Article ID: 1003-6326(2003)01-0073-05

Surface hardening of titanium alloys by oxygen-diffusion-permeation①

MA Hong-yan(马红岩)[1], WANG Mao-cai(王茂才)[1], ZHANG Song(张 松)[2],
XIN Gong-chun(辛公春)[3], WEI Zheng(魏 政)[3]
(1. State Key Laboratory for Corrosion and Protection of Metals,
Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China;
2. School of Materials Science and Engineering,
Shenyang Polytechnic University, Shenyang 110023, China;
3. Shenyang Liming Aero-engine Group Corporation, Shenyang 110043, China)

Abstract: The surface oxygen-diffusion-permeation behaviors of Ti based alloys were investigated. MEF4A optical microscopy and HMV-2000 micro-hardness tester were employed to characterize the microstructure and micro-hardness of the oxygen-permeated alloys. The results show that the micro-hardness of Ti based alloys are sharply enhanced by the permeation of oxygen. The microstructure and micro-hardness of oxygen-permeated layer are strongly related to the oxygen-diffusion-permeation techniques. The solid solution of oxygen in α phase can improve the transformation temperature from α phase to β phase and enlarge the region of α phase so as to improve the micro-hardness of surface layer. Therefore, surface oxygen-diffusion-permeation would be a feasible method to reinforce Ti based alloys based on the solid solution of oxygen in α-Ti. At last, a diffusion-solution model was put forward.

Key words: Ti based alloys; oxygen-diffusion-permeation; reinforcement
CLC number: TG 166.5 **Document code:** A

1 INTRODUCTION

In recent years, the processing industries of Ti and Ti based alloys have been greatly developed[1]. They are reckoned to be "the 21st century steels" for their being used extensively in many fields, such as aviation, navigation, petroleum, chemical industry, medicine, metallurgy, etc. Titanium alloys have high specific strength and excellent hot stability, so they are major used in motors with high pulling ratio. However, their low wear resistance hinders the applications of Ti based alloys. How to improve their surface wearabilities is a key problem. Nowadays, in domestic[2-5], to improve surface micro-hardness, nitriding, ion plating, ion sputtering, carbonization, metalikon, etc are mainly adepted. All these methods are mainly by forming hard coatings adhered to substrate materials to reinforce surface. It's very likely to induce lamination, exfoliation, and cracking, so as to reduce the whole property. High-energy laser beam is a preferable method to enhance micro-hardness, but it is only propitious to harden part of work pieces[6-8]. Therefore, new surface hardening methods with incorporate reinforcement need to be attempted.

It can be seen from Ti-O phase diagram that oxygen has high solid solution in α-Ti and the maximum is up to 14.5%. The solid solution of oxygen can not only improve the transformation temperature from α phase to β phase, stablize α phase, but also engender hardness effect, which can be above HV500. Compared with other surface strengthening technologies, such as nitriding and carbonization, oxygen-diffusion-permeation can improve fretting fatigue resistance and fretting wear resistance and can hardly influence the whole mechanical and chemical functions. Lots of surveys indicate that the present studies are mainly focused on the prevention of oxygen to contaminate Ti based alloys[9-12] and the oxidation of titanium alloys[13-15] and few were done to the oxygen-diffusion-permeation reinforcement both at home and abroad. And no any literature was reported. So in this work, initial study is done in order to study the surface oxygen-diffusion-permeation behaviors of Ti based alloys. This will be useful for further study on oxygen-diffusion-permeation mechanism of Ti based alloys.

2 EXPERIMENTAL

TC11 and BT20 were used as the substrate materials (the nominal composition is listed in Table 1). Coupon specimen of TC11 was about d 11 mm × 3.6 mm. Coupon specimen of BT20 was about 9.0 mm × 14.50

① **Foundation item:** Project(50171073) supported by the National Natural Science Foundation of China
Received date: 2002-02-25; **Accepted date:** 2002-05-20
Correspondence: MA Hong-yan, Ph. D, +86-24-23915863, hyma@imr.ac.cn

mm × 5.30 mm. The specimens were abraded with a series of polishing papers of up to 800-grit without polishing. Oxygen-diffusion-permeation was carried out in H15 air stove at the temperature of T_1 for 10 h and T_2 for 6 h, respectively ($T_0 > T_2 > T_1$, and T_0 is the allotropy transition temperature), by using oxygen-permeation medium.

MEF4A optical microscopy and HMV-2000 microsclerometer were employed respectively to examine the microstructure and micro-hardness of oxygen-permeated layer. Load of the sclerometer was 0.49 N and the duration was 15 s. The element linear analysis on oxygen-permeation-diffusion specimens was characterized by an SEM with an X-ray energy disperse system.

3 RESULTS AND DISCUSSION

3.1 Oxygen-diffusion-permeation in two cases

TC11 and BT20 were oxygen-permeated at temperature of T_1 for 10 h and T_2 for 6 h, respectively. The micro-hardness distributions of oxygen-permeated layer are shown in Fig. 1. It can be seen from Fig. 1 that the oxygen-permeated layers of Ti based alloys have higher micro-hardness than those of the substrate materials. Consequently, the micro-hardness of surface layer can be sharply improved by oxygen-diffusion-permeation. The surface micro-hardness of Ti based alloys, TC11 and BT20, experienced oxygen-diffusion-permeation treatment at T_1 for 10 h can be above 600 GPa; even in 50 μm distance from surface, the micro-hardness can achieve 400 to 450 GPa. Whereas the surface micro-hardness of the same Ti based alloys treated at T_2 for 6 h is approximately close to 550−580 GPa, slightly lower than that treated at the temperature of T_1 and the depth of hardening layer is slightly increased. Observed from surface, when oxygen-permeated at T_2 for 6 h, exfoliation of oxide skin from surface is very serious. The surface-dimensions difference is relatively big so that the surface of alloys has very rough oxide skin. While oxygen-permeated at T_1 for 10 h, the surface-dimensions difference is relatively small and the surface of alloys is comparatively smooth. It can be seen that oxygen-diffusion-permeation at T_1 for 10 h is superior to the one at T_2 for 6 h.

The microstructures of oxygen-permeated layer are shown in Fig. 2. From Fig. 2, it can be seen that there are more α-Ti in surface layer than that in substrate materials and no obvious boundary exists between surface layer and substrate materials. With the distance away from surface, the content of α-Ti is gradually reduced while the content of β-Ti is increased. The microstructures show that the relative ratio of α-Ti to β-Ti in Ti based alloys with α+ β dual phase is changed by the treatment of surface oxygen-permeation. It illustrates that, with increasing the permeation of oxygen, the concentration of oxygen in surface layer is increased and this can be proved in Fig. 3. It can enlarge the region of α-Ti. As we all know, oxygen has high solid solution in α-Ti and the maximum is up to 14.5%. It can improve the allotropy transition point of Ti based alloys and stable α-Ti phase (Fig. 4).

Since oxygen has high solid solution in α-Ti, oxygen enlarged the region of α-Ti and form solid solution in Ti based alloys. Such solid solution has fairly high micro-hardness. It can greatly improve the surface micro-hardness of Ti based alloys. The permeation of oxygen in Ti based alloys formed incorporate reinforcement. It can avoid such problems as the combine intensity and brittl-

Table 1 Chemical compositions of TC11 and BT20 (%)

Ti-based alloy	Ti	Al	Mo	V	Fe	Si	Zr	N	H	O
TC11	Bal.	5.5−7.0	2.8−4.0	–	0.25	0.20−0.35	0.8−3.0	0.05	0.05	0.15
BT20	Bal.	5.0−7.0	0.5−3.0	0.8−2.5	0.30	0.15	1.0−2.5	0.05	0.015	0.15

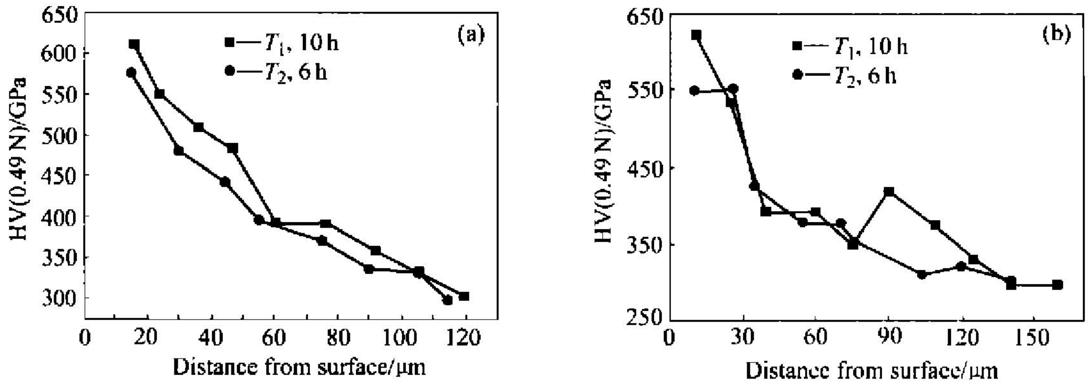

Fig. 1 Micro-hardness of TC11(a) and BT20(b) oxygen-permeated at T_1 for 10 h and at T_2 for 6 h

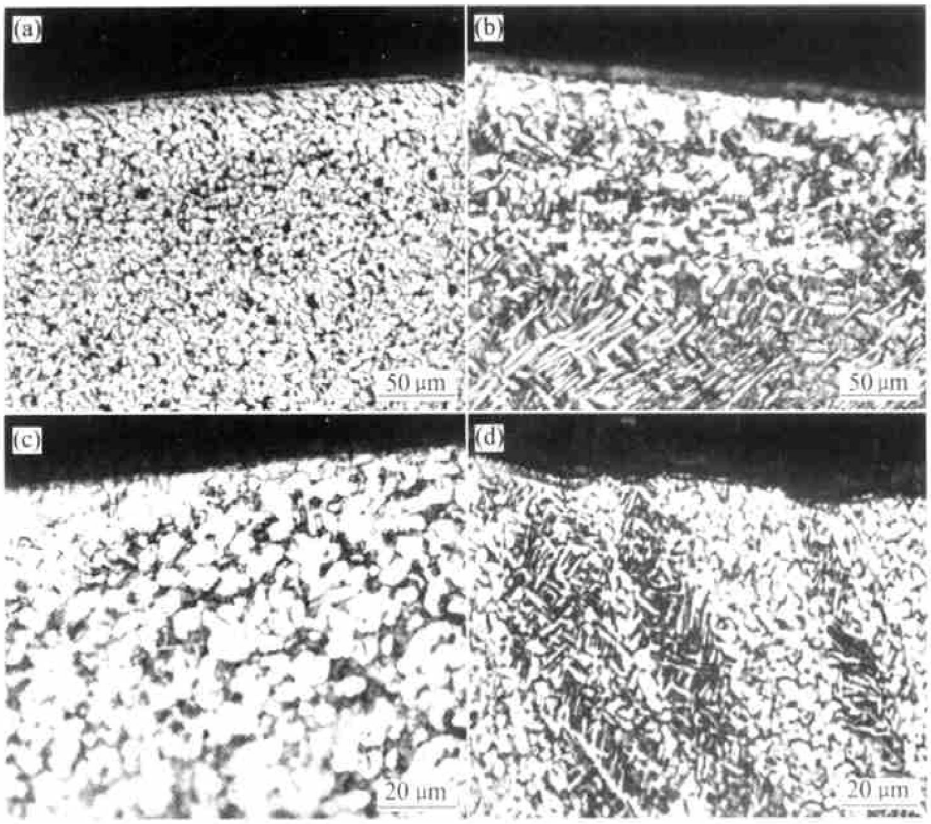

Fig. 2 Oxygen-permeation microstructures of TC11(a), BT20(b) at T_1 for 10 h and TC11(c), BT20(d) at T_2 for 6 h

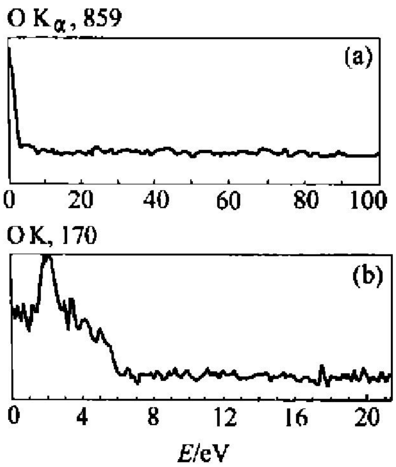

Fig. 3 Oxygen concentration distribution of TC11(a) and BT20(b) from surface to inner

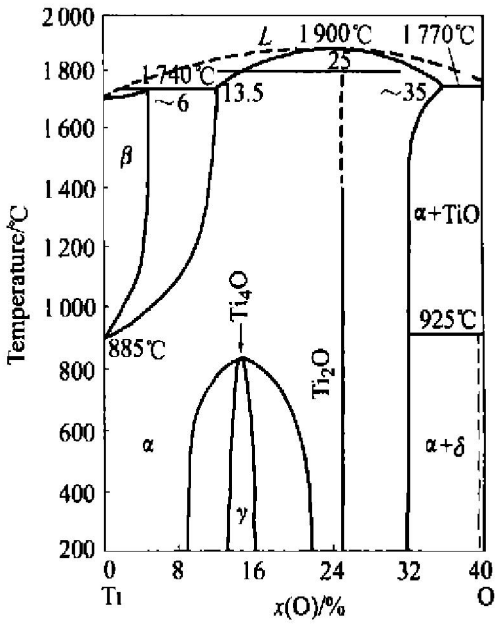

Fig. 4 Ti-O phase diagram

eness existing between adherent coating and substrate materials. Therefore, surface oxygen-diffusion-permeation is a feasible method to reinforce Ti based alloys. Whereas, how to control the solid solution and hardening effect of oxygen in α-Ti to reinforce Ti based alloys needs further study.

3.2 Secondary oxygen-diffusion-permeation

After once oxygen-diffusion-permeation at temperature of T_1 for 10 h, TC11 and BT20 were oxygen-permeated for the second time at the same condition without removing oxide skin. The micro-hardness distribution was shown in Fig. 5. From Fig. 5, it can be seen that the surface micro-hardness of Ti based alloys was higher than that of once oxygen-diffusion-permeation. The maximum can be above 900 or 750 GPa and the depth of hardening layer was also improved. Fig. 6 shows the microstructure of secondary oxygen-diffusion-permeation. It can be seen from Fig. 6 that the α-Ti in surface layer is more than that of once oxygen-diffusion-permeation. It showed that the content of oxygen is accordingly increased with the further permeation of oxygen in Ti based alloys. This en-

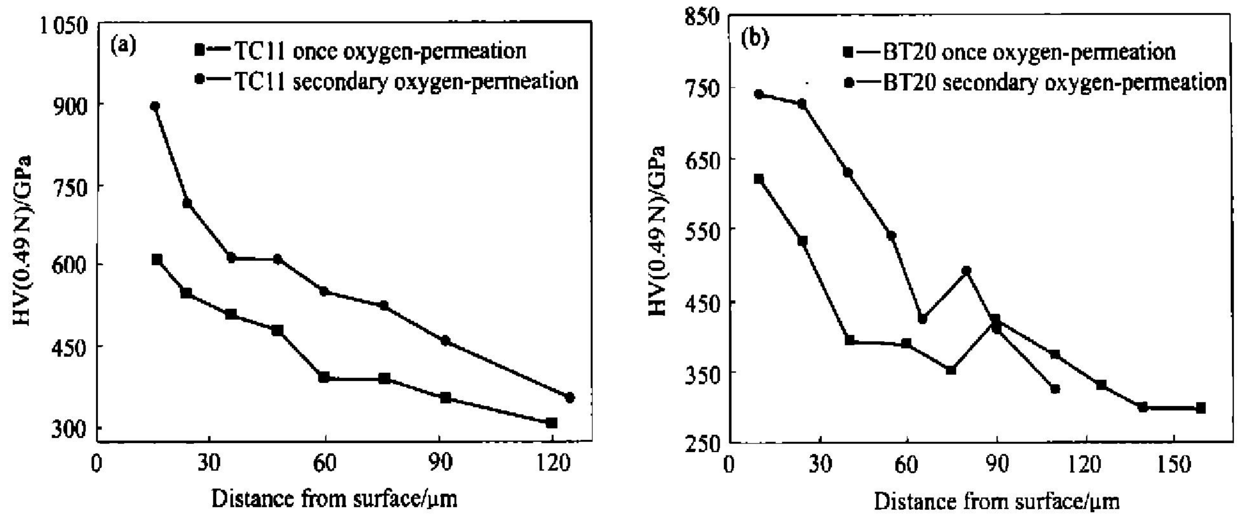

Fig. 5 Micro-hardness of TC11(a) and BT20(b) after once oxygen-permeation and secondary oxygen-permeation at T_1 for 10 h

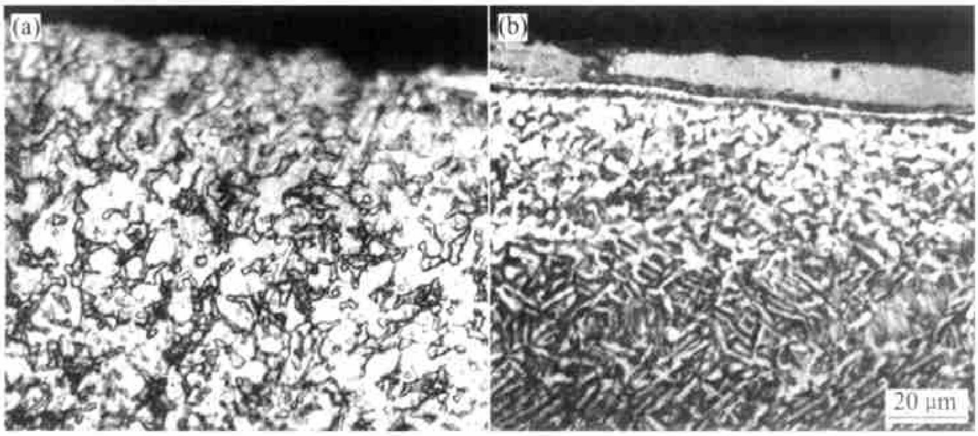

Fig. 6 Oxygen-permeation microstructures of TC11(a) and BT20(b) after secondary oxygen-permeation at T_1 for 10 h

larged the region of α-Ti phase for the more. Therefore, secondary oxygen-diffusion-permeation promoted the micro-hardness of surface layer sharply. But the time for secondary oxygen-permeation won't be too long and a few hours will be suitable. Because the longer the time is, the more serious oxidation the surface will become. Such technology mentioned-above could be a measure to remedy those that haven't achieved enough micro-hardness or depth when oxygen-permeated for the first time. Thus secondary oxygen-diffusion-permeation can improve surface micro-hardness and doesn't change more about the dimension of titanium alloys.

3.3 Diffusion-solution model

From thermal dynamic point of view, during the oxygen-diffusion-permeation process, the following reaction may happen:

$$2Ti + O_2 \rightarrow 2TiO \quad (1)$$

$$2Ti + N_2 \rightarrow 2TiN \quad (2)$$

Oxygen may also form solution in α-Ti as follows:

$$2Ti(\alpha) + O_2 \rightarrow 2Ti\text{-}O(\text{Solution}) \quad (3)$$

In this paper, the oxidation velocity constant of titanium could be expressed by following[16]:

$$K = 0.16\exp(-45\,000/RT) \quad (4)$$

And the nitridation velocity constant of titanium could be expressed as following:

$$K = 3.8\times 10^{-5}\exp(-36\,300/RT) \quad (5)$$

Compare Eqn.(4) with Eqn.(5), it can be seen that, in atmosphere, it is obvious that the reaction of titanium with nitrogen is much slower than that with oxygen. It illustrates that nitridation can hardly occur when titanium is oxidized in air. Therefore, oxygen has priority to be adsorbed on the interface of titanium alloys. Titanium can absorb gases intensively by forming solid solution. Oxide film would be formed until the content of gases go beyond the solution limit[7].

Then a diffusion-solution model can be advanced, just as shown in Fig. 7. That is, when titanium alloys are heated at certain temperature and preserved for a while, surface would be saturated by oxygen in air. In the initial stage, oxygen can diffuse into substrate through interface. Since oxygen have high solution in α-Ti, oxygen can solve in α-Ti and form solution. With the increase of oxygen concentration, the content of α-Ti is enlarged. If the content of oxygen goes beyond the limit of solubility, other titanium oxides can be produced quickly.

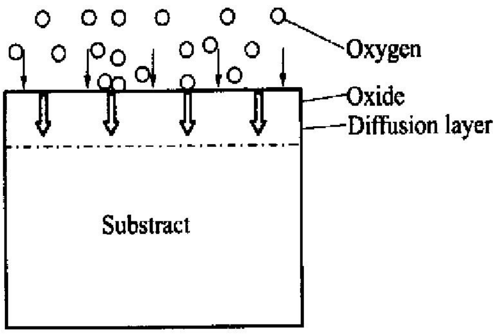

Fig. 7 Diffusion-solution model

4 CONCLUSIONS

1) It is a practicable method to improve surface micro-hardness of Ti based alloys by surface oxygen-diffusion-permeation.

2) Oxygen-diffused-permeation at the temperature of T_1 for 10 h is superior to that at T_2 for 6 h. Oxygen can form solid solution in α-Ti so that it can sharply increase the surface micro-hardness of titanium alloys.

3) Secondary oxygen-diffusion-permeation can not only enhance the micro-hardness but also enlarge the depth of oxygen-permeated layer. Therefore, it could be a measure to remedy those that have not achieved enough micro-hardness or depth when oxygen-permeated for the first time.

4) Diffusion-solution model advanced at the moment is that, at first, oxygen has priority to be adsorbed on the interface; then oxygen diffuses through interface into substrate, and solution of oxygen in α-Ti is formed. If the content of oxygen goes beyond the limit of solubility, other titanium oxides can be produced.

REFERENCES

[1] ZHANG Zhu. Development and application of new titanium alloys[J]. Acta Metallurgica Sinica, 1999, 35(S1): 35 - 38. (in Chinese)

[2] ZHAO Bin, WU Jian-sheng, SUN Jian, et al. High-temperature gas nitridation of TiAl based alloys[J]. Acta Metallurgica Sinica, 2001, 37(8): 837 - 840. (in Chinese)

[3] CHEN Hong-bing, LUO Qi-quan. Study on laser gas alloys for titanium alloy[J]. Laser Journal, 1997, 18(3): 32 - 36. (in Chinese)

[4] LIU Dao-xin, HE Jia-wen. Effect of shot peening factors on fretting fatigue resistance titanium alloy[J]. Acta Metallurgica Sinica, 2001, 37(2): 156 - 160. (in Chinese)

[5] XU Hao, LI Guo-cheng, XU Zhen-sheng. Effect of carburization treatment on microstructure and property of Ti[J]. Acta Metallurgica Sinica, 1999, 35(S1): 463 - 464. (in Chinese)

[6] ZHANG Song, WU Wei-tao, WANG Mao-cai, et al. Laser induced TiC particle reinforced composite layer on Ti6Al4V and their microstructural characteristics[J]. Trans Nonferrous Met Soc China, 2000, 10(1): 6 - 9.

[7] Dutta Majumdar J, Weisheit A, Mordike B L, et al. Laser surface alloying of Ti with Si, Al and Si+ Al for an improved oxidation resistance[J]. Materials Science and Engineering, 1999, A266: 123 - 134.

[8] LÜ Wei-jie, ZHANG Di, ZHANG Xiao-ning, et al. Growth mechanism of reinforcements in in-situ synthesized (TiB + TiC)/Ti composites[J]. Trans Nonferrous Met Soc China, 2001, 11(1), 67 - 71.

[9] JIA Xin-yun, LIU Pei-ying, GUO Bao-lin. High-temperature oxidation and protection of Ti based alloys[J]. Aviation Engineering & Maintenance, 2000, 4: 19 - 21. (in Chinese)

[10] CAI Bo-cheng, LIU Pei-ying, TAO Ye, et al. The isothermal oxidation behavior of Ti60 alloy at elevated temperature [J]. Materials Engineering, 2000, 8: 34 - 36. (in Chinese)

[11] SHIGEJI-Tani, Toshio Shi, Ayumi Mura, et al. Improvement in the oxidation resistance of TiAl by preoxidation in a Cr_2O_3 powder pack[J]. Mater Trans, JIM, 1994, 35(9): 616 - 622.

[12] XIONG Yu-ming, WANG Fu-hui. Effect of enamel coating on oxidation and corrosion resistance of Ti60 alloy[J]. Acta Metallurgica Sinica, 1999, 35(S1): 215 - 219. (in Chinese)

[13] Schmitz-Niederau M, Schütze M. The oxidation behavior of several Ti-Al alloys at 900 ℃ in air[J]. Oxidation of Metals, 1999, 52(3/4): 225 - 240.

[14] Vaquila I, Vergara L I, Passeggi Jr M C G, et al. Chemical reactions at surfaces: titanium oxidation[J]. Surface and Coating Technology, 1999, 122: 67 - 71.

[15] Kiyoshi Kusabiraki, Noriaki Kuroda, Isao Motohira, et al. High-temperature oxidation of pure titanium in CO_2 and Ar-10% CO_2 atmospheres[J]. Oxidation of Metals, 1997, 48 (3/4): 289 - 302.

[16] XIN Xiang-jie, XUE Jun-feng, DONG Min. Corrosion Protection and Engineering Application of Titanium [M]. Hehui: Anhui Science Technologies Press, 1984. 203, 214 (in Chinese)

[17] Rare Metal Manual Editoral Committee. Rare Metal Mannal [M]. Beijing: Metallurgical Industry Press, 1995. 94. (in Chinese).

(Edited by HUANG Jin-song)