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, TiNxOy. The maximum microhardness was obtained, when TiN0.5O1.5 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 TiN0.5O1.5 were recently developed in order to alleviate the tribological problem. Since TiO and TiN are isomorphic and display complete mutual solubility, TiN0.5O1.5 can exist over a wide range of composition. TiO and TiN are isomorphic and display complete mutual solubility. TiN0.5O1.5 can exist over a wide range of composition. The Ti-6Al-4V alloy in the controlled (N, O)-containing atmosphere by the gas diffusion treatment. The Ti-6Al-4V alloy was cut into 10×10×1 mm3, 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 deoxygenated using silica gel filter, and removing oxygen using hot 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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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$_x$O$_y$ 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$_x$N$_y$ [11].
When oxynitriding was carried out in $10^5$ Pa of N$_2$ at 750 °C, weak peaks of rutile-TiO$_2$ and Ti$_2$N were detected in the XRD pattern. The presence of Ti$_2$N 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$_x$O$_y$ thin film through the strong interaction among titanium, oxygen, and nitrogen. At 850 °C, the α-Ti matrix, rutile-TiO$_2$, Ti$_2$N and TiN$_x$O$_y$ were detected as shown in Fig. 5 (a). Here, TiN$_y$O$_x$ was identified as Ti$_{20}$O$_{36}$ 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$_x$O$_y$ 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 N$_2$ 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.
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.

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REFERENCES


