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Effect of Gas-Diffusion Oxynitriding on Microstructure and Hardness of Ti-6Al-4V Alloys

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Abstract**—**The commercially available titanium alloy, Ti-6Al-4V, was oxynitrided in the deoxygenated nitrogen gas at high temperatures followed by cooling in oxygen-containing nitrogen in order to analyze the influence of oxynitriding parameters on the phase modification, hardness, and the microstructural evolution of the oxynitrided coating. The surface microhardness of the oxynitrided alloy increased due to the strengthening effect of the formed titanium oxynitrides, TiN_xO_y. The maximum microhardness was obtained, when TiN_xO_y had near equiatomic composition of nitrogen and oxygen. It could be attained under the optimum oxygen partial pressure and temperature-time condition.

Keywords**—**Oxynitriding, surface microhardness, titanium alloys, Ti-6Al-4V.

I. Introduction

At present, titanium and its alloys are widely used as structural components in the fields of aircraft, medicine, motor, chemistry, and biomedicine, because of their high specific strength, metallic luster and good corrosion resistance. Surface hardness, fatigue strength, durability, and resistances to wear and corrosion are important properties to determine the level of acceptance of titanium alloys in diverse working conditions. Hard coatings based on binary compounds such as TiN, TiC, and TiO not only improve the surface properties of titanium alloys but also provide decorative surface colors [1]-[3]. However, their wear resistance is still not high enough. Hence, functional, hard coatings such as TiN_xO_y were recently developed in order to alleviate the tribological problem. Since TiO and TiN are isomorphic and display complete mutual solubility, TiN_xO_y can exist over a wide range of composition. At the certain N/O ratio range, TiN_xO_y exhibits better hardness, electronic properties and resistances to wear and corrosion than the binary compounds such as TiN, TiC, and TiO [4], [5]. Their properties strongly depend on the composition of TiN_xO_y. This is also a very promising biomaterial because its biomedical properties exceed the binary TiN, TiC, and TiO coating [6].

In this study, TiN_xO_y coatings were deposited on the Ti-6Al-4V alloy in the controlled nitrogen-oxygen-containing atmosphere by the gas diffusion treatment. The Ti-6Al-4V alloy that was used as the substrate in this study accounts for 45% of total titanium production, as compared with 30% for unalloyed grades, and 25% for all other remaining alloys [7]. It belongs to the α+β titanium alloy, which has better strength than either the α or β structure. Gas nitriding is one of the most widely used thermo-chemical treatments for improving the surface properties of titanium alloys by forming hard TiN coating [8]. In the N-containing environments, nitrogen reacts with Ti to form the TiN coating, and also diffuses inwardly interstitially to form the Ti(N) layer. In the (N, O)-containing environments, both nitrogen and oxygen react with Ti to form the TiN_xO_y coating, and similarly diffuse inwardly interstitially to form the Ti(N,O) layer [9]. The gas diffusion treatment has the following advantages: (i) it takes advantage of the high affinity of titanium with nitrogen and oxygen to produce the hardened surface layer which is well bonded to the Ti substrate, (ii) it is ecological clean, and cost-effective, (iii) workpieces of any arbitrary shape can be applied, and (iv) standard vacuum heat equipment can be used.

The purpose of this paper is to synthesize TiN_xO_y coatings on the Ti-6Al-4V alloy in the controlled (N, O)-containing environments at high temperatures by the gas diffusion treatment, and investigate the phases formed, elemental distribution, and microhardness of the oxynitrided Ti-6Al-4V alloy. The understanding of such behavior is essential for the surface hardening and industrial application of titanium alloys.

II. Experimental Procedure

The Ti-6Al-4V alloy with (α+β) phases was cut into dimensions of 15×10×1 mm^3, polished with a 0.1 μm diamond paste to reduce a maximum value of roughness to 0.4 μm, degreased in benzene, washed with deionized water, and oxynitrided using the oxynitriding furnace shown in Fig. 1. This consisted primarily of an electric furnace, rotary and diffusion vacuum pumps, and gas purifying traps. The oxynitriding scheme is shown in Fig. 2. Oxynitriding was carried out by heating at a rate of 0.04 °C/s, holding at 750, 850, and 950 °C for 5 h in deoxygenated nitrogen (total nitrogen pressure = 1 or 10^5 Pa, oxygen amount < 0.01~0.0005 %), cooling in oxygen-containing nitrogen (total pressure = 1 Pa) down to 500 °C at a rate of 0.03 °C/s, and furnace cooling under vacuum. Deoxygenated nitrogen was obtained by removing moisture using silica gel filter, and removing oxygen using hot titanium chips. The oxynitrided Ti-6Al-4V alloy was inspected using an X-ray diffractometer (XRD) with CuKα-radiation, and its Vickers microhardness was measured under 0.49 N load. Its hardness was measured using the nanoindentor, using the CSM method (Continuous Stiffness Measurement) with the point interval of 10 μm and total distance of 140-150 μm.

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Fig. 1 Oxynitriding equipment

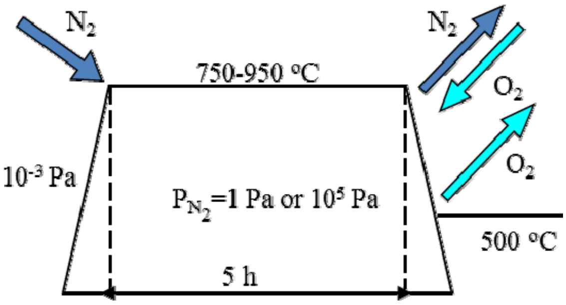

Fig. 2 Oxynitriding process of Ti-6Al-4V alloy

III. Results and Discussion

Fig. 3 shows the EPMA image and the corresponding elemental maps of the Ti-4Al-6V substrate. The α-Ti phase was rich in Al, and continuous, while β-Ti islands were rich in V. It is noted that aluminum is an α stabilizer, while vanadium is a β stabilizer.

During oxynitriding in oxygen-containing nitrogen, oxygen interacts with titanium actively and the surface oxide films forms because TiO and TiO_2 are more stable than TiN. In a closed system, the oxygen partial pressure in nitrogen-containing gas decreases with time. Then, nitrogen dissolution and nitride formation as well as dissociation and partial dissolution of oxide films take place simultaneously. Due to the limited solubility between TiN and TiO, the oxynitride phases form. With an increase in temperature and process time, oxynitrides transform gradually into titanium nitrides [10]. Oxygen partial pressure and the process temperature-time determine the composition of surface phases. In case of the high oxygen partial pressure, the higher temperature and longer processing time are needed to dissolve and transform the oxide films to oxynitrides or nitrides.

SEM top view and fracture surface of the oxynitrided Ti-6Al-4V alloy are shown in Fig. 4. The surface was covered with bumpy TiN_xO_y coating, as shown in Fig. 4 (a). The sample exhibited the brittle fracture, as shown in Fig. 4 (b).

Table I lists the dependence of surface microhardness of Ti-6Al-4V alloy on the oxynitriding temperature and gas pressure. Oxynitriding formed the outermost thin oxide film (mainly rutile-TiO_2 with 1~2 μm in thickness) and the underlying diffusion layer (10~20 μm in thickness) at the surface. When oxynitrided in 10^5 Pa of N_2 gas, the microhardness increased owing to the strengthening effect of oxynitrides with an increase of temperature from 750 to 850 °C. However, at 950 °C, the formed oxynitrides did not provide the highest level of surface strengthening owing to the softening effect. When oxynitrided in 1 Pa of N_2 gas, the surface microhardness became lower than that obtained in 10^5 Pa of N_2 gas because a lesser amount of oxynitrides formed. However, oxynitriding at 850 and 950 °C in 1 Pa of N_2 gas was effective in increasing the surface microhardness due to the intensive formation of oxynitrides. Particularly, when oxynitrided at 850 °C in 1 Pa of N_2 gas, the maximum surface microhardness was obtained. This may be related with the optimal composition of oxynitrides, TiO_xN_y [11].

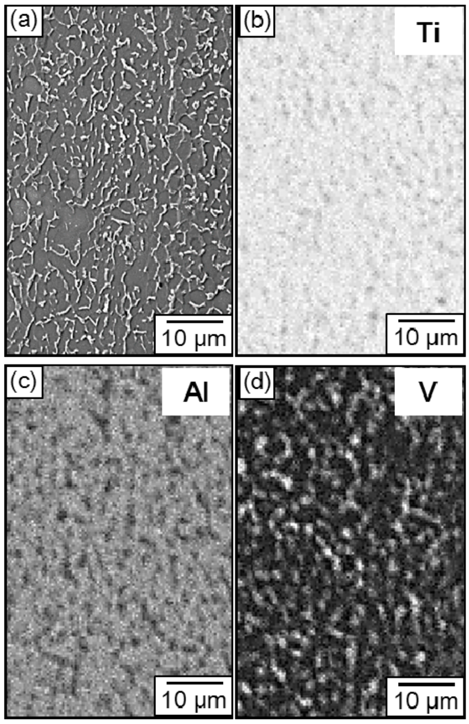

Fig. 3 Ti-6Al-4V alloy before nitriding (etched with Kroll's etchant): (a) EPMA image, and maps of (b) Ti, (c) Al, and (d) V

TABLE I
VICKERS MICROHARDNESS (GPA) OF TI-6AL-4V ALLOY AS A FUNCTION OF THE OXYNITRIDING TEMPERATURE AND GAS PRESSURE

	750 °C	850 °C	950 °C
$P_{N2}=10^5$ Pa	10.9	13.5	11.5
$P_{N2}=1$ Pa	7.2	17	16.2

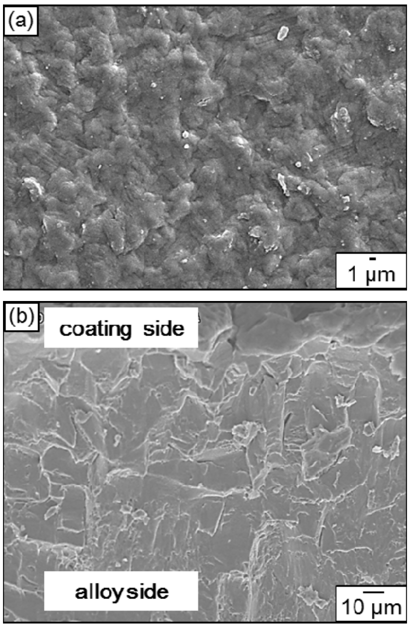

Fig. 4 SEM microstructures of the Ti-6Al-4V alloy after oxynitriding at 750 °C under $P_{N2}=10^5$ Pa: (a) top view, (b) fracture surface

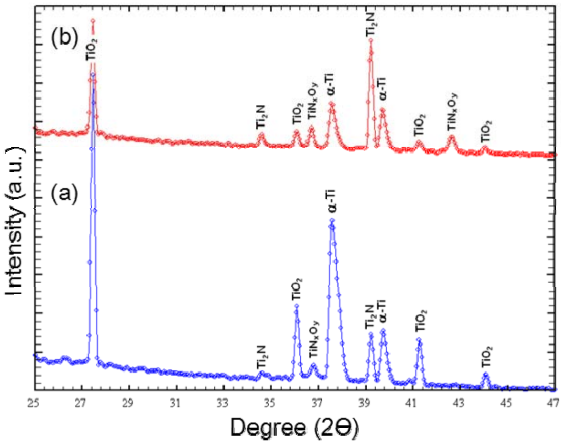

Fig. 5 X-ray diffraction patterns of Ti-6Al-4V alloy after oxynitriding for 5 h at (a) 850 °C, (b) 950 °C

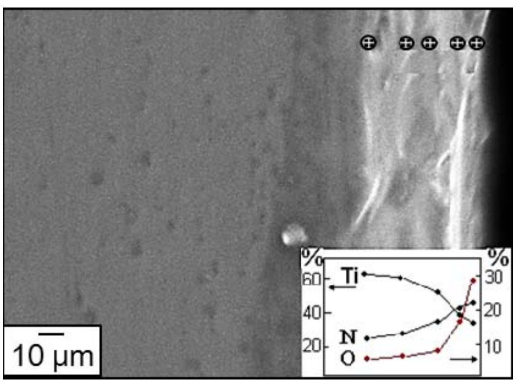

Fig. 6 Cross-sectional microstructure and line profiles of Ti-6Al-4V alloy after oxynitriding at 850 °C for 5 h

When oxynitriding was carried out in 10^5 Pa of N_2 at 750 °C, weak peaks of rutile-TiO_2 and Ti_2N were detected in the XRD pattern. The presence of Ti_2N peaks indicated the beginning of nitride formation at 750 °C. Above 750 °C, nitrogen began to dissolve in TiO_2 to form the outermost TiN_xO_y thin film through the strong interaction among titanium, oxygen, and nitrogen. At 850 °C, the α-Ti matrix, rutile-TiO_2, Ti_2N and TiN_xO_y were detected as shown in Fig. 5 (a). Here, TiN_xO_y was identified as $TiN_{0.44}O_{0.56}$ with a lattice parameter of 4.2382 Å based on the amount of shifting from the TiN pattern. With increasing the temperature to 950 °C, the intensity of rutile-TiO_2 decreased and that of oxynitride increased, as shown in Fig. 5 (b).

When oxynitriding was carried out in 1 Pa of N_2 at 850 °C, the XRD analysis indicated the weak rutile-TiO_2 and TiN_xO_y peaks and the shift of α-Ti matrix peaks. It seemed that most of oxygen atoms diffused through the outermost thin surface film (mainly, rutile and oxynitride) into the underlying diffusion layer to form the hard Ti(O,N) solid solution.

Fig. 6 shows the elemental distribution of Ti-6Al-4V alloy around the surface after oxynitriding at 850 °C in 10^5 Pa of N_2. As moving from the surface toward the matrix, the amount of oxygen and nitrogen decreased, whilst that of Ti increased. It is worth noting that the amount of oxygen was larger than that of nitrogen at the surface layer. This behavior reversed in the inner layers.

Maximum microhardness was obtained when the sample was oxynitrided at 850 °C, because oxynitrides have near equiatomic compositions formed. The maximum level of surface strengthening did not correspond with the maximum processing temperature. The fact that hardening effect of oxynitriding is more effective at the lower temperatures can be explained by the more intensive oxynitride formation, because at low temperatures the oxynitride composition is close to the lower limit of homogeneity.

The specimen that was oxynitrided in 1 Pa of N2 at 750 °C was mounted, polished, and its hardness and Young's modulus were measured from the surface, as shown in Fig. 7. There was some fluctuation in the hardness values. The average hardness was 7 GPa and Young's modulus was 145 GPa. While Young's modulus was nearly constant, the hardness tended to decrease as moving toward the interior. Nitrogen and oxygen that diffused inward interstitially increased the hardness through the solid solution strengthening and the formation of oxynitrides at the surface [11].

Fig. 8 shows the hardness and Young's modulus of the specimen that was oxynitrided in 10^5 Pa of N_2 at 750 °C. Again, there was some fluctuation in the measured values. As moving toward the interior, both Young's modulus and the hardness tended to approach the Young's modulus and the hardness of the matrix in the unsaturated core. Figs. 7 and 8 indicate that the higher the nitrogen pressure was, the higher the microhardness was.

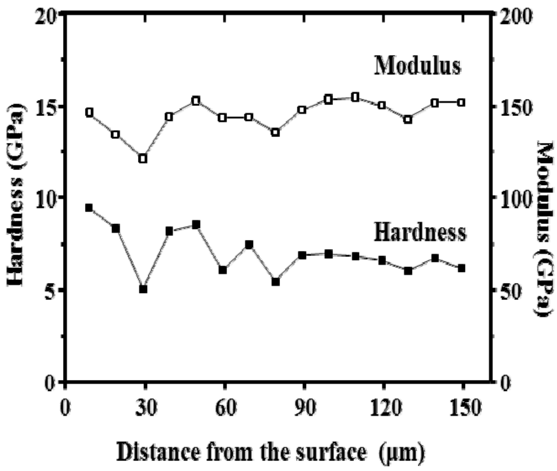

Fig. 7 Hardness and Young's modulus of the Ti-6Al-4V alloy after oxynitriding at 750 °C under P_{N2}=1 Pa

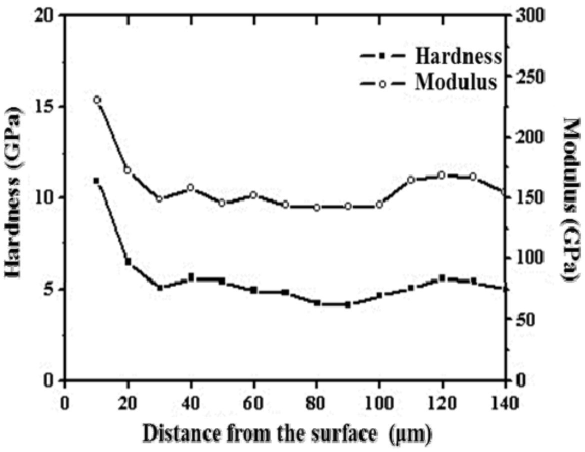

Fig. 8 Hardness and Young's modulus of the Ti-6Al-4V alloy after oxynitriding at 750 °C under P_{N2}=10^5 Pa

IV. Conclusion

The Ti-6Al-4V alloy was oxynitrided at 750-950 °C for 5 h in order to study the phase modification, the microstructural morphology change and the hardness evolution.

1. Oxynitride layers of Ti alloys could be formed by processing in deoxygenated nitrogen followed by cooling in oxygen-containing nitrogen.
2. Oxynitride layers were obtained by controlling the oxygen partial pressure and optimization of temperature-time parameters at the temperature range of 750-950 °C.
3. Oxynitriding increased the surface microhardness due to the strengthening effect of interstitial nitrogen and oxygen as well as the formation of titanium oxynitrides. The hardness at the surface was high, and decreased in the diffusion zones to approach the hardness of the matrix.

Acknowledgment

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