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Effects of pre-heat conditions on diffusion hardening of pure titanium by vacuum rapid nitriding

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ABSTRACT

The pre-heat treatment in vacuum rapid nitriding process was introduced to improve the surface hardening characteristics such as thick depth, high hardness and particularly to reduce the processing time. The pre-heat treatment was maintained for 30 min with an interval of 10 °C at the temperatures of 700– 800 °C under a high vacuum to allow the absorption of oxygen atoms on the titanium surface into the inner side. The following nitriding processes were equally performed at the same condition as 800 °C for 1 h. As a result, the depth of a hardened layer in the sample, which was treated at 800 °C for 1 h with the pre-heat treatment at 760 °C for 30 min, was similar to that of the treated sample at 800 °C for 3 h without pre-heat treatment and the depth was about 40 μm. The processing time can be largely reduced by introducing the pre-heat treatment process. The pre-heated specimens showed a longer wear lifetime by more than three times and higher friction resistance than that of PVD or non-nitrided specimens. The surface gradient-hardened layers exhibited excellent wear resistance and could prevent separation or debonding between matrix and the coated layer effectively.

1. Introduction

Titanium and its alloys have excellent corrosion resistance because it exhibits not only a large effect of preventing corrosions penetrated inside a material due to its dense oxidized titanium film but also an immediate reproduction of damaged passive films within several micro seconds in the air [1–4]. In particular, titanium shows excellent corrosion resistance against chloride ions and can be used in marine structures and chemical process industries under severe environments. In addition, as titanium has no harmful reaction with human blood and superior bio-compatible characteristics to other metal materials, titanium and its alloys represent some advantages in bio-medical fields [5–8].

In spite of these excellent characteristics, titanium alloys show some disadvantages in their hardness and wear resistance. Thus, studies on the surface modification to improve such weaknesses have been attracted. Regarding the improvement in the surface characteristics of titanium, it was reported that the protective films which have excellent mechanical properties in low temperatures could be obtained by coating TiN onto the base material of titanium [9]. The TiN coating that has been most largely studied in wear resistive coating materials shows excellent oxidation resistance and surface roughness and ductility. Also, it exhibits an elegant gold color and has been largely used in not only wear resistance protective films but also corrosion resistive and ornament coating materials [10,11].

For improving the surface hardness and wear resistance of titanium using excellent coating materials, interstitial element hardening (using C, N, and O, etc.), plasma, Physical Vapor Deposition (PVD) and Chemical Vapor Deposition (CVD) methods are used as general surface hardening methods [12–15]. Studies on applying the PVD method such as Ion Plating, Cathode Arc Deposition, Reactive Sputtering, and the CVD to coat the titanium surface, have been largely conducted. The CVD process is useful to vapor complex shapes because the CVD process has no dense coating microstructures, high adhesiveness, etc. Although it exhibits advantages of controlling the composition of coating materials and coating thickness, it may cause some changes in microstructures at an interface between a thin film coating layer and titanium matrix because vapor deposition processes are usually performed at high temperatures. Thus, it has been known that these changes significantly affect the mechanical and corrosion properties [16,17].

The PVD process has some advantages such as excellent wear resistance, heat resistance, oxidation resistance, and corrosion resistance. Whereas, it has some disadvantages such as a weak adhesive strength between the thin film coating layer and the matrix, high price equipments, a long processing time, separations in coated layers, and some cracks between layers, etc.

In this study, a thermo-chemical treatment (TCT) processing is introduced in order to generate the hardened inner-layers with continuous

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hardness gradient. It enables some interstitial elements such as nitrogen, oxygen, and carbon to diffuse and penetrate into the matrix of titanium. By applying this method, it is expected that the wear resistance of the titanium surface is improved and the separation between the coating layer and the matrix as well as some cracks caused by external factors are restricted. Various pre-heat treatments are applied to implement the fast and effective absorptions of the TiO_2 oxidized film which is existed on the titanium surface, under a high vacuum atmosphere. And the influences of some factors on the changes in surface hardness, surface gradient-hardened layers, and surface wear resistance are investigated.

2. Materials and methods

The specimen for applying the surface hardening was a commercial product of pure titanium with a size of $10 \times 12 \times 10$ mm^3 (from TIMET) and its bulk chemical composition was presented in Table 1. The TCT processes were applied by the different processing conditions. For obtaining the surface gradient-hardened layers on the surface of titanium, a gas controlled vacuum furnace (GCVF) system was used, which is designed to control temperature, vacuum level, and gas flow, etc.

Nitrogen was used as a reactive gas and the surface hardening process was implemented by decreasing the pressure to 5×10^{-5} Torr initially by the GCVF system, and then controlling the partial pressure in the chamber as 5×10^{-1} Torr through inserting nitrogen gas, followed as heating it up to 800 °C (Fig. 1). As titanium has a large affinity with nitrogen, it makes possible to easily form titanium nitride. The TCT process involves a pre-heat treatment process as shown in Fig. 1 in order to remove the passive oxide film existed on the titanium surface and effectively present such a nitriding process. The pre-heat treatment was maintained for 30 min in a specific temperature range in the initial heating stage and the nitriding process was carried out at 800 °C for 1 h. The pre-heat treatment was applied at four different temperatures in a range between 700 and 800 °C, such as 710 °C, 740 °C, 760 °C, and 790 °C. In addition, some TiN vapor deposited specimens using the PVD method were used for comparing them with the TCT specimens.

For verifying the effects of the surface modification in these specimens, surface hardness, cross-sectional hardness, surface wear characteristics, and cross-section coating layers were analyzed as well as the morphologies of the hardened layers. The hardness characteristics of the cross-section were measured from the surface to the center of the specimens by a micro Vickers hardness tester (by FUTURE-TECH, Model FM-700). Wear characteristics were evaluated by using a Ball on Disk type wear tester (by J&L, Model JLTB-02 tribometer) in which a SUS304 stainless ball with a diameter of 1 mm was used as a counterface material. By generating frictional wear with a rotational radius of 3 mm between the ball and the specimen, the friction coefficients in each specimen were measured under a rotational speed of 100 rpm and a load of 1N, and the frictional behaviors were also investigated. Room-temperature X-ray diffraction analysis was carried out on a Philip X'PERT Diffractometer utilizing radiation at 30 kV and 40 mA, the scanning range being $2\theta = 20°–80°$. In addition, through observing the sections of the specimens by a scanning electron microscope (SEM, by JEOL, JSM-6610LV), the compound layers generated on the surface and the diffused layers of nitrogen gas and their boundaries were analyzed.

Table 1
Chemical composition of commercially pure titanium material (wt.%).

Components	C	Fe	H	N	O	Ti
wt.%	0.05	0.3	0.008	0.02	0.2	Bal.

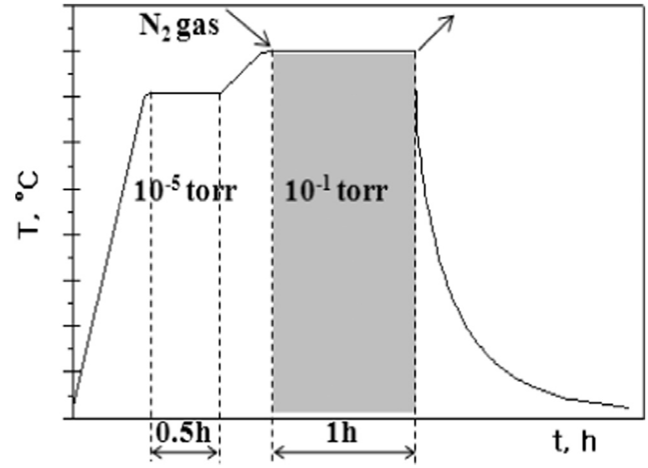

Fig. 1. Schematic diagram of the TCT process for nitriding titanium according to variable pre-heat treatment conditions.

3. Results and discussion

3.1. Surface gradient-hardened layers

An XRD analysis was performed for verifying the compounds generated on the surface hardened layers (Fig. 2). It was possible to observe titanium matrix and TiN phases in the PVD specimens. In the case of the specimens in the TCT process, the generation of α-Ti, $TiN_{0.26}$, and Ti_2N phases was verified in all four specimens even though there were no generations and changes of other compounds according to pre-heat treatment temperatures. The peak of α-Ti phase in all TCT specimens was slightly moved from the original peak to a lower angle. This slightly shifts of α-Ti peak, which has a hexagonal close-packed (HCP) structure, is connected with the expansion or distortion of lattices due to the insertion of the interstitial element, nitrogen atoms [18].

For confirming the titanium nitrides analyzed by the XRD, the surface hardened layers were investigated by SEM analysis, as shown in Fig. 3. For the PVD process, TiN compound layer with a thickness of about 1.7 μm was only observed. For the TCT-ed specimens, it was verified that all specimens presented three layers. The results revealed that the compound generated at the most outside was Ti_2N based on the studies performed by S. Gokul Lakshmi et al. [19], Erol Metin et al. [20], and S. Taktak et al. [21] and the hardened layer generated at the

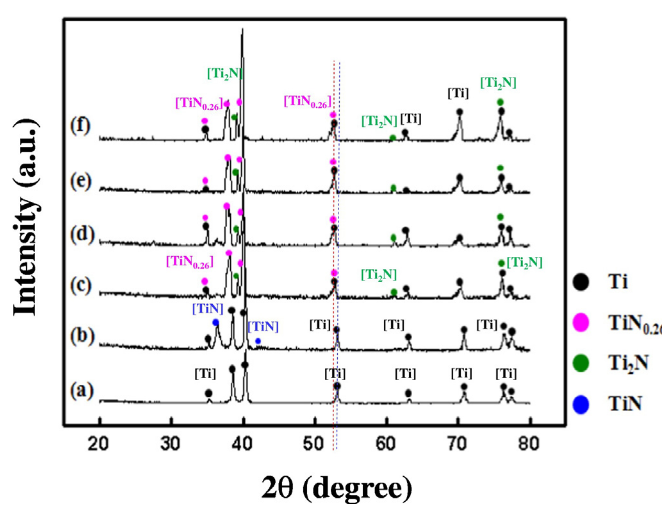

Fig. 2. X-ray diffraction patterns of the nitrided surface compound layers according to the various pre-heat treatment temperatures; (a) as-received, (b) PVD (TiN), pre-heating at (c) 710 °C, (d) 740 °C, (e) 760 °C, and (f) 790 °C (the TCT treated at 800 °C, 1 h).

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