

Surface hardening of titanium by thermal oxidation

W. YAN, X. X. WANG

Materials Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China

E-mail: mse_wangxx@dial.zju.edu.cn

Titanium and titanium alloys have been widely used in industrial and medical fields due to their excellent corrosion resistance and biocompatibility. Poor wear resistance, however, is one of the major problems of these alloys and restricts them from wider application. Nitriding has been the major surface hardening method used for titanium alloys so far [1–4]. Oxygen can also strengthen titanium by solid solution, but reports of the oxidation strengthening of titanium are lacking. In the present study, the oxygen diffusion layers of titanium, which were obtained after thermal oxidation at 700–900 °C for 1–4 hr, were systemically investigated in order to explore the feasibility of an oxygen diffusion hardening process as an alternative surface modification technique for titanium.

Specimens of size 10 mm × 10 mm × 2 mm were cut from commercially pure titanium sheet of TA2 grade (Northwest Nonferrous Metal Institute, China). All the specimens were annealed at 800 °C for 1 hr, and then pickled in HF aqueous solution to remove the surface oxide layers and the underlying oxygen diffusion layers. The thermal oxidation was carried out at 700–900 °C for 1–4 hr in an air atmosphere. The surface hardness of the oxygen diffusion layers was measured using an HV-1000 Vickers microhardness tester (Shanghai Materials Tester Machine Company, China) with 50–1000 g indenter loads. The cross-sectional hardness profile was measured using a 50 g indenter load. The crystal structure was analyzed using a PHILIPS X-ray diffractometer with Cu-K α radiation at a scan speed of 4 ° min⁻¹. The microstructure of the diffusion layers was observed using a LEICA MPS60 optical microscope and a HITACHI S-570 scanning electron microscope (SEM).

The surface oxide on all the specimens was identified as rutile TiO₂, as indicated by the X-ray diffraction (XRD) pattern of the oxide film on the 700 °C/1 hr treated specimen shown in Fig. 1. By quenching in water following oxidation, the oxide films on all of the specimens could be removed by gently grinding with SiC paper, exposing the underlying oxygen diffusion layers. Fig. 1 shows the XRD patterns of the oxygen diffusion layers of the specimens with various treatments. It can be seen that with increasing treatment temperature or period of time, all the diffraction peaks, corresponding to α -Ti, move to lower angles, suggesting increased lattice parameters. Detailed analyses reveal that the (002) peak, representing the *c* axis, shifts the most, while the (100) peak, representing the *a* axis, moves the least. This can be attributed to the fact that the solution of oxygen atoms in octahedral

interstices of α -Ti causes mainly the elongation of the *c* axis and hardly affects the *a* axis [5, 6]. Table I lists the lattice parameters that were calculated from the 2θ values of (002) and (101) diffraction peaks and the estimates of the associated oxygen concentrations [6]. The higher the treatment temperature and the longer the period of time, the higher the oxygen concentration. However, under the treatment conditions involved in the present research, the oxygen concentration did not reach the highest value of 34 at.%, as reported in Reference [6].

The micrographs in Fig. 2 show the oxygen diffusion layers of the specimens after 800 °C/1 hr and 900 °C/1 hr treatments. It can be seen that in the region near to the surface there is a black line (indicated by an arrow) that runs across the grain boundaries. The hardness indenter marks in Fig. 2 indicate an obvious hardening effect, even on the interior side of the black line, suggesting that the black line is not the boundary between the diffusion layer and the metal substrate. In

TABLE I The lattice parameters and the oxygen concentrations of diffusion layers of titanium specimens after various treatments

Treatments	<i>a</i> (nm)	<i>c</i> (nm)	<i>c/a</i>	Oxygen concentrations (at.%)
Untreated	0.29511	0.46843	1.5873	0
700 °C/1 hr	0.29520	0.47426	1.6066	18
700 °C/2 hr	0.29553	0.47478	1.6065	21
700 °C/4 hr	0.29655	0.47580	1.6045	23
800 °C/1 hr	0.29549	0.47448	1.6057	20
900 °C/1 hr	0.29506	0.47526	1.6107	22

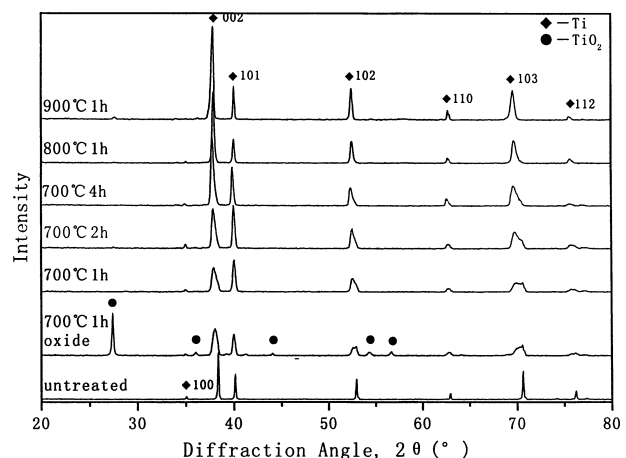


Figure 1 XRD patterns of the oxygen-diffusion layers of specimens with various heat treatments.

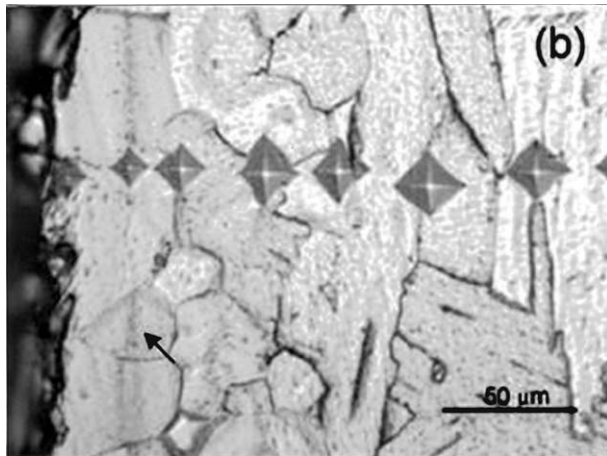
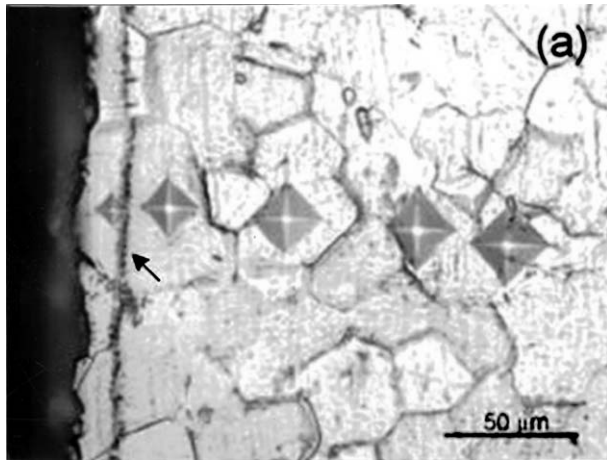


Figure 2 Reflected light micrographs of cross sections of diffusion layers in (a) 800 °C/1 hr and (b) 900 °C/1 hr treated specimens. The microhardness indentations which were made at a load of 50 g, show the hardening effect of the diffusion layers and the arrows indicate the line separating the inner and outer diffusion zones.

this paper, the zone outside the line will be referred to as the outer oxygen diffusion zone, and the zone between the line and the metal substrate will be the inner oxygen diffusion zone. The SEM micrographs in Fig. 3 reveal the characteristics of the line between the outer and inner oxygen diffusion zones of the 700 °C/1 hr and 4 hr treated specimens. It can be seen in Fig. 3a that a line (indicated by an arrow), which is fairly thin, already exists in the diffusion layer of the 700 °C/1 hr treated specimen. While in Fig. 3b, the line in the 700 °C/4 hr treated specimen is much thicker. In conjunction with the XRD results, it can be concluded that both the outer and inner oxygen diffusion zones are Ti-O solid solutions of α phase. According to QI *et al.* [7], a black line also formed in the diffusion layer of the 600 °C/100 hr oxidized titanium specimen. The mechanism of its formation still remains unknown.

The low hardness of close-packed hexagonal α -Ti is related to its relatively low c/a ratio. In the diffusion layer, the c/a ratio of α -Ti increases because of the lattice distortion caused by the dissolved oxygen, which consequently leads to the increase in hardness. The treatment temperature and time dependence of the cross-sectional hardness–depth profile and the surface hardness–load profile are shown in Figs 4 and 5, respectively. It should be noted in Fig. 4 that the diffusion layers in the 700 °C/1 hr and 2 hr treated

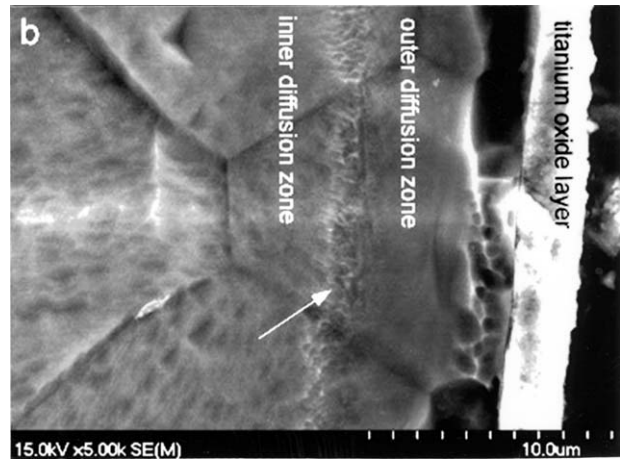
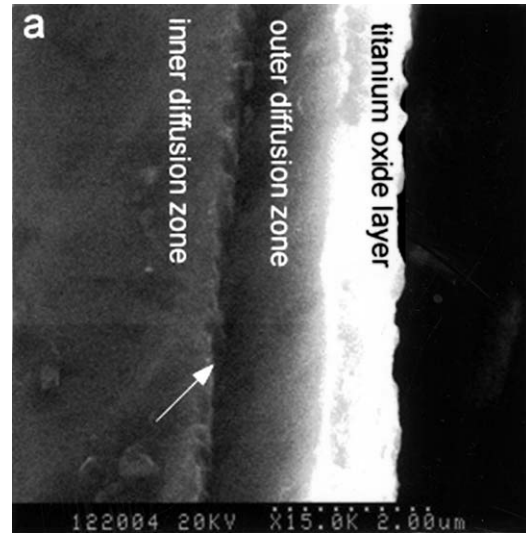


Figure 3 SEM micrographs of cross sections of diffusion layers in the specimens treated at 700 °C for (a) 1 hr and (b) 4 hr. The arrows indicate the line separating the inner and outer diffusion zones.

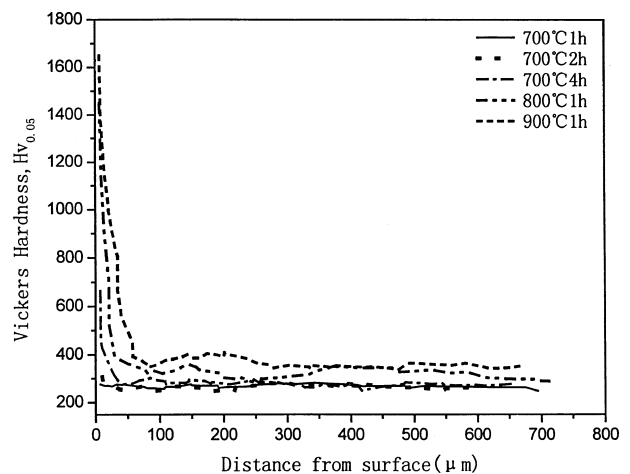


Figure 4 The cross-sectional hardness–depth profile of the oxygen diffusion layers for the specimens after various treatments.

specimens are too thin to be detected by the microhardness tester used in the present research. The hardened layers can be detected in the 700 °C/4 hr, 800 °C/1 hr, and 900 °C/1 hr treated specimens. The 800 °C/1 hr and 900 °C/1 hr treated specimens exhibit remarkable hardening with the highest hardnesses being above HV1400 and HV1600, respectively. According to the

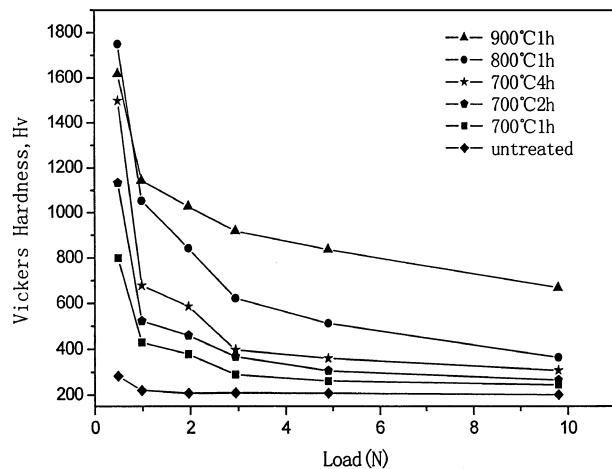


Figure 5 The surface hardness-load profile of the oxygen diffusion layers for the specimens after various treatments.

microstructure analyses in Figs 2 and 3, the thicknesses of the outer diffusion zones of the 700°C/4 hr, 800°C/1 hr, and 900°C/1 hr treated specimens are about 7, 8, and 25 μm , respectively. If a hardness above HV400 is used to define the total diffusion layer, from Fig. 4 the thicknesses of the total oxygen diffusion layers are about 15, 25, and 55 μm for the 700°C/4 hr, 800°C/1 hr, and 900°C/1 hr treated specimens, respectively. Thus, it can be estimated that the inner diffusion zone is a little thicker than the outer diffusion zone. In Fig. 5, the surface hardness of the oxygen diffusion layers decreases with increasing indenter loads, which is the typical behavior of the thin hard layers. It is interesting to observe that for the 700°C/1 hr and 2 hr

treated specimens, a surface hardening effect is exhibited clearly in Fig. 5, but not in Fig. 4. This suggests that the surface microhardness analysis is more sensitive to the presence of surface hardening layers than the cross-sectional hardness analysis.

Based on the above analyses of the oxygen diffusion layers in titanium, it can be concluded that the thermal oxidation provides titanium with an oxygen diffusion layer beneath the oxide layer. The oxygen diffusion layer, being α phase with elongated c axis, consists of the outer and inner zones that are separated by a line. With increasing treatment temperature or time, the thickness and the oxygen content of the diffusion layer increase, and accordingly the hardening effect is enhanced.

References

1. K. MATSUURA and M. KUDOH, *Acta Materialia* **50** (2002) 2693.
2. R. W. HANZEL, *Metal Progress* **3** (1954) 89.
3. H. L'ENFANT, P. LAURENS, M. C. SAINTE CATHERINE, T. DUBOIS and J. AMOUROUX, *Surf. Coat. Technol.* **96** (1997) 169.
4. A. SHENHAR, I. GOTMAN, S. RADIN and P. DUCHEYNE, *Ceram. Int.* **26** (2000) 709.
5. CHUANLIN ZHENG, ZHONG XU, XISHAN XIE, ZHIYONG HE and JIANXIN DONG, *J. Univ. Sci. Technol. Beijing* **24** (2002) 44.
6. W. ROSTOKER, *J. Metals* **9** (1952) 981.
7. P. Y. QI, X. Y. LI, H. DONG and T. BELL, *Mater. Sci. Eng. A* **326** (2002) 330.

Received 30 September 2003
and accepted 6 April 2004