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Hard Ti-N Film Coating of Titanium-Based Materials by Magnetron DC Sputtering

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Coating of titanium-based materials such as Ti-6Al-4V alloy with Ti-N films was examined by magnetron DC sputtering, in order to improve their blood compatibility aiming at the application of the titanium-based metal to the material for totally implantable artificial hearts, as well as their hardness and thereby their abrasion resistance. In this study, the effects of discharge voltage on the formation of the Ti-N film deposited with the reactive sputtering in an Ar-N_2 gas mixture was investigated. Under visual observation, the films deposited at various voltages appeared to be uniform and adhesive, while their colour tone varied with the voltage and the films obtained under a voltage higher than 400 V looked yellow gold (typical colour of TiN). According to AES in-depth profiles, the Ti/N ratio in depth direction was nearly constant for each of the films. It was found from XRD analysis that a Ti_2N phase was predominantly formed in the films deposited under 350V, while a TiN phase was predominantly formed in the films deposited under a voltage higher than 400 V, and that the crystallinity of these phases was developed by heating the substrates over 400℃. Furthermore the Vickers hardness reached over Hv2700 GPa for the films obtained at 450 V onto the substrates heated at 430℃.
Key words: titanium-based materials, nitride coating, reactive sputtering, titanium nitride, blood compatibility

1. INTRODUCTION

Titanium-based materials such as Ti-6Al-4V alloy attract attention as a biomaterial due to features such as excellent mechanical properties and corrosion resistance, and super plasticity, thus enabling the forming of denture bases of complicated shapes. However, this alloy contains aluminium and vanadium liable to do serious harm to human bodies [1,2], so its actual use will require prevention of direct contact with biological tissues. In our previous study, a method of coating the alloy surface with a pure titanium film of excellent biocompatibility as a barrier layer was developed by DC sputtering in argon atmosphere to improve the dental applicability of the alloy [3,4]. The pure titanium barrier layer prevents such harmful substances from leaching out to biological tissues.

The alloy coated with titanium layer is, however, not suitable for the medical implant materials exposed to the blood stream such as artificial heart valves or artificial hearts, because titanium is not only poor in the blood compatibility but also soft and easily damaged [5]. Therefore, it is necessary to improve both the hardness and the blood compatibility of the barrier layer. Y. Mitamura *et al.* reported good blood compatibility of titanium nitride films [6].

In the present work, aiming at the application of the titanium-based metal to the material for totally implantable artificial hearts as well as their hardness and thereby their abrasion resistance, we performed coating of the Ti-6Al-4V alloy substrate with Ti-N film by reactive DC sputtering in an Ar-N_2 gas mixture, expecting an improvement not only of the hardness but also of the blood compatibility of the barrier layer. Furthermore, we investigated the effects of discharge voltage on the properties of formed Ti-N films.

2. EXPERIMENTAL

A planar magnetron sputtering system (ANELVA Corp. type SPF-210H) with a 200 mm-diameter, 130 mm-height stainless chamber was used. The planar target used for this study was a 100 mm-diameter 99.99 mass% pure titanium disk. A schematic diagram of the reactive DC sputtering system is shown in Fig. 1. The magnetic field to confine the discharge area for the magnetron sputtering was 2.5×10^{-2} T. Ti-6Al-4V alloy substrates (13×9 mm^2, thickness 0.55 mm) cleaned with organic solvent were mounted on the substrate holder, water-cooled or heated at 430℃. The heating rate and time were 5℃/min and around 90 min respectively. The pressure in the vacuum chamber was around 1.0×10^{-2} Pa. The discharge voltages ranged from 350 V to 450 V, while the current for sputtering was fixed at 1 A. Ti-N films were deposited onto the substrate by reactive DC sputtering under an Ar-N_2 atmosphere, in which the nitrogen content was regulated by adjusting the nitrogen flow rate at just before the critical flow rate under its sputtering condition, i.e., approximately at 1.2 ml/min for 350 V, 1.6 ml/min for 400 V or 2.0 ml/min for 450 V respectively, while the argon flow rate was fixed at 1.4 ml/min where the argon gas pressure was around 1.0 Pa. Deposition time for sputtering under such discharge voltage was adjusted to obtain the same thickness of 3 μm, so that we can ignore the effects of the different thickness on the measurement of the film hardness.

The thickness of the deposited films was measured by tracing the substrate-film step using a surface roughness tester [7]. The surface morphology of the films was studied on SEM images. In-depth profiles of the chemical composition (Ti/N ratio) of the film were analysed by AES with an ion sputter etching method using an argon ion beam. Characterization of the film was accomplished by XRD. Hardness was measured using a Vickers hardness tester under 10 g load.

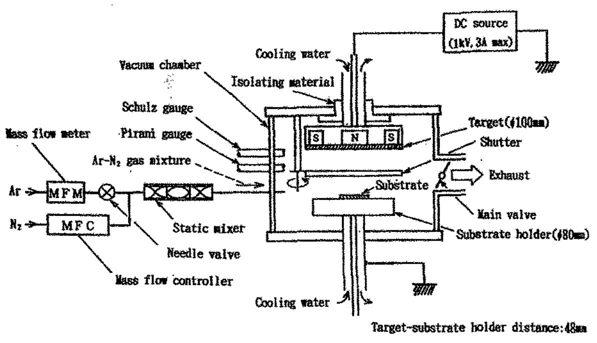

Fig. 1. Schematic diagram of the magnetron DC reactive sputtering.

Furthermore, to verify the blood compatibility of the films, the surface thrombogenicity of Ti-N films obtained using magnetron sputtering with a TiN target at 420 V was evaluated by a cone-stirring-type platelet adhesion test with plasma of the blood drawn from health volunteers. The number of platelets adhered to the surface of the Ti-N films for 15 minutes was compared with that of titanium substrates, where an acrylic resin was used as a negative control.

3. RESULTS AND DISCUSSION

Under visual observation, the films deposited under various discharge voltages appeared to be uniform and adhesive, while their colour tone varied with the voltage. The films obtained under a voltage higher than 400 V looked yellow gold. Therefore the formation of TiN in the films was assumed. In regard to the mechanical durability, the films was hard and durable without being damaged by a tip of pincette.

A typical SEM image of the surface of a Ti-N film is shown in Fig. 2. Under SEM, the surface of the films under various voltages were observed to consist of fine particles.

J. Y. Park *et al.* reported that the number of adherent platelets increases with the increase of surface roughness for pure titanium materials [8]. Thus it was guessed that such granular film surfaces obtained in this study might not have so good blood compatibility as smooth ones although the films were not of pure titanium but of Ti-N. Therefore it is necessary to investigate further the depositing conditions who could realize the smooth film surfaces.

In AES analysis, Auger spectra were acquired in N(E) mode using the Beam Brightness Modulation (BBM) method [9,10], to overcome the problem of the peak overlap of the principal Auger nitrogen transition peak (N-KLL) with one of titanium peaks (Ti-LMM). Thus the overlapped peaks in the N(E) spectra were resolved into the nitrogen peak and the titanium peak using the Least-Squares Fitting (LSF) procedure after the prefiltering of spectra, developed by Sekine et al. [11,12]. The AES signal of Al-KLL was also acquired to determine the position of the interface between the film and the substrate, where an increase in aluminium concentration in depth direction might be detected.

AES in-depth profiles of titanium and nitrogen for a typical film are shown in Fig. 3. In the figure, the abscisa indicates the depth from the film surface while the ordinate indicates the relative concentration (atomic%) of titanium or nitrogen.

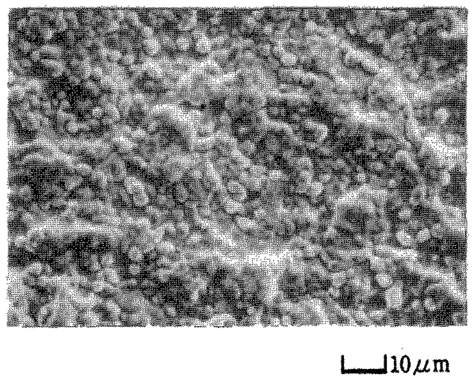

Fig. 2. A SEM image of the surface of the Ti-N film obtained in this study.

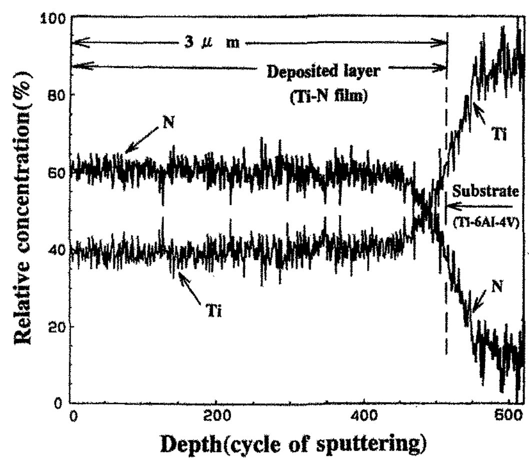

Fig. 3. The AES in-depth profiles of titanium and nitrogen for the Ti-N film deposited at 400 V onto the substrate heated at 430℃.

They show that the concentration of titanium and nitrogen are nearly constant in depth direction, and for the Ti-N films obtained under the other conditions, their concentrations of titanium and nitrogen are also nearly constant in-depth direction. Therefore it was found that the Ti/N ratio in depth direction was nearly constant in each of the films.

The in-depth profiles of the other obtained films were similar. Therefore it was found that the Ti/N ration in depth direction was nearly constant in each of the films.

Figures 4 and 5 show the X-ray diffraction patterns of the films deposited under 350 V and 400-450 V, respectively. In each figure, the diffraction patterns of the films deposited onto the water-cooled substrate and the heated one at 430℃, respectively were shown. For the film deposited under 350 V, not only Ti_2N phase but also ζ-Ti_4N_{3-x} phase and η-Ti_3N_{2-x} phase were detected. On the other hand, for the films deposited under 400-450 V, not only TiN phase but also ζ-Ti_4N_{3-x} phase and η-Ti_3N_{2-x} phase were detected. Therefore it was concluded that Ti_2N phase were predominantly formed in the film under 350 V, while TiN phase were predominantly formed in the films under 450 V, and that the crystallinity of these phases was developed by heating the substrates over 400℃.

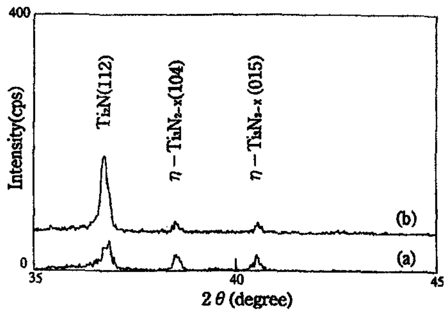

Fig. 4. X-ray diffraction pattern of the films deposited at 350 V onto the substrates cooled by water (a) and heated at 430℃ (b).

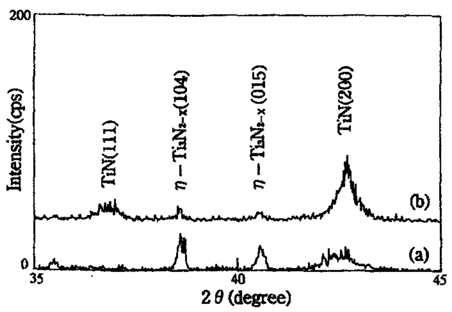

Fig. 5. X-ray diffraction pattern of the films deposited at 450 V onto the substrates cooled by water (a) and heated at 430℃ (b).

Considering the difference in the diffraction angle (2θ) and the shape of the peak for TiN(200) between Ti-N films deposited onto the substrates cooled by water and those heated at 430℃, it was guessed that the TiN phase has larger grains and more compressive internal stress in the films deposited onto the substrates heated at 430℃ than in those cooled by water.

I. Tsyganov *et al.* reported that TiN showed higher blood compatibility than pure titanium or titanium oxides [13]. Thus it was expected that the obtained Ti-N film coatings could improve the blood compatibility of titanium-based materials.

The Vickers hardness of the films deposited under various discharge voltages onto the substrates water-cooled and heated at 430℃ is shown in Fig. 6. It was found that the hardness of the films increased with the increase in voltage, and that the hardness of the films deposited under a voltage higher than 400 V was remarkably enhanced by heating the substrate over 400℃.

The hardness of the titanium dissolving nitrogen atoms increases with the increase of nitrogen [14,15], and also for TiNx films (where x is the nitrogen/titanium composition ratio) deposited by reactive sputtering, it was reported that their hardness roughly increased with the increase of the x value [16]. On the other hand, the x value, with which the TiNx phase was predominantly formed in the Ti-N films obtained in this study, increased with the increase of discharge voltage, as shown in Figures 4 and 5. Thus it was confirmed that the magnetron-sputtered Ti-N films consisting of TiNx phases also had a similar tendency to the TiNx films, i.e. their hardness increased with the increase of x value.

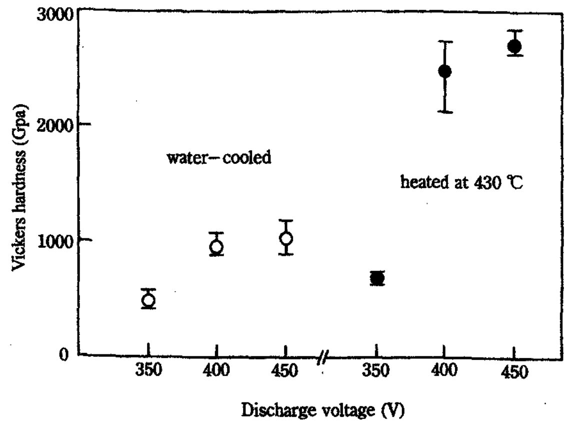

Fig.6. Vickers hardness of the Ti-N films deposited under various voltages onto the substrates cooled by water (○) and those heated at 430℃ (●).

It was found that the maximum hardness reached over Hv=2700 GPa for the films deposited at 450 V onto the substrate heated at 430℃. This very high hardness will improve the abrasion resistance.

Figure 7 shows the result of the platelet test for the acrylic resin, Ti-N films and titanium substrates for 15 minutes, where the acrylic resin was used as a negative control.

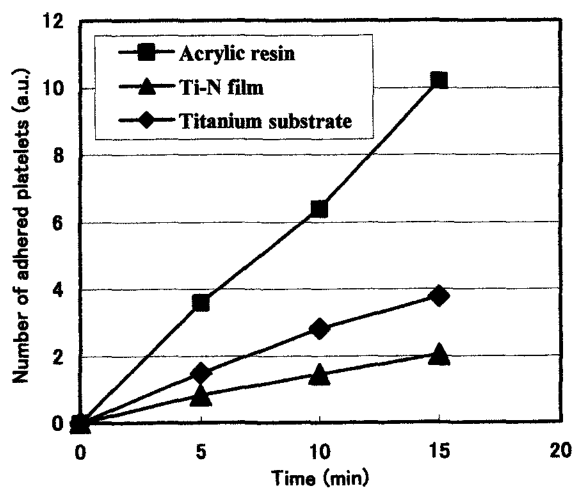

Fig. 7. Result of the platelet test for the acrylic resin, titanium substrates and Ti-N films deposited using magnetron sputtering with TiN target.

Comparing the number of adhered platelets for the Ti-N film with that for the titanium substrate, the ratio of the Ti-N film's number to the titanium substrate's one was estimated to be 0.59. Thus it was found that the platelet adhesion of the Ti-N film was much smaller than the titanium, confirming that the TiN coatings improved the blood compatibility.

4. CONCLUSIONS

Coating of Ti-6Al-4V alloy substrates with Ti-N films was carried out by reactive DC sputtering in Ar-N_2 gas mixture. Under visual observation, the films deposited at various voltages appeared to be uniform and adhesive, their colour tone varied with the voltage, and the films obtained under a voltage higher than 400V looked yellow gold. With SEM, the surface of the films deposited under various voltages were observed to consist of fine particles. According to AES analysis, the Ti/N ratio in depth direction was nearly constant in each of the films. On the basis of XRD, it was concluded that Ti_2N phases were predominantly formed in the films deposited below 350 V, while TiN phases were predominantly formed in the films deposited at a voltage higher than 400 V, and that the crystallinity of these phases was developed by heating the substrates over 400℃. Furthermore, it was found that the maximum hardness reached over Hv=2700 GPa for the films deposited at 450 V onto the substrate heated at 430℃.

Therefore it was expected that the Ti-N films deposited onto the alloy substrates heated 400℃ at voltages higher than 400 V could be served to improved not only the hardness and thereby the abrasion resistance of the alloy but also the blood compatibility.

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REFERENCES

[1] S. G. Steinemann and S. M. Perren, *Titanium Sci. Technol.*, **2** , 1327-34 (1985).
[2] P. Galle, *Compt. rend.*, **299**, 535-39(1984).
[3] T. Sonoda, A. Watazu, J. Zhu, A. Kamiya, K. Ushiki, K. Naganuma and M. Kato, *Vacuum*, **60**, 197-199(2001).
[4] T. Sonoda, A. Watazu, J. Zhu, W. Shi, K. Katou and T. Asahina, *Thin Solid Films*, **459**, 212-215(2004).
[5] Y. Mitamura, *J. Surface Finishing Society of Japan*, **43**, 739-48(1992).
[6] Y. Mitamura, T. Yuhta and T. Mikami, *High Tech. Ceramics*, **1**, 127-38(1987).
[7] M.Numoto, *J. Surface Finishing Society of Japan*, **40**, 241-49 (1989).
[8] J. Y. Park, C. H. Gemmell and J. E. Davies, *Biomaterials*, **22**, 2671-2682(2001).
[9] M.P.Seah, *Surface Science*, **32**, 703-12(1972).
[10] T. Sekine, A. Mogami, M.Kudoh and K.Hirata, *Vacuum*, **34**, 631-42 (1984).
[11] T.Sekine and A.Mogami, *Surf. Inerface Anal.*, **7**, 289-97 (1985).
[12] T. Sekine, Y. Ando and H. Tokumasu, *J. Vac. Sci. Technlol.*, **A4**, No.3, 1557-68 (1986).
[13] I. Tsyganov, M. F. Maitz and E. Wieser, *Applied Surface Science*, **235**, 156-163(2004).
[14] W. L. Finley and J. A. Snyder, *Trans. ASME*, **188**, 1950, 277-85 (1950).
[15] R. I. Jaffee, H. R. Ogden and D. J. Maykuth, *Trans. ASME*, **188**, 1261-73 (1950).
[16] R. Manory, *Surf. Eng.*, **3**, 233-48 (1987).

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