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X-ray diffraction measurements of plasma-nitrided Ti–6Al–4V

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Abstract

A systematic study was undertaken with samples of commercial Ti–6Al–4V nitrided in a conventional d.c. plasma equipment. As treatment parameters, we have used: nitriding time (from 15 to 360 min); nitriding atmosphere (H_2–20% N_2 and H_2–60% N_2); total pressure (from 10 mPa to 1 kPa) and cathode temperature (from 673 to 943 K). X-ray diffraction measurements show that the effect of nitriding on the near-surface composition of ($\alpha+\beta$)–Ti–6Al–4V is a very complex function of the process parameters. Among these, it appears that the sample temperature plays the more dramatic role. For temperatures below 773 K, ϵ-Ti_2N and δ-δ-TiN are clearly present only for a long period of treatment in a N/H = 3/2 atmosphere. For the N/H = 1/4 atmosphere, these nitrides are not present in the XRD pattern of samples treated at 773 K, even for a long treatment time such as 240 min. However, samples treated at 943 K show well-resolved ϵ-Ti_2N and δ-TiN reflections, even for short treatment times such as 15 min.

Keywords: Plasma nitriding; Ti–6Al–4V; X-ray diffraction

1. Introduction

Ti–6Al–4V has been used for orthopedic devices because it has several beneficial properties such as a low density, a low modulus of elasticity, excellent corrosion resistance and biocompatibility. However, the low wear performance of Ti and its alloys in abrasive and adhesive wearing conditions has been an obstacle for its extensive use in surgical procedures. A considerable amount of effort has been made to overcome this obstacle. Conventional ion implantation [1–4], plasma source nitrogen ion implantation [5], conventional plasma nitriding [6], intensified plasma ion nitriding [7], and reactively sputtered thin films [8] have been recently reported. It has been shown that surface treatment with nitrogen improves the wear [1,3–5,7] and the hardness [1,2,4,6–8] performance of Ti–6Al–4V. Although these results can be indicative of the potential use of the different techniques, a comparison between them is very difficult because the chemical surface properties are strongly dependent on the deposition process parameters. For a review, see Ref. [9].

X-ray diffraction results reported by Konuma and Matsumoto [10], concerning the nitriding of titanium in a radio frequency discharge, show that for treatment times between 1 and 8 h, the surface composition consists of cubic δ-TiN and tetragonal ϵ-Ti_2N for every experimental condition used in their investigation. For $t > 8$ h, only the δ phase was present at the compound layer. Konuma and Matsumoto used sample temperatures between 1073 and 1223 K. However, in a similar experiment, but using a d.c. glow discharge at a higher temperature (from 1073 to 1273 K), Badini et al. [11] have shown the formation of both phases. Therefore, even materials prepared by similar techniques are different if the process parameters are not well controlled.

In this work, we report X-ray diffraction measurements on Ti–6Al–4V submitted to d.c. glow discharge as a function of the following parameters: nitriding time, gaseous mixtures of nitrogen and hydrogen, sample temperature and total pressure during treatment.

2. Experimental

Samples from the same ingot of commercial Ti–6Al–4V were ground flat and mechanically polished to a 0.5 μm alumina finish and nitrided in conventional d.c. plasma-nitriding equipment. Treatments were performed

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in more than 30 samples, with time in the range of 15–360 min. Two mixtures of nitrogen and hydrogen (ratios in vol.%: N/H = 1/4 and N/H = 3/2) under a total pressure from 10 mPa to 1 kPa were used. Voltages in the range from 370 to 600 V and currents from 200 to 400 mA were adjusted to maintain the cathode temperature between 673 and 943 K. Auxiliary heating was not used. The treatment chamber was cleaned through a four-step filling–evacuation process with nitrogen. After nitriding, the samples were cooled in the treatment chamber with a nitrogen atmosphere.

X-ray diffraction (XRD) measurements, in $\theta-2\theta$ geometry (Bragg–Brentano goniometer), were carried out in a Siemens diffractometer with monochromated Cu Kα radiation. All the XRD patterns were obtained with scan step of 0.05°2θ with a counting time of 2 s.

Table 1
X-ray diffraction data for the as-received Ti–6Al–4V sample

2θ (grad)	d (nm)	I	hkl-α	hkl-β
35.40	0.2536	100	100	
38.50	0.2338	12	002	
39.45	0.2284	18		110
40.45	0.2230	78	101	
53.30	0.1719	2	102	
57.00	0.1614	1		200
63.55	0.1464	2	110	
71.00	0.1328	2	103	211
74.90	0.1268	7	200	
76.80	0.1241	3	112	
78.10	0.1224	21	201	
82.50	0.1169	1	004	220
84.95	0.1141	1	202	
87.50	0.1114	2	104	

3. Results and discussion

3.1. As-received Ti–6Al–4V

Fig. 1 displays the XRD pattern for the as-received material. Since there is no JCPDS standard for this material, and the known results from the literature are not sufficiently numerous for a detailed comparison, we will fit our results to those reported for the hexagonal α-Ti (JCPDS file #44-1294) and for the cubic β-Ti (JCPDS file #44-1288). From this qualitative fitting, the as-received material was indexed, as shown in Table 1. The β phase is clearly characterized by the (110) and (200) reflections, with $d = 0.2284$ nm and $d = 0.1614$ nm, respectively.

3.2. Treatment effect on β-Ti–6Al–4V

It is known that the lattice parameters of the α phase increase linearly with the nitrogen concentration when titanium is nitrided at temperatures higher than 1573 K [12]. Our measurements show no significant line shift of the α phase for any sample. Conversely, the β phase shows clear evidence of a line shift, suggesting lattice distortion after nitriding. It is well known that this lattice distortion correlates with the internal stress [13], but our measurements are not appropriate for this kind of investigation. However, we can obtain a qualitative view by plotting the lattice parameter (a_{hkl}) against the diffractometer function ($DF = \cos\theta \cot\theta$). In a stress-free sample, the so-plotted lattice parameter will vary linearly. The linear fit would give the true lattice parameter, a_0, corrected for systematic experimental effects. Scattering of the a_{hkl} data from the linear plot can be related to several crystal defects and to changes in the near-surface microstructure [14].

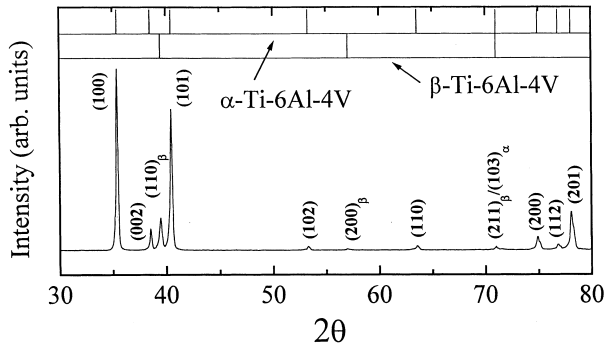

Fig. 1. θ–2θ XRD pattern for the as-received Ti–6Al–4V. The α and β phase reflections are indicated at the top.

In Fig. 2 several plots of a_{hkl} vs. DF are shown. As can be seen, the as-received β phase presents considerable lattice deformation, probably due to the polishing procedure. The lattice parameter roughly estimated from this plot is about 0.3330 nm, similar to that ascribed to β-Ti, i.e. 0.3306 Å (JCPDS file #44-1288). After nitriding, this lattice parameter is increased for all the samples, presenting values between 0.3346 and 0.3353 Å. This corresponds to an increase of about 0.6%. As a comparison, it is interesting to keep in mind the values reported for the α phase [12]. Similar increases correspond to a solid solution with a nitrogen concentration from about 5 to 9 at.%.

3.3. Treatment effect on the near-surface composition

Fig. 3 illustrates the effect of nitriding time for samples treated in a mixture of H_2–60%N_2 (vol.%), at 0.27 kPa and 773 K. There is no signal for titanium nitride for $t < 90$ min. For $t = 90$ min, besides a line shift of the β phase, we observed a reflection at $2\theta = 38.10$ ($d \cong 0.2362$ nm), not ascribable to any titanium nitride. This could be attributed to orthorhombic TiO_2, but this reflection accounts only for 6% in intensity for powder pattern (JCPDS file #29-1360). The patterns for the

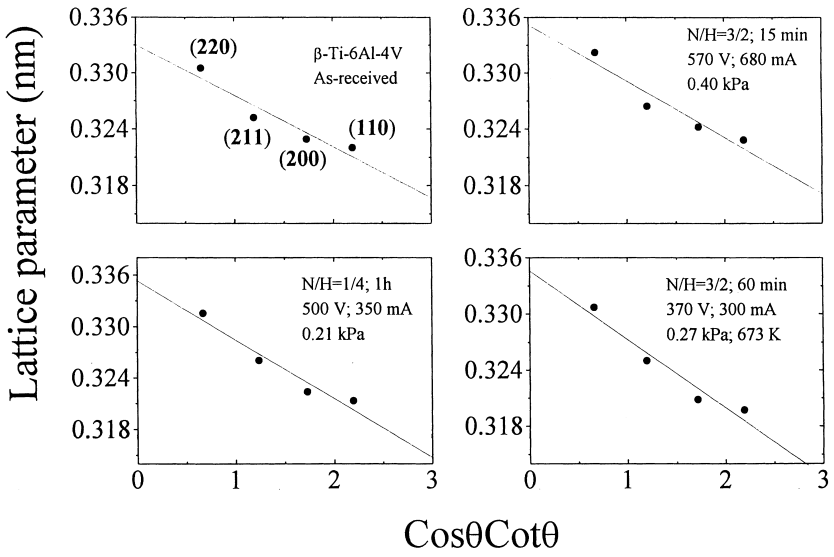

Fig. 2. Lattice parameter a_{hkl} as a function of $\cos\theta\cot\theta$, for the β phase present in the as-received Ti–6Al–4V and in samples nitrided with experimental conditions as indicated.

samples treated during time $t > 240$ min indicate the presence of δ-TiN and ϵ-Ti_2N.

The effect of the treatment duration on the near-surface composition depends on the other parameters. For instance, Fig. 4 shows the results obtained for samples treated in a chamber for which the measured current was used as an indirect temperature control. With atmosphere nitriding N/H = 1/4, treatment for 1 h induced nitride formation at the surface. The amount of precipitates is clearly dependent on the pressure and current (temperature). The sample treated with 0.47 kPa and 420 mA shows highly distorted ϵ-Ti_2N and δ-TiN, as well as the nitrogen deficient ζ-Ti_4N_{3-x} nitride. This is suggested by the reflection at $2\theta \cong 38.20$, corresponding to the (015) reflection of the nitride referred to. The line at $2\theta \cong 44.70$ cannot be assigned to any known titanium nitride. It could be attributed to the (420) reflection of V_2O_3 (JCPDS #39-0774).

The effect of the sample temperature is more clearly illustrated in Fig. 5. These samples were nitrided in N/H = 1/4 atmosphere at 0.40 kPa. At a high temperature (943 K), 20 min was a sufficient length of time to considerably increase the contribution from ϵ-Ti_2N and δ-TiN to the XRD pattern. Fig. 5 confirms the results reported for δ-TiN synthesized by low-energy ion-assisted deposition [14]: at a high temperature, the preferred orientation is that corresponding to (200). This trend is independent of the nitriding atmosphere used and was reproducible in different treatment chambers, as illustrated in Fig. 6. The results displayed in this figure were obtained from samples treated with a

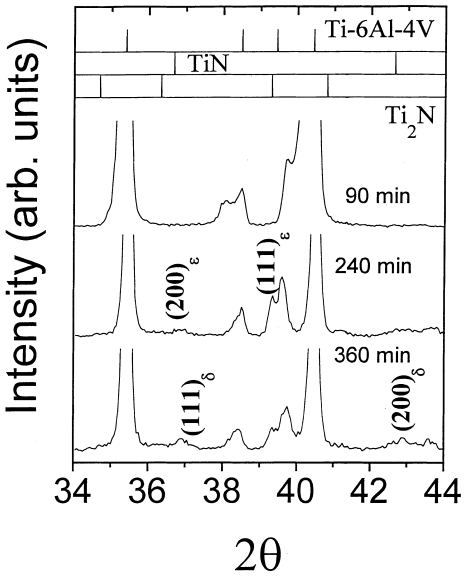

Fig. 3. θ–2θ XRD pattern for samples nitrided over a period of 90, 240 and 360 min in gaseous mixture H_2–60 vol.% N_2, with 0.27 kPa and 773 K. The Ti–4Al–6V, δ-TiN and ϵ-Ti_2N reflections are indicated at the top.

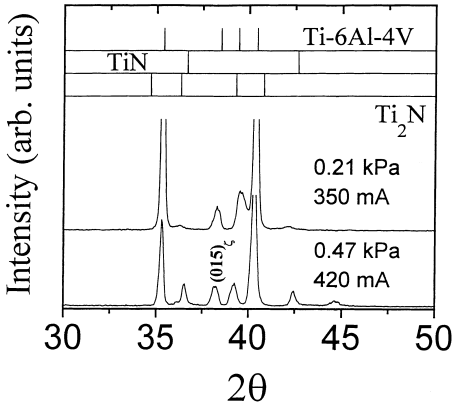

Fig. 4. θ–2θ XRD pattern for samples nitrided during 60 min in gaseous mixture H_2–20 vol.% N_2, with pressure and current as indicated.

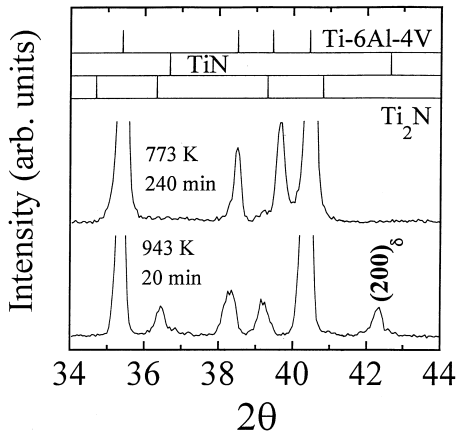

Fig. 5. θ–2θ XRD pattern for samples nitrided in gaseous mixture H_2–20 vol.% N_2, with 0.40 kPa, for the temperatures and times as indicated.

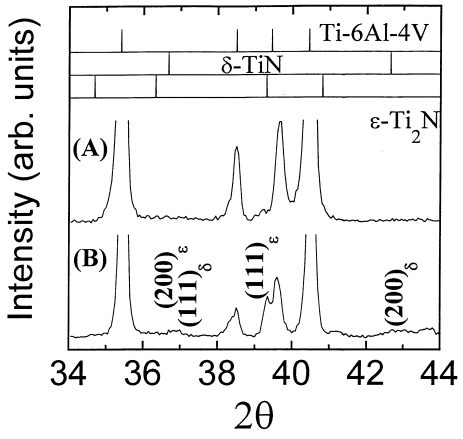

Fig. 7. θ–2θ XRD pattern for samples nitrided with 0.40 kPa, at 773 K during 240 min, in a gaseous mixture (A) H_2–20 vol.% N_2 and (B) H_2–60 vol.% N_2.

N/H = 3/2 atmosphere at 0.27 and 0.40 kPa. Although prepared with different pressures, these samples are comparable because the effect of this parameter is very small within the range used. As can be seen, the sample treated at the lower temperature (270 mA) shows no indication of titanium nitride, even after 90 min, whereas that treated at the higher temperature (680 mA) shows a considerable amount of titanium nitride after 15 min.

Fig. 7 displays the results from samples treated with different nitriding atmospheres, keeping constant the other parameters (0.40 kPa, 773 K, 240 min) but the nitriding atmosphere. Despite the prolonged treatment used, the XRD pattern of the sample nitrided in the N/H = 1/4 atmosphere shows only a small degree of $(111)_\epsilon$ reflection at $2\theta \cong 39.35$ and no signal of δ-TiN. In contrast, the pattern of the sample treated at the N/H = 3/2 atmosphere shows a well-defined $(111)_\epsilon$ reflection as well as an indication of δ-TiN reflections.

From the penetration depth of the Cu Kα radiation into titanium nitride [13], the thickness of the produced layers is estimated to be less than 5 μm. This result is consistent with that reported earlier for the same alloy, treated with a similar method, e.g. for a sample nitrided at 1073 K for 8 h, the thickness of the compound layer was ≈7.5 μm [11].

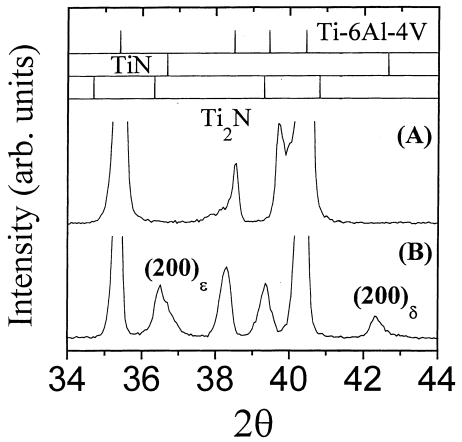

Fig. 6. θ–2θ XRD pattern for samples nitrided in a gaseous mixture H_2–60 vol.% N_2, with: (A) 0.27 kPa, 270 mA, during 90 min; (B) 0.40 kPa, 680 mA, during 15 min.

4. Conclusions

The effect of d.c. glow discharge with a nitrogen–hydrogen mixture on the near-surface composition of (α + β)-Ti–6Al–4V is a very complex function of the process parameters: treatment time, proportion of nitrogen, sample temperature and total pressure during treatment. Among these parameters, and within the experimental conditions used in the present experiment, it appears that the sample temperature plays the more dramatic role. For temperatures below 773 K, ε-Ti_2N and δ-TiN are clearly present only for the N/H = 3/2 atmosphere, after a treatment longer than 240 min. Samples treated at 943 K show well-resolved ε-Ti_2N and δ-TiN reflections even after short treatment times such as 15 min.

Besides the titanium nitride precipitation, plasma nitriding induces considerable lattice distortion on the β phase of the as-received Ti–6Al–4V. XRD line shifts are observed for almost all samples. The addition of nitrogen increases the lattice parameter by about 0.6%, an indication that at least 5 at.% N is introduced into the surface for each experimental condition used here.

Acknowledgements

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