COATING OF PURE TITANIUM WITH TiN/Ti MULTI-LAYERED FILMS BY SPUTTER-DEPOSITION FOR IMPROVING BLOOD COMPATIBILITY

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Titanium-based materials have been utilized as biomaterials in dental or orthopedic field such as denture clasps and artificial dental roots or artificial joints, fixing plates and screws for broken bone, and its prostheses or implants exhibit excellent biocompatibility [1,2]. However, the pure titanium is not suitable for the medical materials exposed to the blood stream such as artificial heart valves, because titanium is poor in the blood compatibility [3]. Therefore, it is necessary to improve both the hardness and the blood compatibility of the barrier layer. Y.Mitamura, et al. reported the good blood compatibility of titanium nitride films [4]. In the present work, we performed the coating of pure titanium substrates with TiN/Ti multi-layered films using sputter-deposition in Ar gas atmosphere, aiming at the application of pure titanium to the material for totally implantable artificial hearts, in order to improve not only the blood compatibility of pure titanium but also the adhesion between the deposited TiN(titanium nitride) coating and the pure titanium substrate. The effects of the thickness of the Ti(pure titanium) layer on adhesion of TiN coatings to the pure titanium substrate were investigated. Furthermore the effects of the TiN coating obtained in this study on blood compatibility were also investigated.

A planar magnetron sputtering system (ANELVA Corp. type L-332S-FHS) with 2 cathodes was used. The planar targets used for this study were a pure titanium disk and a titanium nitride disk of 80mm-diameter, respectively. Pure titanium substrates (14mm diameter disk with 0.50mm thick) were mounted on the water-cooled substrate holder. TiN/Ti multi-layered films were deposited onto the pure titanium substrates by sputtering in sequence the pure titanium target and the titanium nitride one using the planar magnetron sputtering system. The sputter-deposition of the multi-layered films was carried out in the atmosphere of argon (Ar). The sputtering conditions examined in this study were as follows. The electric power source supplying to each sputter cathode with the pure titanium target or the titanium nitride one was of DC (direct current). The discharge voltage and current for sputtering the pure titanium target were 380V and 0.78A respectively. On the other hand, the discharge voltage and current for sputtering the titanium nitride target were 520V and 0.58A respectively. A Ti layer and a Ti-N layer were deposited onto the same pure titanium substrate in sequence by sputtering pure titanium target and titanium nitride one respectively. Thus the Ti-N/Ti multi-layered films were formed through the accumulation of these layers during the sputter-deposition. For the investigation of the effects of the thickness of Ti (pure titanium layer) on adhesion of TiN coatings to the pure titanium substrate, the thickness of pure titanium layer was varied from 0 to 200nm, while that of TiN layer was fixed at 200nm. Thereby the multi-layered film might be from 200nm thick to 400nm thick in total.

To investigate the blood compatibility of the obtained TiN/Ti multi-layered films, their surface thrombogenicity 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 TiN/Ti multi-layered film for 15min was compared with that of the pure titanium substrate, where an acrylic resin was used as a negative control.

Under visual observation, the obtained multi-layered films with the pure titanium layer 200nm thick looked yellow gold and appeared to be uniform and adhesive, while both TiN monolithic films deposited directly onto the titanium substrate under the same sputtering conditions and the multi-layered films with the pure titanium layer 100nm thick peeled off partly. Thus the formation of TiN (titanium nitride) layer at the surface was assumed because of their color tone, and it was found that the TiN/Ti multi-layered film with a Ti layer more than 200nm thick was adhesive to the pure titanium substrate. I. Tsyganov et al. reported that TiN showed higher blood compatibility than pure titanium or titanium oxides [5]. Thus it was expected that the obtained Ti-N/Ti multi-layer film coatings could improve the blood compatibility of titanium-based materials. Figure 1 shows the result of the platelet test for the acrylic resin and for the TiN/Ti multi-layered film for 15min. Figure 2 shows the result of the platelet test for the acrylic resin and for titanium substrates for 15 minutes in the same way. And besides, the number of platelets adhered to the surface of the titanium substrates for 15 minutes was the factor of 0.34, comparing to that of the acrylic resin used as and negative control. On the other hand, the number of platelets adhered to the surface of the obtained TiN/Ti films for 15 minutes was the factor of 0.22, comparing to that of the acrylic resin used as a negative control. Based on these results of the platelet test, the ratio of the number of adhered platelets for the obtained TiN/Ti film to that for the titanium substrate was estimated to be 0.65. Thus it was found that the platelet adhesion of the obtained TiN/Ti film was much smaller than the pure titanium, concluding that the TiN/Ti multi-layer coating improved the blood compatibility. Therefore it was found that both the blood compatibility of pure titanium and the adhesion between the deposited TiN coating and the pure titanium substrate were improved by this method.

References:

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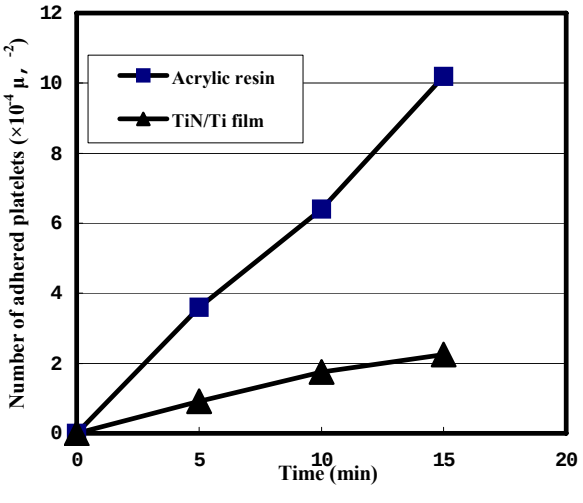

Fig.1. Result of the platelet test for the acrylic resin and for the TiN/Ti multi-layered film.

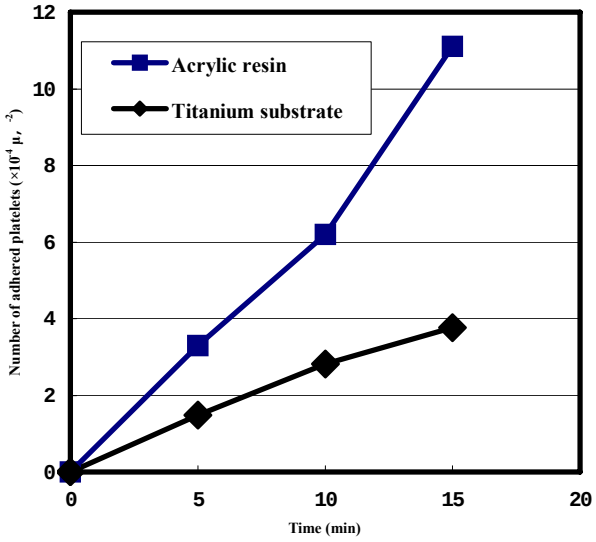

Fig.2. Result of the platelet test for the acrylic resin and for the titanium substrate.