Formation of Oxynitride Layers on Titanium Alloys by Gas Diffusion Treatment

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Titanium alloys were oxynitrided in controlled nitrogen-oxygen gas atmospheres between 650 °C and 950 °C for 5 h to 10 h with two different techniques of gas diffusion treatment. One technique was performed in an oxygen-containing (oxygen amount ≥ 0.4 %) nitrogen environment. The other technique was performed in a deoxygenated (oxygen amount < 0.01 % to 0.0005 %) nitrogen environment with subsequent cooling in an oxygen-containing nitrogen environment (with an oxygen pressure of 1 Pa). The surface microhardness of oxynitrided samples increased due to the strengthening effect of titanium oxynitrides (TiN_xO_y). The maximum microhardness of the titanium oxynitrides was obtained with a near-equiatomic composition of nitrogen and oxygen in TiN_xO_y under optimal oxygen partial pressure and temperature-time conditions.

Keywords: titanium alloy, oxynitriding, surface microhardness

1. INTRODUCTION

Titanium alloys are widely used in the fields of aircraft, medicine, motors, chemistry and biomedicine [1]. The surface hardness, fatigue strength, durability, wear-resistance, and corrosion-resistance are important factors for determining the level of acceptance of titanium alloys in diverse working conditions. Hard coatings based on binary compounds such as TiN, TiC, and TiO improve the surface properties of titanium alloys and provide decorative surface colors [2-4]. Hard coatings based on ternary titanium oxynitrides, such as TiN_xO_y, display superior hardness, electronic properties, wear-resistance, and corrosion-resistance [5,6]. These benefits come from the electronic structure of oxynitrides and the chemical bonds of atoms in the lattice. The hardness, corrosion-resistance and color depend strongly on the composition of TiN_xO_y. This compound is also a very promising biomaterial because its biomedical properties (thrombocytes adhesion and blood clotting) are superior to binary compounds [7].

Films of TiN_xO_y are representative transition-metal oxynitrides and can be deposited by various coating techniques such as magnetron sputtering [5,6,8,9], ion-assisted deposition [10], evaporation [7,11], ion implantation [12] and the gas diffusion treatment [13]. The last technique takes advantage of the high reactivity of titanium with nitrogen and oxygen to produce hardened surface layers that are well bonded to a tough matrix. The purpose of this article is to develop the fundamentals of the oxynitriding technique, which involves gas diffusion treatment of titanium alloys in controlled media that contain nitrogen and oxygen.

2. EXPERIMENTAL PROCEDURE

The base metals were commercially available pure titanium, pseudo-α-alloy (Ti-Al-Mn), (α+β)-alloy (Ti-Al-V) and β-alloy (Ti-Al-Mo-Cr-Fe-Si). Their compositions are listed in Table 1. The samples were cut into dimensions of 15 mm × 10 mm × 1 mm, polished with 0.1 μm diamond paste to reduce the maximum value of roughness, R_a, to 0.4 μm, degreased in benzene, and washed with deionized water prior to the oxynitriding.

Figure 1 shows the two kinds of gas diffusion treatments schemes for the oxynitriding in this study. The first oxynitriding scheme is shown in Fig. 1(a). The samples were heated to a temperature range of 650 °C to 950 °C, held for 10 h, and then cooled in oxygen-containing nitrogen (total pressure = 10^5 Pa; oxygen amount ≥0.4 vol.%). The second oxynitriding scheme is shown in Fig. 1(b). The reaction chamber was initially vacuumed down to 10^{-3} Pa and heated in a temperature range of 750 °C to 950 °C for 5 h in deoxygenated nitrogen (total pressure = 1 or 10^5 Pa; oxygen amount < 0.01 % ~0.0005 %). It was subsequently cooled to 500 °C

Table 1. Chemical composition of titanium alloys, mass.%

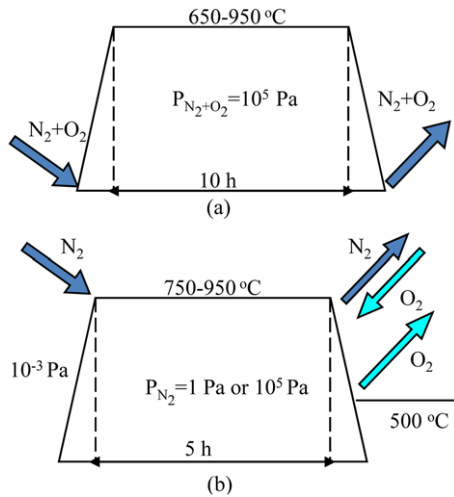| Alloy	Alloying elements	Interstitial elements (max. content)
Ti	none	0.07C-0.20Zr-0.10Fe-0.12Si-0.04O-0.01N
Ti-Al-Mn	Ti-(3.5~5.0)Al-(0.8~2.0)Mn	0.1C-0.3Zr-0.3Fe-0.15Si-0.15O-0.05N-0.012H
Ti-Al-V	Ti-(5.3~6.5)Al-(3.5~4.5)V	0.1C-0.3Zr-0.25Fe-0.15Si-0.15O-0.05N-0.015H
Ti-Al-Mo-Cr-Fe-Si	Ti-(5.5~7.0)Al-(2.0~3.0)Mo-(0.8~2.3)Cr-(0.2~0.7)Fe-(0.15~0.4)Si	0.1C-0.5Zr-0.18O-0.05N-0.015H

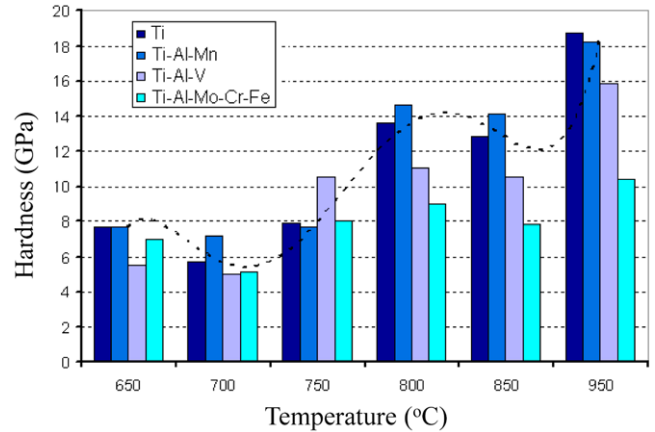**Fig. 1.** Oxynitriding process for titanium alloys: (a) scheme 1 and (b) scheme 2.

Fig. 2. Vickers surface microhardness of titanium alloys versus the oxynitriding temperature. Oxynitriding via the first scheme. Dotted line = general tendency.
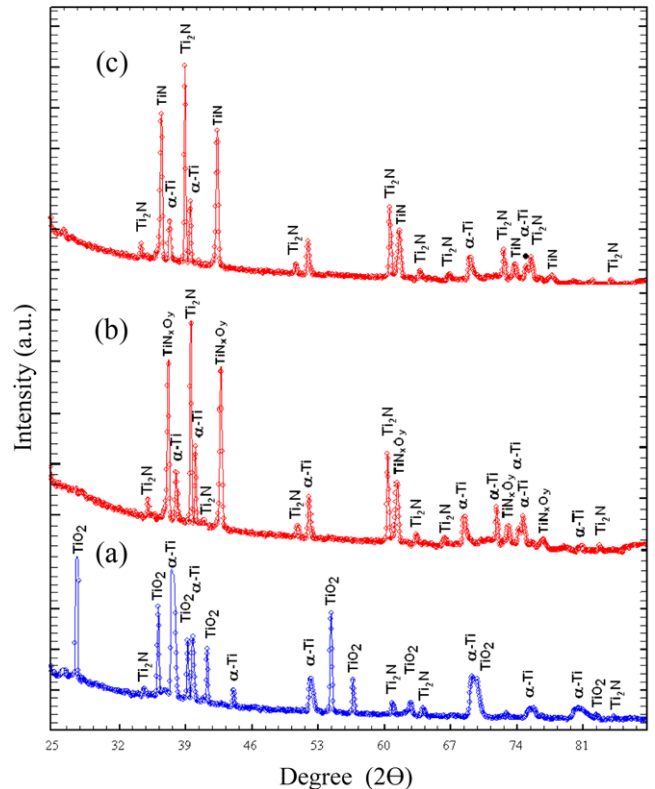
in oxygen-containing nitrogen (total pressure = 1 Pa) by the removal of deoxygenated nitrogen and the addition of oxygen and then exhausted to 10^{-3} Pa while being cooled to room temperature. Deoxygenated nitrogen was obtained by filtration of the moisture and oxygen through a silica gel filter and hot titanium chips. As shown in Fig. 1, the heating rate was 0.04 °C/s and the cooling rate was 0.03 °C/s. The oxynitrided specimens were inspected with an X-ray diffractometer (XRD) with a CuK$_\alpha$-radiation with 35 kV and 20 mA. The tube focusing was made by the Bregg-Brettano method. The scan step was 0.05° with 5 s endurance. The Vickers microhardness of the oxynitrided titanium alloys was measured under a load of 0.49 N.

3. RESULTS

3.1. Oxynitriding via the first scheme

Figure 2 shows how the surface microhardness of titanium alloys depends on the oxynitriding temperature. The surface hardness is as low as 5.5 GPa to 7.5 GPa at 650 °C and 5.0 GPa to 7.0 GPa at 700 °C, depending on the alloy grade. Oxynitriding leads to the formation of an outermost thin oxide film (mainly rutile TiO$_2$ with a thickness of 1 μm to 2 μm) and an underlying diffusion layer (with a thickness of 10 μm to 20 μm) at the surface of titanium alloys.

Figure 3 shows X-ray patterns of the oxynitrided Ti-Al-V alloy. Rutile TiO$_2$ peaks can be seen in Fig. 3(a) together

Fig. 3. X-ray diffraction patterns of the Ti-Al-V alloy that was oxynitrided via the first scheme for 10 h at (a) 700 °C, (b) 800 °C, and (c) 950 °C.

with Ti$_2$N peaks and an α-Ti matrix. The presence of the Ti$_2$N peaks indicates the beginning of the nitride formation at

700 °C. At 750 °C and 800 °C, the nitrogen begins to dissolve inside TiO_2 to form the outermost TiN_xO_y thin film (Fig. 3(b)) as a result of the strong interaction between titanium and nitrogen at high temperatures. The XRD analyses indicate that the oxynitrides that form at 750 °C and 800 °C are $TiN_{0.4}O_{0.6}$ with a cell parameter of 4.236 Å and $TiN_{0.45}O_{0.55}$ with a cell parameter of 4.239 Å, respectively [14]. The increment of nitrogen content in TiN_xO_y causes the surface microhardness to reach a maximum value of 14.5 GPa at 800 °C (Fig. 2). Titanium oxynitrides no longer form at temperatures greater than 850 °C. Instead, as shown in Fig. 3(c), the outermost surface film consists of titanium nitrides such as TiN and Ti_2N. At 950 °C, the surface microhardness increases to 18.7 GPa owing to intense nitride formation, and the underlying diffusion layer is about 150 μm.

3.2. Oxynitriding via the second scheme

During isothermal holding in deoxygenated nitrogen at 750 °C to 950 °C, nitrides form in the outermost surface of the alloy. During the subsequent cooling in oxygen-containing nitrogen, the nitrides are transformed to oxynitrides, which is the principle of the formation of oxynitrides on Ti alloys.

When oxynitriding is conducted in 10^5 Pa of N_2, weak rutile peaks and Ti_2N peaks can be detected in the XRD pattern at 750 °C. At 850 °C, α-Ti, TiO_2, Ti_2N and TiN_xO_y can be detected (Fig. 4(a)). TiN_xO_y with a lattice parameter of 4.2382 Å is identified as $TiN_{0.44}O_{0.56}$; this value is based on the amount of shifting from the TiN pattern. As shown in Fig. 4(b), when the temperature is increased to 950 °C, the intensity of the rutile peaks decreases and the intensity of the oxynitride peaks increases.

When oxynitriding is conducted in 1 Pa of N_2 at 850 °C, the XRD analysis indicates weak rutile and oxynitride peaks and a shift in the titanium peaks. Most oxygen atoms appear to be diffused through the outermost thin surface film (mostly, rutile and oxynitride) into the underlying diffusion layer to form a hard solution of Ti(O,N).

Figure 5 shows the results of an analysis of the elemental composition of the near surface layers of the Ti-Al-V alloy after oxynitriding at 850 °C in 10^5 Pa of N_2. The amount of oxygen and nitrogen decreases with changing the position from the top surface toward the matrix. At the outermost surface, the amount of oxygen exceeds the amount of nitrogen. This situation is reversed at the inner layers.

Figure 6 shows that the surface microhardness of samples oxynitrided in 10^5 Pa of N_2. When the temperature is increased from 750 °C to 850 °C, the surface microhardness increases due to the strengthening effect of the oxynitrides. Note, however, that the oxynitrides that form at 950 °C don't have the highest level of surface strengthening. The oxynitride coating that forms at 850 °C has the maximum microhardness.
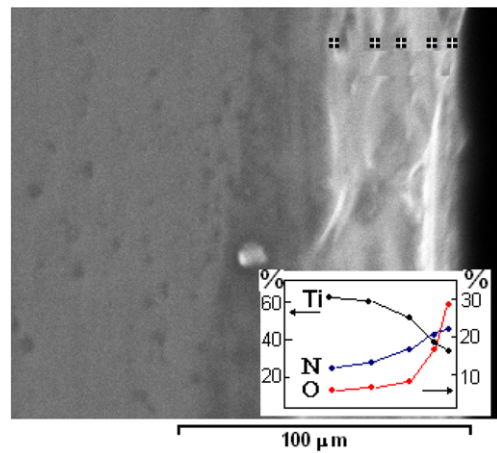

Fig. 5. Cross-sectional micrograph and distribution of Ti and interstitial elements of the Ti-Al-V alloy that was oxynitrided at 850 °C for 5 h via the second scheme.
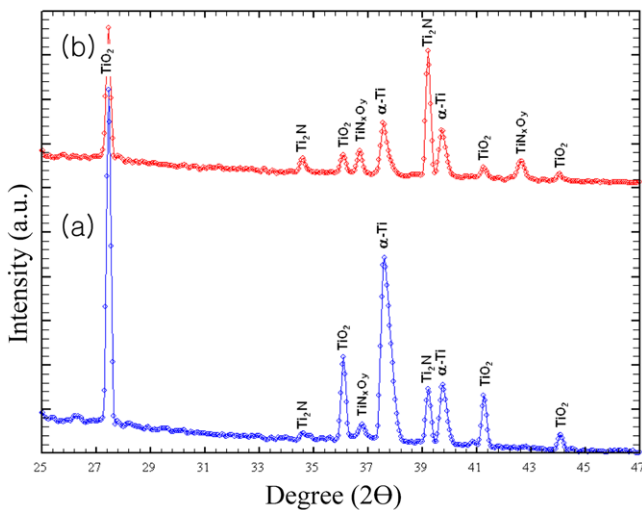

Fig. 4. X-ray diffraction patterns of the Ti-Al-V alloy that was oxynitrided via the second scheme for 5 h at (a) 850 °C, and (b) 950 °C.
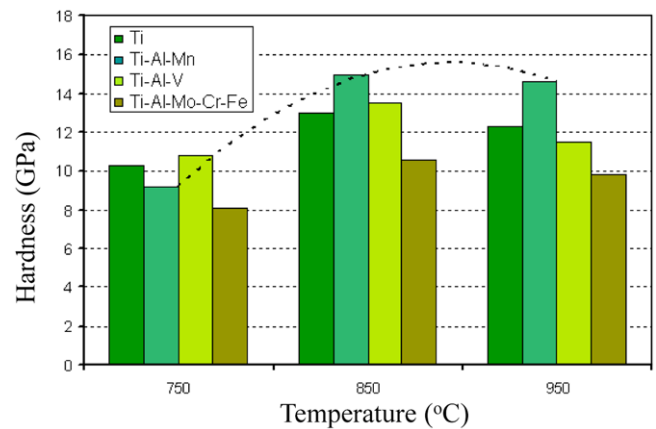

Fig. 6. Vickers surface microhardness of titanium alloys versus the oxynitriding temperature. Oxynitriding in 10^5 Pa of N_2 via the second scheme. Dotted line = general tendency.
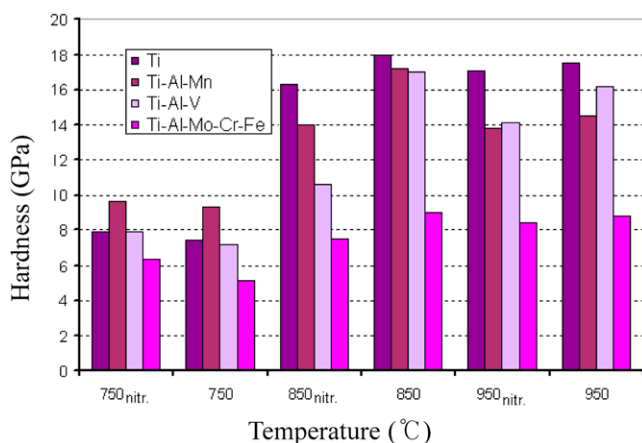
Fig. 7. Vickers surface microhardness of titanium alloys versus the oxynitriding temperature. Oxynitriding in 1 Pa of N_2 via the second scheme. "nitr." subscript indicates nitriding under the same process parameters.

Figure 7 shows the surface microhardness of samples oxynitrided in 1 Pa of N_2. For the sake of comparison, the nitriding was performed under identical conditions (that is, at a temperature range of 750 °C to 950 °C, a process time of 5 h, and nitrogen partial pressure of 1 Pa). The surface microhardness obtained after the oxynitriding at 750 °C is slightly less than that of the corresponding nitriding. However, due to the intensive formation of oxynitrides, oxynitriding at 850 °C and 950 °C is more effective than nitriding in terms of increasing the surface microhardness. Figures 6 and 7 show the results of the maximum surface microhardness obtained from the samples processed at 850 °C. These results may be related to the optimal composition of the oxynitride compound because the hardness of the oxynitrides depends strongly on their composition [14].

4. DISCUSSION

During oxynitriding in oxygen-containing nitrogen, oxygen actively interacts with titanium, and surface oxide films form because TiO and TiO_2 are more stable than TiN [15]. In a closed system, the oxygen partial pressure in a nitrogen-containing medium decreases with time owing to the consumption of oxygen. There is then a simultaneous occurrence of nitrogen dissolution, nitride formation, and a dissociation and partial dissolution of oxide films. The oxynitride phases form as a result of the limited solubility between TiN and TiO [15]. With an increase in temperature and process time, the oxynitride phases transform gradually into titanium nitrides [16]. The oxygen partial pressure and process temperature-time appear to determine the composition of the surface phases. When the oxygen partial pressure is high, a higher temperature and longer process time are needed to dissolve the oxide films and transform them into oxynitrides

or nitrides.

As shown in Figs. 2 and 6, the maximum microhardness is obtained from samples oxynitrided at 800 °C (scheme 1) and 850 °C (scheme 2). During the processing of scheme 1, the oxynitride forms at 800 °C and the nitride forms at 950 °C. The maximum microhardness is likely due to the fact that the oxynitrides have near-equiatomic compositions. This composition is the reason the maximum process temperatures fail to provide the maximum level of surface strengthening. The fact that the hardening effect of oxynitriding is more effective at lower temperatures (Figs. 2 and 6) can be explained by the more intensive oxynitride formation because at low temperatures the oxynitride composition is close to the lower limit of homogeneity.

5. CONCLUSIONS

1. Oxynitride layers can be formed through processing in either oxygen-containing nitrogen or deoxygenated nitrogen followed by cooling in oxygen-containing nitrogen.

2. Oxynitride layers are obtained by controlling the oxygen partial pressure and optimizing the temperature-time parameters at a temperature range of 750 °C to 950 °C.

3. The maximum microhardness is obtained at a near-equiatomic composition of x and y in TiN_xO_y. The fact that the hardening effect of oxynitriding is more effective at around 800 °C (scheme 1) and 850 °C (scheme 2) can be explained by the more intensive oxynitride formation because at these temperatures the oxynitride is closer to the equiatomic composition.

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