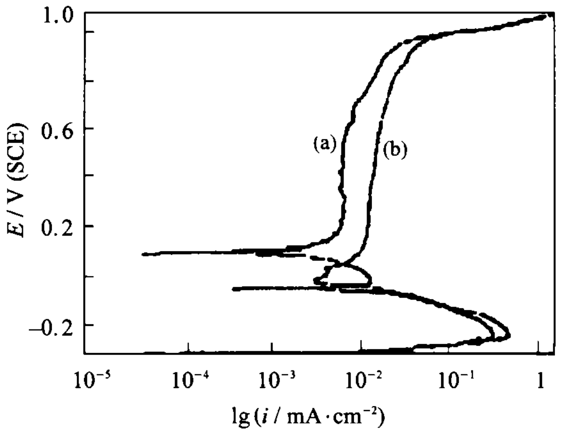

Figure 1 Polarization curves of stainless steel 317L in 5% H_2SO_4+2%NaCl solution at 30℃. (a) prepassivated, and (b) non-passivated.

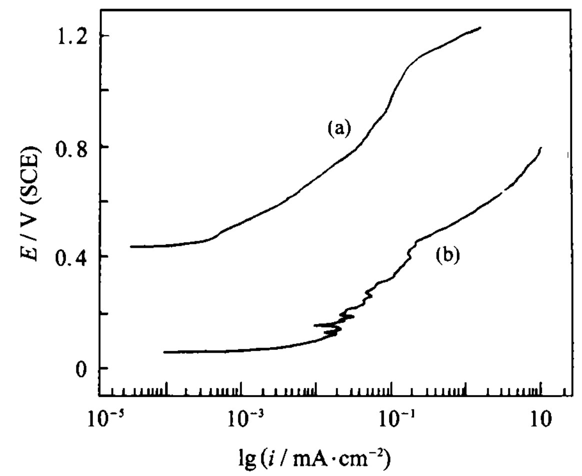

Figure 2 Polarization curves of stainless steel 317L in 5% NaCl+0.1%H_2O_2 solution at 22℃. (a) prepassivated, and (b) non-passivated.

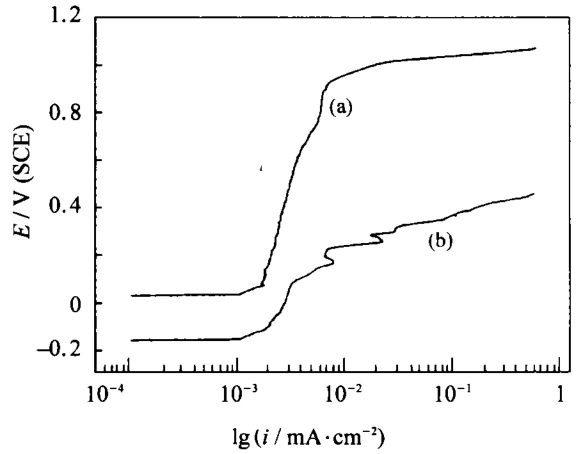

Figure 3 Polarization curves of stainless steel 317L in 2% NaCl solution at 30℃. (a) prepassivated, and (b) non-passivated.

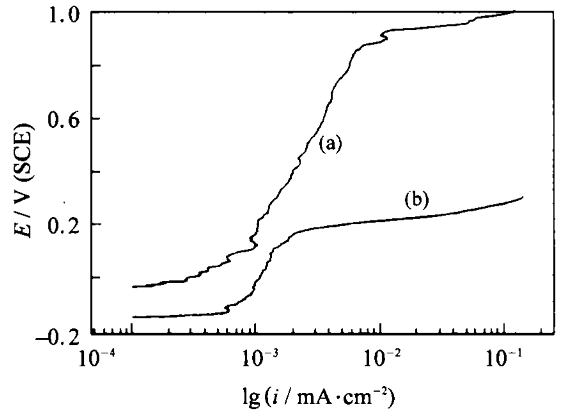

Figure 4 Polarization curves of stainless steel 317L in 0.9% NaCl solution at 37℃. (a) prepassivated, and (b) non-passivated.

specimens approached each other (see table 1), and that it was difficult to distinguish the passivated state from the non-passivated state. Being a basic testing medium for an evaluation test, the solution should first have sensitive response to different passivation-quality state of the stainless steel surface. Especially for the prepassivated and non-passivated 317L, in order to differentiate its different surface states apparently different pitting potential E_b values should be shown. However, in 5% H_2SO_4+2% NaCl solution at 30℃, the measured polarization curves approached the pitting potential E_b. There was no way to differentiate the prepassivated state and the non-passivated state. Therefore, this solution could not be selected as the basic testing medium for the evaluation of the methods used.

In the immersion solution 5% NaCl + 0.1% H_2O_2 used in the present Professional Standard ZBC 35005-86 [1], the polarization curves of the prepassivated and non-passivated specimens showed no apparent passivation behaviors. There was no apparent pitting potential either (In this paper E_b was only estimated approximately according to the relative increase of the current). The prepassivated and non-passivated state could not be distinguished clearly in this solution, so it could not be selected as a testing medium for the evaluation of electrochemical methods.

Whereas the polarization curves of 317L in 2% NaCl (30℃) and 0.9% NaCl (37℃) testing solution possessed typical electrochemical passivation behaviors and showed apparent pitting potential yielding points. For prepassivated and non-passivated specimens, their pitting potential E_b had apparent difference, which were the normal response characteristics required for a testing medium as an electrochemical evaluation testing method. Therefore, the two solutions could be included. In consideration of the professional range and referring to related international standards, 0.9% NaCl (37℃) solution was recommended as a testing medium in defining testing method in order to discriminate passivated, non-passivated states and different passivation qualities of stainless steel surface states.

2.2 Determination of testing method and evaluation criteria of passivation quality

In order to test and evaluate whether the passivation quality of 317L could meet the requirement, an uniformed standard testing method should be established and the evaluation parameters should be defined. In the electrochemical polarization measurement, the most important parameter representing the pitting resistant quality (pitting corrosion susceptibility) of passivation films of stainless steel was the pitting potential E_b. As the potentiodynamic scanning measurement was performed, the applied anodic polarization potential moved positively until reaching a certain characteristic potential value, at which the stainless steel surface film was broken down and the polarization current increased drastically. The characteristic potential was the pitting potential E_b. The value of E_b was reliable and sensitive in representing the corrosion resistance, stability and anti-breakdown of surface passivation films of the stainless steel [3,4]. Therefore, E_b could be selected as the evaluation parameter for testing the surface state including passivated, non-passivated and the ones of different passivation quality.

In order to realize the measurement of polarization curves and E_b by dynamic potential scanning, testing media were first selected. The solution 0.9% NaCl (37℃) as a testing medium was recommended.

In the measurement of polarization curves by potentiodynamic scanning, different potential scanning rates had great influence on polarization behaviors and E_b. Based on the results researching on pitting corrosion and electrochemistry of stainless steel before, we selected 20 mV/min as the potential scan rate in the potentiodynamic scanning measurement.

The results indicated that the electrochemical testing method of potentiodynamic scanning is an effective passivation quality testing and evaluating method because of its sensitivity and reliability in testing. This method recommends that the starting potential be the free corrosion potential E_{corr} and the scanning rate 20 mV/min. Meanwhile, the potential value at which the current rises drastically is selected as the pitting potential E_b; the testing medium is 0.9% NaCl solution at 37℃. As an evaluating parameter, E_b, a quantitative index should be recommended to evaluate the passivation quality of 317L. **Figure 5** shows the measured electrochemical polarization curves of the 317L specimens in the testing medium 2% NaCl solution (30℃) at three states: surface mechanically polished, mech-

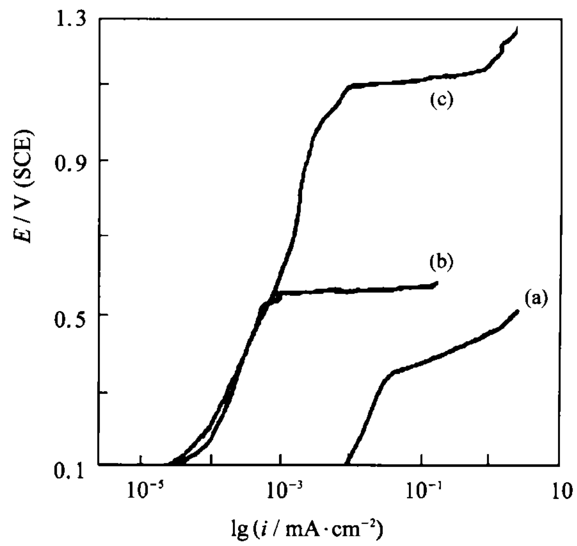

Figure 5 Polarization curves of stainless steel 317L in 2% NaCl at 30℃. The three different surface states are: (a) mechanically polished, (b) mechanically +elctrolytically polished, and (c) passivation treated (30%HNO_3, 35℃, 6 h) after mechanically polished.

anically and electrolytically polished, and mechanically polished followed by passivation treatment (passivated in another HNO_3 solution with 30% HNO_3 at 35℃ for 6 h), respectively. E_b of the specimens undergone mechanical polishing can reach 294 mV (SCE), while that of the specimens through mechanical and electrolytic polishing can reach 557 mV (SCE). However, the results of mechanical polishing followed by passivation treatment can cause E_b increase to 1 097 mV (SCE).

Based on the statistical analysis of a large amount of experimental results, E_b> 850 mV (SCE) should be recommended as a criterion for eligibility of surface passivation treatment of 317L. Generally, the medical stainless steel 317L undergone appropriate passivation treatment could satisfy this requirement.

The authors carried out some confirmation tests on actual products made by 317L. In the experiment, the products were passivated in 30% HNO_3 solution at 35℃ for 6 h, cleaned in water, dried by blowing, and sealed by 704 glue with an exposure surface area of 0.05 cm^2. Then, they were tested by the prescribed potentiodynamic scanning method for the polarization curves in 0.9% NaCl (37℃) solution, the starting potential being the free corrosion potential E_{corr} and the scanning rate being 20 mV/min. The results were listed in **table 2**. For comparison, this table also includes the measured E_b of the 317L products undergone by different passivation treatments obtained through sampling from several corporations. These results effectively prove that the method studied in this paper is an effective and practical, quick and simple, sensitive and reliable testing method. The recommended evaluation criterion is also reasonable.

Table 2 Pitting potential E_b of passivation treated practical products of medical stainless steel 317L in 0.9% NaCl at 37℃.

Name of products	Manufacturer	Passivation technique	Sample code	E_b / mV (SCE)
Plum-flower-shaped needle	Company A	30% HNO_3, 35℃, 6 h	1, 2, 3	1 051,1 060,1 004
Lath nail	Company A	30% HNO_3, 35℃, 6 h	1, 2, 3	982,972,974
Bone-connecting sheet	Company A	30% HNO_3, 35℃, 6 h	1, 2, 3	981,957,982
Plum-flower-shaped needle	Company B	HNO_3+$K_2Cr_2O_7$	Average value of three samples	324
Triangle-shaped needle	Company C	12 L HNO_3+16 L H_2O_2	Average value of three samples	586
Bone-connecting bolt	Company D	65% HNO_3,ambient temperature,2 h	Average value of three samples	750

3 Conclusions

(1) The electrochemical potentiodynamic scanning method studied in this paper is an effective and practical, quick and simple, and sensitive and reliable method for testing and evaluating surface passivation qualities of the medical stainless steel 317L. Additionally, the 0.9% NaCl solution (30℃) is introduced as the testing medium in the testing method.

(2) The pitting potential E_b can be used as the evaluation parameter and E_b> 850 mV (SCE) is recommended the evaluation criterion. All materials meeting this requirement should be considered as having eligible passivation treatment. This criterion can be satisfied by normal chemical passivation treatment in nitrate acid solution.

Acknowledgements

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References

[1] *ZBC35005-86, the Corrosivity Testing Methods for Bone-connecting Sheets and Bolts*. 1986.

[2] ASTM F746-87 Standard Test Method for Pitting or Crevice Corrosion on Metallic Surgical Implant Materials. *Annual Book of ASTM Standards*, Vol.03.02., 1994.

[3] S. Song: *Corrosion Electrochemistry Study Methods*. Chemical Industry Press, Beijing, 1988, p.66-77.

[4] Y. Wu, *et al.*: *Corrosion Experiment Methods and Anti-corrosion Testing Technology*. Chemical Industry Press, Beijing, 1996, p.31-35, 90-92.