Room Temperature Nitriding of Pure Titanium Using Atmosphere Controlled Scanning Cyclic Press

Yuta Funaki[1,*1], Nao Fujimura[2], Takashi Nakamura[2], Kosuke Takahashi[2] and Tatsuki Wajima[3]

[1] *Division of Mechanical and Space Engineering, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan.*
[2] *Division of Mechanical and Aerospace Engineering, Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan.*
[3] *Hybridge Co. Ltd., Sapporo, 065-0021, Japan*

The scanning cyclic press (SCP) developed in our laboratory refines the microstructure of metallic materials by scanning the surface using a vibrating indenter. In the previous study, we conducted SCP to pure titanium in a nitrogen gas environment and found that the TiN layer formed even at room temperature. In this study, we investigated the detailed characteristics of the TiN layer and the refined microstructure beneath it created by the combination of SCP and nitrogen environment. Observation and crystal structure analysis were conducted by transmission electron microscopy and hardness measurement by nanoindentation tester. As a result, we clarified that the TiN layer consisted of extremely fine grains ranging from several to a few dozen nanometers. At the same time, we recognized that the interior beneath the TiN layer kept the titanium microstructure with approximately 0.1 to 0.3 μm sized grains that were also drastically refined from the base material. The hardness significantly increased at the surface and gradually decreased around 10 to 40 μm depth, and finally approached that of the base material. The TiN and the refined microstructure of the modified layer reasonably explained the tendency of hardness distribution.

Keywords: *Surface modification, Nitriding, Grain refinement, Titanium, Scanning cyclic press.*

1. Introduction

Titanium and its alloys are widely used in the industrial field owing to their excellent specific strength, corrosion resistance, and heat resistance. However, their wear resistance is unsatisfactory, and particular surface modification is often required for sliding components application. Nitriding, as typified by gas nitriding and plasma nitriding, is one of the methods to improve the wear resistance of metals. In the nitriding of titanium, wear resistance is enhanced by forming nitrogen compounds, such as TiN and Ti_2N, on the surface layer[1, 2]. Generally, high temperatures and a long operating time are necessary for nitriding treatment to diffuse nitrogen into the titanium microstructure. However, they may also cause unintentional changes in the strength properties due to heat[3, 4]. Therefore, research on nitriding at lower temperatures has been conducted[5-7].

Recently, we developed a new surface modification technique, scanning cyclic press (SCP), which scans the metal surface with a vibrating indenter to refine the microstructure by applying cyclically compressive load[8]. In the previous study, we conducted SCP to pure titanium in a nitrogen gas environment and found that the TiN layer formed even at room temperature[9]. In this study, observation and crystal structure analysis by transmission electron microscopy and hardness measurement by nanoindentation tester were conducted to clarify the detailed characteristics of the surface layer created by the combination of SCP and nitrogen environment at room temperature.

2. Experimental procedure

2.1 Material and specimen

The material used was pure titanium (JIS H 4650). Table 1 shows the chemical composition, and Figure 1 shows an SEM image of the microstructure consisting of polycrystalline α-phase. The average α-grain size was 13.1 μm. The specimen was a round bar with a diameter of 4 mm and a length of 52 mm. The specimen surface was polished using #800-#2000 grit emery paper and then finished by buffing with 1 μm grain size alumina and diamond abrasives.

Table 1 Chemical composition (mass %).

O	N	C	Fe	H	Ti
0.113	0.003	0.001	0.028	0.0007	Bal.

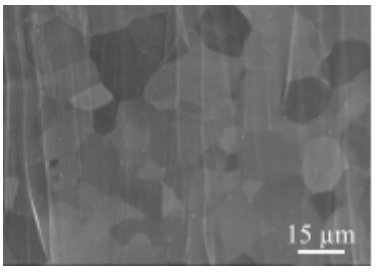


Figure 1 SEM image of microstructure of pure titanium.

2.2 Surface modification equipment

Figure 2 shows a schematic diagram of the SCP. An indenter at the top of the hydraulic actuator applies a cyclic compressive load to the specimen supported by a reaction receiver connected with a load cell. Thanks to the feedback system, precise load control is achieved during surface modification. The entire specimen surface can be modified by applying feed and rotation movement. The system has a vacuum chamber with an oil rotary pump and a

[1]* Graduate Student, Hokkaido University

turbomolecular pump, allowing modification in a vacuum or any gas environment.

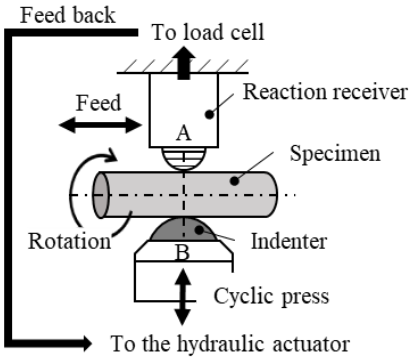


Figure 2 Schematic representation of surface modification using scanning cyclic press.

2.3 Surface modification condition

Table 2 shows the condition of the surface modification. In this study, the chamber was evacuated to 3.4 $\times 10^{-4}$ Pa, and nitrogen gas was introduced up to atmosphere pressure. A sinusoidal compressive load from 0 to 58.8 N was applied to the specimen at 200 Hz frequency. The rotation and feed speeds of the specimen were 1.3 rpm and 10 μm・s^{-1}, respectively. The number of loading cycles was set to 5×10^7 cycles. The modified surface area was 8 mm along the specimen axis direction. The room temperature during the surface modification was in the range from 23 to 28 ℃.

Table 2 Condition of the surface modification.

Compressive load, c_p/N	58.8
Frequency, *f*/Hz	200
Rotation speed, r_s/rpm	1.3
Feed speed, F_s/μm·s^{-1}	10
Number of loading cycles	5×10^7
Temperature, *T*/℃	23~28
Environment	Nitrogen

2.4 TEM analysis and hardness measurement

A TEM sample with a thickness of 0.1 μm was prepared from the surface-modified area using a focused ion beam (FIB) apparatus (JEM-9320FIB, JEOL). Observation and crystal structure analysis were conducted using 200kV transmission electron microscopy (JEM-2000FX, JEOL).

A nanoindentation tester (ENT-NEXUS-KT, ELONIX) was used for hardness measurement. A cylindrical specimen approximately 5 mm in length was cut from the modified area, and the nanoindentation test was conducted from the edge of the cross-section toward the interior.

3. Result and discussion

3.1 TEM analysis

Figure 3 shows a bright-field image of the surface layer of the sample. The surface layer was divided into two regions. One is a mottled appearance consisting of bright and dark irregular patterns framed by the two white dashed lines. The other is a slightly darker area than the mottled region, showing a granular microstructure. The depth of the mottled pattern layer was approximately 1.5 μm and the granular microstructure was observed below this layer. The grain size of the granular microstructure was about 0.1~0.3 μm, which was extremely fine compared to the average grain size of the pristine sample (13.1 μm). To identify the crystal structures of these two regions, the electron diffraction images at points A and B in Figure 3 were taken as shown in Figures 4 (a) and (b), respectively. The electron diffraction image at point A was a ring pattern consisting of multiple overlapping spots (Figure 4 (a)). Considering the beam diameter (approx. 0.09 μm) and the sample thickness (0.1 μm), this result suggested that a polycrystalline structure with grain sizes ranging from several to a few dozen nanometers was formed at Point A. In contrast, the electron diffraction image at point B shows several clear spots (Figure 4 (b)) indicating that two or three single crystals were contained within point B. From Figures 4(a) and (b), the lattice constant of each region was calculated by measuring the distances from the transmitted light to the two diffraction spots. The results are listed in Table 3 and Table 4. From Table 3, the lattice constant at point A was found to be a = 0.444 nm, which approximately equaled the lattice constant of TiN, a = 0.424 nm. From Table 4, the lattice constants at point B were a = 0.313 nm and c = 0.483 nm, which approximately equaled the lattice constants of Ti, a = 0.295 nm and c = 0.469 nm, respectively. These results indicate that TiN was formed in the mottled pattern layer and that the Ti crystalline structure was kept in the granular microstructure region.

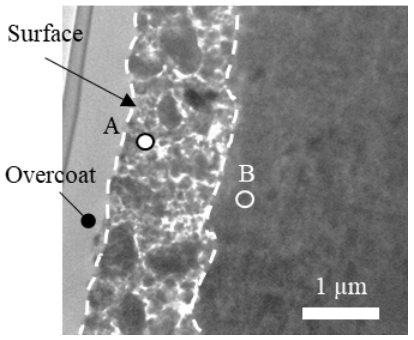
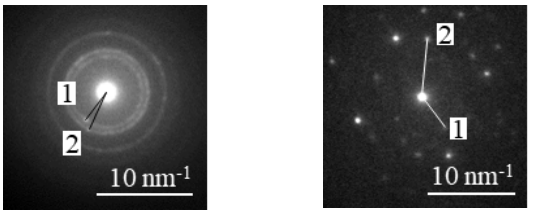


Figure 3 TEM bright-field image of the surface layer of the sample.



(a) Point A (b) Point B

Figure 4 Electron diffraction image at points A and B in Figure 3.

Table 3 Calculated lattice constant at point A.

Lattice constant,	*a* / nm
Calculated value	0.444

TiN	0.424

Table 4 Calculated lattice constant at point B.

Lattice constant,	*a* / nm	*c* / nm
Calculated value	0.313	0.483
Ti	0.295	0.469

3.1 Hardness measurement

Figure 5 shows the results of the nanoindentation test. The indentation hardness of the 1 µm depth from the surface was 6.5~8.0 GPa, which was significantly higher than the average value of 4.3 GPa at the center of the sample. On the other hand, the hardness in the region of 10~40 µm from the surface was 4.5~6.0 GPa, a slight increase from the center of the sample. Considering the result of TEM analysis, increasing hardness at a depth of 1 µm from the surface likely resulted from the formation of TiN to a depth of 1.5 µm from the surface. The slight increase in hardness of 10 ~40 µm inside the surface is considered to be attributed to the finer microstructure of the titanium region.

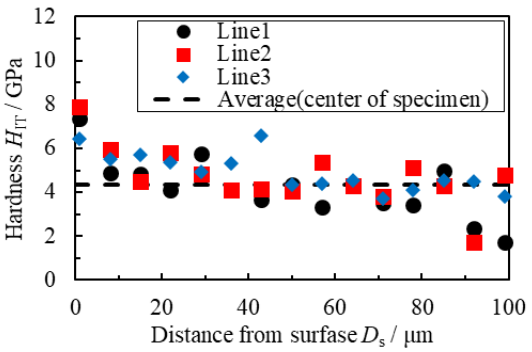


Figure 5 Result of nanoindentation test.

4. Conclusion

In this study, the surface of pure titanium was modified using the SCP in a nitrogen gas environment at room temperature. The observation and crystal structure analysis by TEM, and the hardness measurement by nanoindentation tester were conducted to investigate the characteristics of the modified surface layer. As a result, the following conclusions were obtained.

1) TEM analyses clarified that a TiN layer with a grain size ranging from several to a few dozen nanometers was formed just beneath the surface. The grain size of the titanium microstructure below the TiN layer was refined to about 0.1~0.3 µm.

2) Nanoindentation tests clarified that the hardness at the surface increased significantly. This phenomenon likely resulted from the formation of the TiN layer. A slight increase in hardness was observed at 10~40 µm inside the surface, which was attributed to the finer microstructure of the titanium region.

Acknowledgments

This study was supported by Northern Advancement Center for Science & Technology (R03 H-4-2) and THE AMADA FUNDATION (AF-2019018-B2). Crystal structure analysis was performed at the High-Voltage Electron Microscope Laboratory, Hokkaido University.

References

1) D. G. Bansal, O. L. Eryilmaz and P. J. Blau: Wear **271** (2011) 2006-2015.
2) M. P. Kapczinski, C. Gil, E. J. Kinast and C. A. d. Santos: Mater. Res. **6** (2003) 265-271.
3) M. Akita, Y. Uematsu, T. Kakiuchi, M. Nakajima, Y. Bai and K. Tamada: Mater. Sci. Eng. A 627 (2015) 351-359.
4) K. Tokaji, T. Ogawa and H. Shibata: J. Mater. Eng. Perform. **8** (1999) 159-167.
5) S. Kikuchi, Y. Nakamura, A. Ueno and K. Ameyama: Mater. Trans. 56 (2015) 1807-1813.
6) O. Unal, E. Maleki and R. Varol: Vacuum **150** (2018) 69-78.
7) K. Fujita, M. Ijiri, Y. Inoue and S. Kikuchi: Adv. Mater. **33** (2021) 2008298.
8) T. Nakamura, K. Miyazaki, N. Fujimura and T. Wajima: METAL PROCESSING METHOD, JP2018-40046 A (2018).
9) Y. Funaki, T. Nakamura, N. Fujimura, K. Takahashi and T. Wajima: Collected Abstracts of Mechanical Engineering Congress 2022 Japan (2022) J163p-06.