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Tribological Behavior of Titanium-Sintered Composites with Ring-Shaped TiN Dispersoids

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Abstract: The wide applicability of titanium (Ti) has prompted the analysis to improve its mechanical strength through the addition of different alloying elements. Among these, Ti materials with pre-mixed pure Ti and titanium nitride (TiN) powders as the starting materials have exhibited improved mechanical properties and tribological performance. In this study, the tribological properties of Ti matrix composites with ring-shaped TiN dispersoids were evaluated. The materials were fabricated from pre-mixed pure Ti powder and core-shell structured Ti-(N) powder, which were prepared by heat treatment at 1273 K under N₂ gas. The tribological behavior of the Ti-TiN composites was studied by varying the applied load using a ball-on-disk wear test under oil lubrication conditions. The initial familiarity period of the Ti-TiN composites decreased. Subsequently, compared to the pure Ti specimen employed as a reference material, the friction coefficient was significantly lower and more stable. This is attributed to the ring-shaped, hard TiN dispersoids, which prevented the adhesion phenomenon and improved the oil film formability owing to the increase in microhardness and abrasive wear resistance of the nitrogen solid solution in the core region.

Keywords: core-shell structured TiN powder; ring-shaped TiN dispersion; tribological properties; titanium matrix composite; powder metallurgy; spark plasma sintering; friction coefficient; abrasive wear behavior; oil lubricant



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1. Introduction

As an oxide mineral, Ti is a resource-rich element, and it is the ninth most abundant crustal element. It has a high specific strength, good corrosion resistance, and biocompatibility. Therefore, Ti and its alloys are widely employed in various industries, such as aircraft components, medical devices, and chemical plant products. Several researchers have reported wear and tribological properties of Ti matrix composites reinforced by titanium boride (TiB), titanium carbide (TiC), and silicon nitride (Si₃N₄) that were evaluated by the PM process [1–3]. They concluded that increasing the contents of the reinforcement is the best way to improve the friction characteristics and decreasing the wear loss. Surface modifications have also been made to improve the wear resistance of Ti alloys [4–7]. For example, silicon carbide (SiC) coating on a Ti-6Al-4V alloy obtained a low and stable coefficient of friction due to good adhesion between the Ti matrix and SiC [4].

Additional alloying elements are effective in improving the mechanical strength of Ti; however, they are often expensive rare metals or harmful and toxic to humans, such as vanadium (V), niobium (Nb), tantalum (Ta), and chromium (Cr) [8]. As substitutes for these elements, the addition of oxygen, nitrogen, iron, silicon, carbon, and hydrogen (referred to as “ubiquitous elements”) has been reported to achieve solid solution and grain refinement strengthening of Ti fabricated by powder metallurgy (PM) processes [9–13]. For PM-fabricated Ti materials with pre-mixed pure Ti and titanium nitride (TiN) powders as the

starting materials, a previous study [14] clarified that nitrogen (N) solid solution strengthening has successfully improved their mechanical properties and tribological performance.

A core-shell-structured Ti-(N) powder is developed by the heat treatment of spherical pure Ti powder in an N₂ gas atmosphere [10]. TiN layers are formed as shells at the top surface of the Ti powder, and N atoms are dissolved in its center region (core) as solid solutes. This unique powder has been used in fabricating Ti materials with large amounts of N solutes through an additive manufacturing process, resulting in superior tensile strength and good ductility, owing to the refined martensite (α') grains and homogeneous N solid solution [15].

In our previous study [16], aluminum (Al) matrix composites dispersed with Al₃Zr particles were fabricated from the pre-mixed pure Al and zirconium hydride powder, and their tribological properties were evaluated under oil lubrication. The friction coefficient and wear volume of the Al–Al₃Zr composites are significantly lower than those of monolithic pure Al specimens. This is attributed to the uniform dispersion of Al₃Zr hard particles protruding from the matrix, which prevents direct contact between the Al matrix and counter material surface. Moreover, the oil film formation around the Al₃Zr dispersoids effectively control the direct contact of the materials, thereby reducing the friction coefficient.

In this study, core-shell structured Ti-(N) powder was used to fabricate PM Ti composites with ring-shaped TiN dispersoids using the optimum consolidation temperature to prevent a reaction between the TiN phases and Ti matrix. The tribological properties of the Ti–TiN composite specimens were evaluated under lubrication conditions. In particular, the effects of the circular TiN dispersoids on the friction coefficient and abrasive wear behavior were investigated by varying the applied load in the wear test with a pure Ti specimen as the reference material.

2. Materials and Methods

Spherical, commercially pure (CP)-Ti powder (purity: 99.7%, median diameter: 24.2 μ m, TILOP-45, Osaka Titanium Technologies, Amagasaki, Japan) fabricated by gas atomization was used as the raw material in this study, as shown in Figure 1a. The O, N, and H contents of the CP-Ti powder measured by an elemental analyzer (EMGA-830, HORIBA, Kyoto, Japan) were 0.119, 0.003, and 0.004 wt%, respectively. Core-shell structured Ti-(N) powder was prepared by the heat treatment of the CP-Ti powder at 1273 K for 0.6 ks in a horizontal tube furnace at a heating rate of 20 K/min and a N₂ gas flow rate of 5 L/min. A nitrogen content of 10.51 wt% was obtained, which is significantly higher than that of raw CP-Ti powder (0.003 wt%). Figure 1b shows the same spherical shape as the received powder.

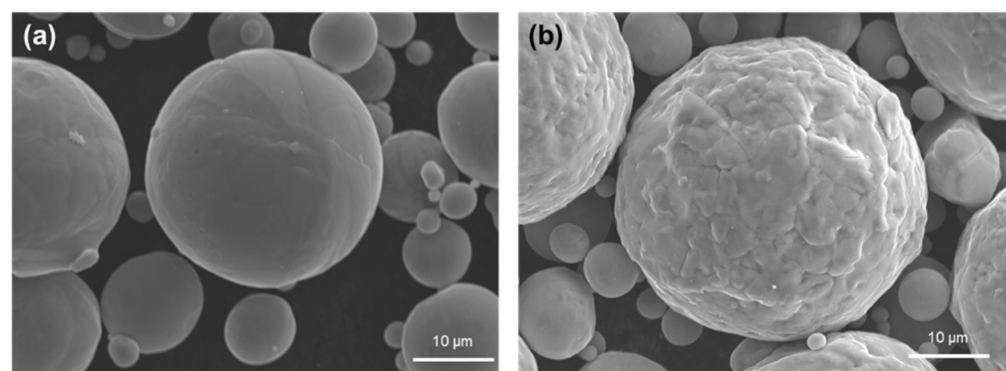


Figure 1. SEM images of (a) as-received pure Ti powder and (b) core-shell structured Ti-(N) powder heat treated in N₂ atmosphere at 1273 K for 10 min.

To prepare the starting powder, CP-Ti powder was mechanically mixed with core-shell structured Ti-(N) using tabletop ball-milling equipment (AV-2, Asahi, Chiba, Japan) at a rotation speed of 90 rpm for 3.6 ks with a weight ratio of 8:2 (CP-Ti:Ti-(N) powder). Yttria-stabilized zirconia (Y-ZrO₂) balls with a 10 mm diameter were used in the ball-milling

process. A graphite mold ($\Phi 36$ mm) was filled with the pre-mixed powder and consolidated by spark plasma sintering (SPS1030s, SPS Syntex, Yokohama, Japan) at 1123 K for 10 min under an applied pressure of 30 MPa and a vacuum atmosphere of 6 Pa. This sample was denoted as “SPS Ti–20%Ti(N)”. The density of the fabricated samples was measured using the Archimedes method and was presented as a percentage of pure Ti (4.51 g/mm^3). The N and O contents of the SPS samples were also measured. The microstructures and elemental distributions were examined by scanning electron microscopy (SEM, JSM-7600F, JEOL, Akishima, Japan) with energy-dispersive X-ray spectroscopy (EDS, JED-2300, JEOL). The microstructure analysis samples were prepared for metallography using a standard polishing procedure with SiC paper up to 4000 grit, polishing with a 1- μm alumina suspension, and electrochemical polishing in a solution consisting of 95 vol% acetic acid (CH_3COOH) and 5 vol% perchloric acid (60% HClO_4) for 120 s at room temperature. The samples were immediately rinsed with ethanol and air dried. The phase structures of the powders and sintered materials were analyzed using X-ray diffraction (XRD, XRD-6100, Shimadzu, Kyoto, Japan) with Cu $K\alpha$ radiation at 40 kV and 50 mA, and with a step size of 0.02° . The hardness of the materials was randomly measured by a Vickers microhardness tester (HMV-G, Shimadzu) with 0.025 N applied, and the measurement number was 20 for each sample. The average hardness value was used as the representative one of the specimens.

The tribological properties of the sintered materials were investigated using a ball-on-disk wear test (FPR-2100, Rhesca, Hino, Japan) under lubrication conditions using engine oil (SAE30, MOBILE, Tokyo, Japan) at 293 K to evaluate the friction coefficient and wear loss. SPS CP-Ti and Ti–N materials were machined as disk specimens, and two types of SUS304 (304) and SUS440C (440C) stainless balls were employed as the counter materials. The applied load of 2.45, 4.9, and 9.8 N, rotating speed of 31 mm/s, track radius of 10 mm, and wear test time of 10.8 ks were used in this study, based on a previous work [16]. The total sliding distance of this wear test was 334.8 m. The average friction coefficient calculated from the two test results was used as the representative value for each disk specimen. After the wear test, the damaged sliding surface of each specimen was investigated using the SEM–EDS system to investigate the effects of the circular TiN dispersoids in the Ti matrix on the wear behavior of the samples. The surface morphology and roughness of the disk specimens were investigated using a digital microscope (DSX, DSX500, Olympus, Shinjuku, Japan) after the wear test. The wear track values of each specimen were measured four times, and the average values were used as the representative value.

3. Results and Discussion

3.1. Materials Characterization

The cross-sectional microstructure of the core–shell structured Ti–(N) powder after heat treatment at 1273 K for 10 min under N_2 atmosphere is shown in Figure 2. Compared to raw CP-Ti powder, the N content of the Ti–(N) powder increased by 0.003 wt% to 10.51 wt%, and a small increment from 0.119 wt% to 0.182 wt% was noted for the O content. The EDS analysis mapping and line-scanning analysis results clearly indicate the N concentration near the surface of the Ti powder, as shown in Figure 2(a-2), which corresponds to the bright area of the SEM image in Figure 2(a-1). A N-rich region was detected as shells with a thickness of 4–6 μm around the raw Ti powder, and some N elements were dissolved in the matrix as solid solutes. This is attributed to the diffusion of N atoms through the top surface of the CP-Ti powder into the center area during the heat treatment in N_2 . Simultaneously, Ti_2N /TiN were formed at the surface owing to the larger N amount from the N_2 atmosphere than that in the diffusion of N atoms, as reported in our previous study [10].

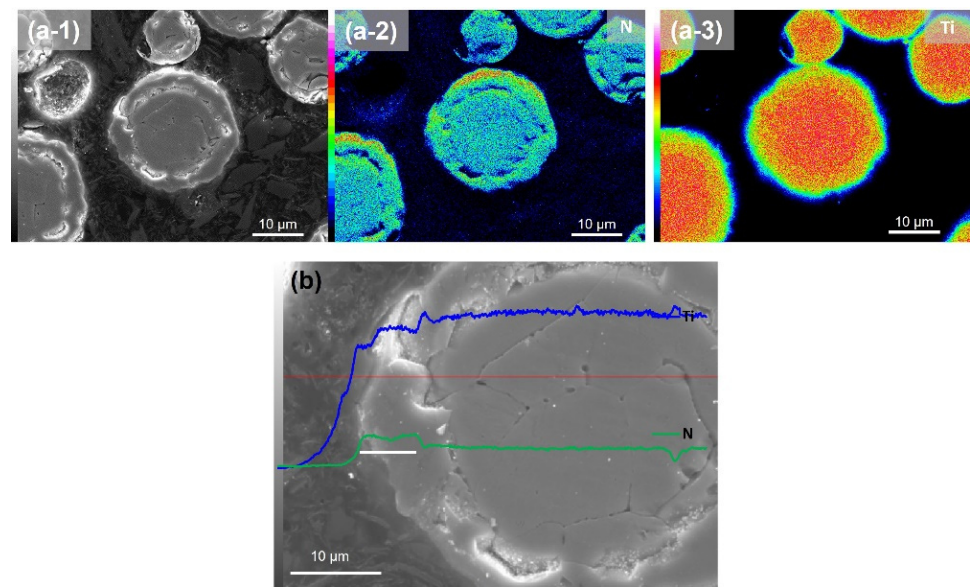


Figure 2. Cross-sectional EDS results of the N_2 -treated Ti powder in N_2 atmosphere at 1273 K for 10 min (a) Mapping result and (b) line-scan image.

The relative density of the SPSed samples was 99.4% and 99.2% for the SPS pure Ti and Ti–20%Ti(N), respectively. Figure 3 shows the SEM–EDS results of the SPS pure Ti and Ti–20%Ti(N) materials used as disk specimens in the wear test. The N-concentrated area was not detected in the SPS pure Ti with 0.003 wt% N, as shown in Figure 3(a-2). However, using the core-shell structured Ti–(N) powder, the bright-green colored area clearly revealed the ring-shaped N atom distribution in the matrix, as shown in Figure 3(b-2), corresponding to high N content. Further, the ring diameter is approximately equal to that of the core-shell-structured Ti–(N) powder, indicating that the original TiN shells of the Ti–(N) powder remained in the SPS Ti–(N) material. The EDS line-scanning profiles and point analysis results quantitatively show three regions with different N contents, as shown in Figure 4, namely, the ring-shaped region with 14.4–15.1 wt% N (No. 1 and 2), the N-rich layer with 5.6–7.4 wt% N (No. 3 and 4), and the interior core area with 1.8–2.2 wt% N (No. 5 and 6). Although EDS analysis is not quantitatively accurate, it is sufficient for the relative comparison of nitrogen contents in these three regions, and the N content of shells and N-rich layers is significantly larger than that of the Ti matrix (1.1–1.4 wt%; No. 7 and 8).

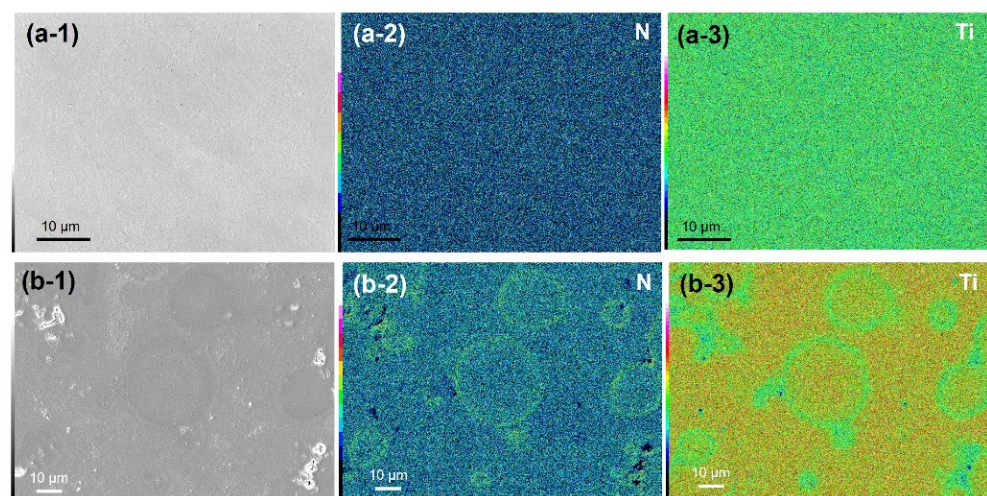


Figure 3. Cross-sectional EDS mapping result for the SPS (a) pure Ti and (b) Ti–20%TiN materials.

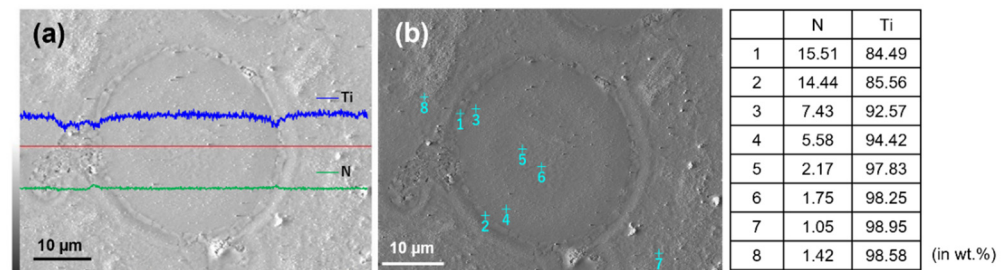


Figure 4. Cross-sectional EDS results for the SPS Ti-20%Ti(N) materials: (a) line-scan image and (b) point analysis.

XRD analysis was conducted to identify the formation of a TiN and N atom solid solution in the α -Ti phase of the four samples: raw pure Ti powder, core-shell structured Ti-(N) powder, SPS pure Ti, and Ti-20%Ti(N) materials. As shown in Figure 5, the raw Ti and SPS Ti samples consist of a single α -Ti phase, and Ti_2N and TiN diffraction peaks were detected in the Ti-(N) powder after the nitriding heat treatment of the raw Ti powder. Compared to the raw pure Ti powder, a peak shift of the main α -Ti (0002) to a low diffraction angle was clearly observed in the core-shell-structured Ti-(N) powder because of the lattice expansion in the c-axis direction by the N atom solution [17]. SPS Ti-20% Ti(N) exhibits a diffraction peak of the Ti_2N compounds, originating from the core-shell structured Ti-(N) powder, which corresponds to the EDS analysis results in Figure 3(b-2,b-3). Furthermore, no peak shifts were observed for the main α -Ti in the SPS Ti-20% Ti(N) sample; that is, the N atoms originating in the Ti-(N) powder were not dissolved in the Ti matrix consisting of raw pure Ti powder (a).

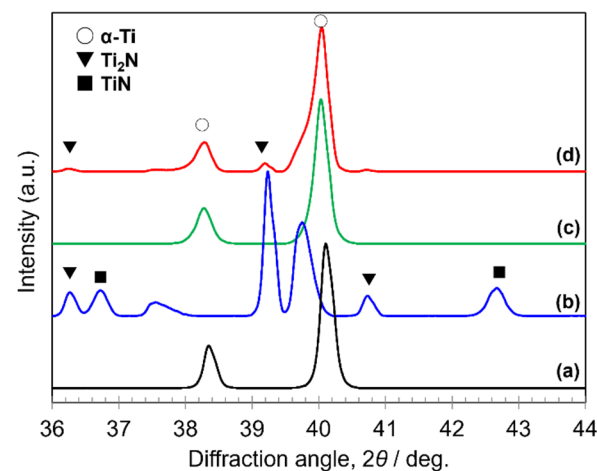


Figure 5. XRD results for the starting powder and SPS materials: (a) pure Ti powder, (b) core-shell-structured Ti(N) powder, (c) SPS pure Ti, and (d) SPS Ti-20%Ti(N).

3.2. Tribological Properties of the Ti Composites with Ring-Shaped Ti_2N

Figure 6 shows the changes in the friction coefficient of the pure Ti and Ti-20%Ti(N) disk specimens from the ball-on-disk wear test. For the pure Ti disk specimen, the period of the unstable initial stage with large changes in the friction coefficient was approximately 2 ks using the SUS304 ball, which is longer than obtained when using the SU440C ball (approximately 1 ks). This unstable behavior is mainly ascribed to the slight stick-slip behavior at the contact interfaces of the specimens during the initial familiarity stage. Considering the average Vickers microhardness measurement of 171, 291, and 653 HV for pure Ti, SUS304, and SUS440C, respectively, the large difference in the microhardness between pure Ti and SUS440C shortens the initial familiarity period because the topmost surface of the soft Ti disk can easily be shaved by a hard SUS440C ball. The friction coefficient profiles obtained using the Ti-20%Ti(N) disk specimen also showed similar

results as that of the pure Ti disk. However, the unstable period in the sample for both ball materials is extremely short, and the friction coefficient variation ($\Delta\mu$) is significantly smaller than that of the pure Ti specimen. This is attributed to the ring-shaped hard TiN dispersoids with a hardness of 793 ± 59 Hv in the matrix [18], which effectively prevented a stick-slip behavior, resulting in the shortened initial familiarity phenomena.

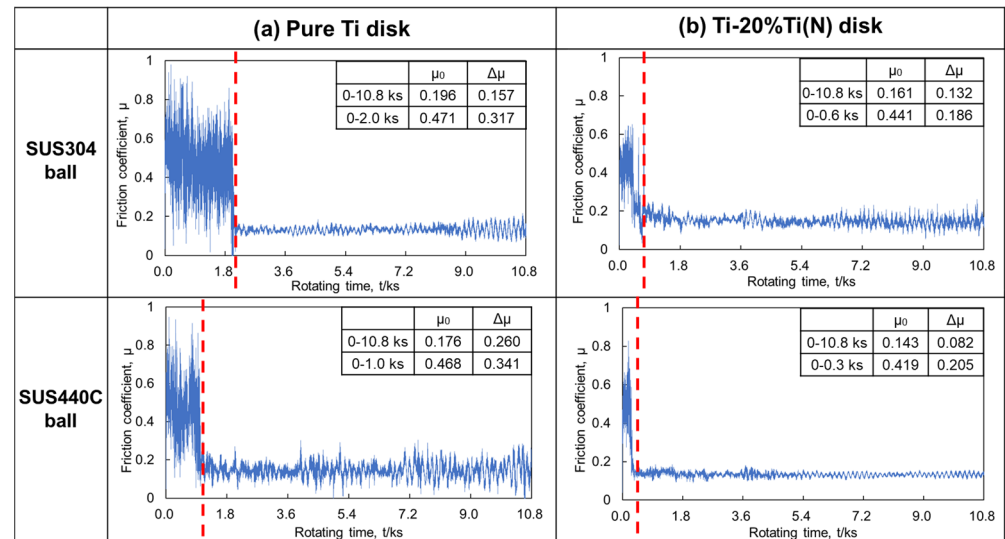


Figure 6. Changes in the friction coefficient and sliding surface profiles of (a) pure Ti and (b) Ti-20%Ti(N) from the ball-on-disk wear test using SUS304 and SUS440C balls as the counter material.

Figure 7 shows the changes in the friction coefficient and sliding surface roughness of the pure Ti disk specimens after the wear test using the SUS440C ball with the applied loads of 2.45, 4.90, and 9.80 N. With the applied load of 2.45 N, the friction coefficient fluctuated throughout the wear test owing to the adhesive wear behavior; the mean friction coefficient (μ_0) and its mean variation ($\Delta\mu$) were 0.191 and 0.385, respectively. In comparison, μ_0 and $\Delta\mu$ had values of 0.153 and 0.220 at 4.90 N, and 0.176 and 0.260 at 9.80 N, respectively. With an increase in the applied load, an initial familiarity phenomenon occurred, followed by the gradual stabilization of the μ value. The wear damage of the disk specimen increased remarkably because of the abrasive wear phenomenon caused by the hard SUS440C ball material.

Using the Ti-20%Ti(N) disk specimens, the mean value of the friction coefficient and its variations were significantly smaller than those of the pure Ti disk (Figure 7), as shown in Figure 8, resulting in lower values of μ_0 and $\Delta\mu$. For example, μ_0 and $\Delta\mu$ had values of 0.147 and 0.045 at 2.45 N, 0.146 and 0.108 at 4.90 N, and 0.143 and 0.082 at 9.80 N, respectively. In addition, the dependence of the μ_0 and $\Delta\mu$ values on the applied load is extremely low; that is, the tribological behavior of the Ti-20%Ti(N) disks with ring-shaped hard TiN dispersoids was stable even with changes in the applied load. The wear damage gradually increased with an increase in the applied load. A significantly smaller increase was observed for than Ti-20%Ti(N) disks than that for the pure Ti disk sample. For the Ti-20%Ti(N) disk sample, the percent decrease of μ_0 and $\Delta\mu$ at 9.80 N were values of 19% and 70%, respectively, compared with that of the pure Ti disk sample. The Ti-20%Ti(N) disk sample consisted of (i) a pure Ti matrix, (ii) ring-shaped hard TiN dispersoids, and (iii) interior core regions with N solid solution hardening, as shown in Figures 3b and 4. The mechanically improved regions strengthened by the TiN compounds and N solutes effectively increased the wear resistance, thereby decreasing the friction coefficient and its variations. In addition, ring-shaped hard TiN dispersoids protruding from the sliding surface, shown in Figure 9, increased the formability of an oil lubricant film around the TiN circular compounds, resulting in a low and stable friction coefficient. These results are in good agreement with the strengthening effect of hard particles in the matrix composite [16,19].

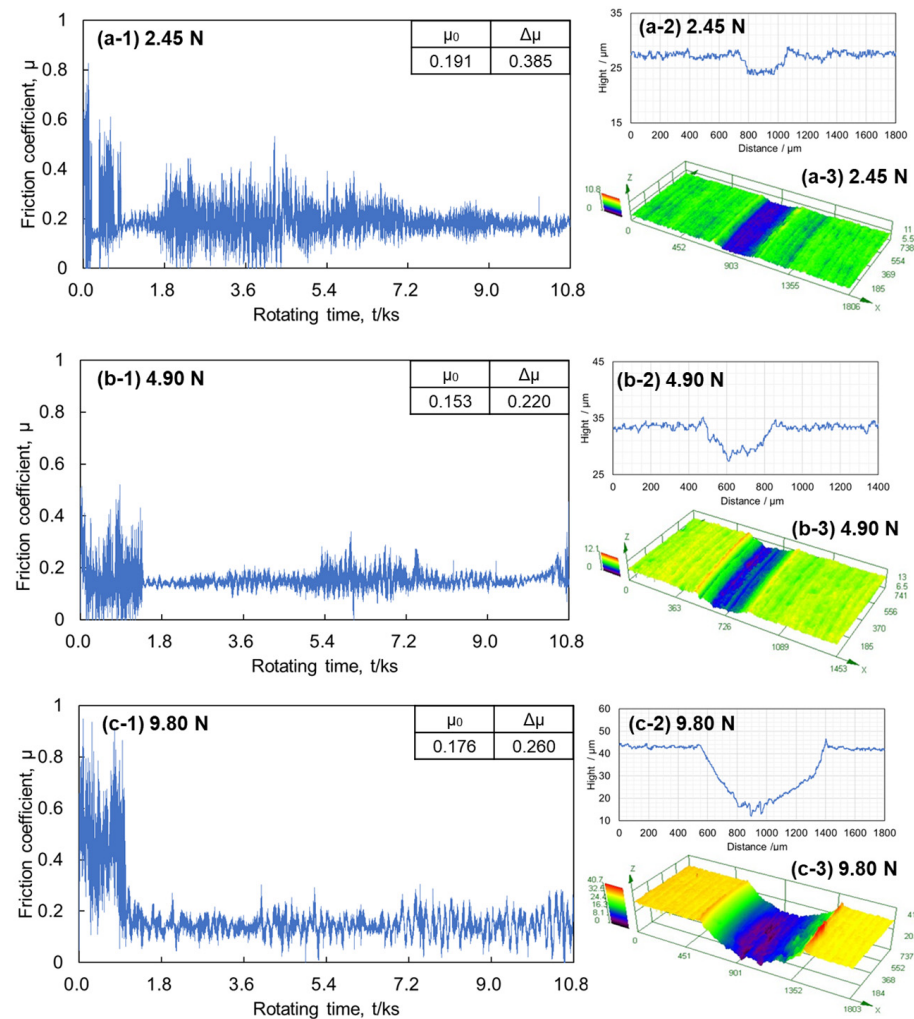


Figure 7. Changes in the friction coefficient and sliding surface profile of the pure Ti plate using SUS440C ball under an applied load of (a) 2.45 N, (b) 4.90 N, and (c) 9.80 N.

Figure 10 summarizes the tribological and wear properties of the pure Ti and Ti–20%Ti(N) disk specimens. Compared to the monolithic Ti sample, the mean friction coefficient and its variations in the Ti–20%Ti(N) disk were significantly smaller and more stable with an increase in the applied load. In both disk specimens, the amount of wear loss and sliding width tended to increase with an increase in the applied load. In particular, when a load of 9.80 N was applied, the wear resistance of the Ti–20%Ti(N) samples was superior to that of pure Ti owing to the hard TiN dispersoids.

Surface damage observations were performed on the sliding tracks of each disk specimen and a SUS440C ball after the wear test while changing the applied load, as shown in Figure 11. The pure Ti disk specimen had numerous abrasive wear scratches, as shown in Figure 11(a-1). The EDS analysis results revealed that the adhesion area of Fe, originating from the SUS440C ball, gradually increased with an increasing applied load. Scratches were observed along the sliding direction of the counter SUS440C balls. Moreover, Ti adhesion and wear debris from the disk specimen were noted. In contrast, the Ti–20%Ti(N) disk surface exhibited slight scratches and a small amount of Fe adhesion on the sliding track, as shown in Figure 11(b-1). With an increase in the applied load, the track width gradually increased; however, severe seizure phenomena were not observed in any of the disk specimens. The SUS440C balls, as shown in Figure 11(b-2), also exhibited a slight Ti adhesion on the sliding surface, indicating mild wear at the sliding interface with the use of the Ti–20%Ti(N) disk sample. As a result, when a load of 9.8 N was applied to the pure titanium disk, the values of disk wear loss and the disk wear width increased significantly,

showing 1.9 mg and 763 μm , respectively, as shown in Figure 10. In comparison, those values of the Ti–20%Ti(N) disk were 0.5 mg and 609 μm , respectively.

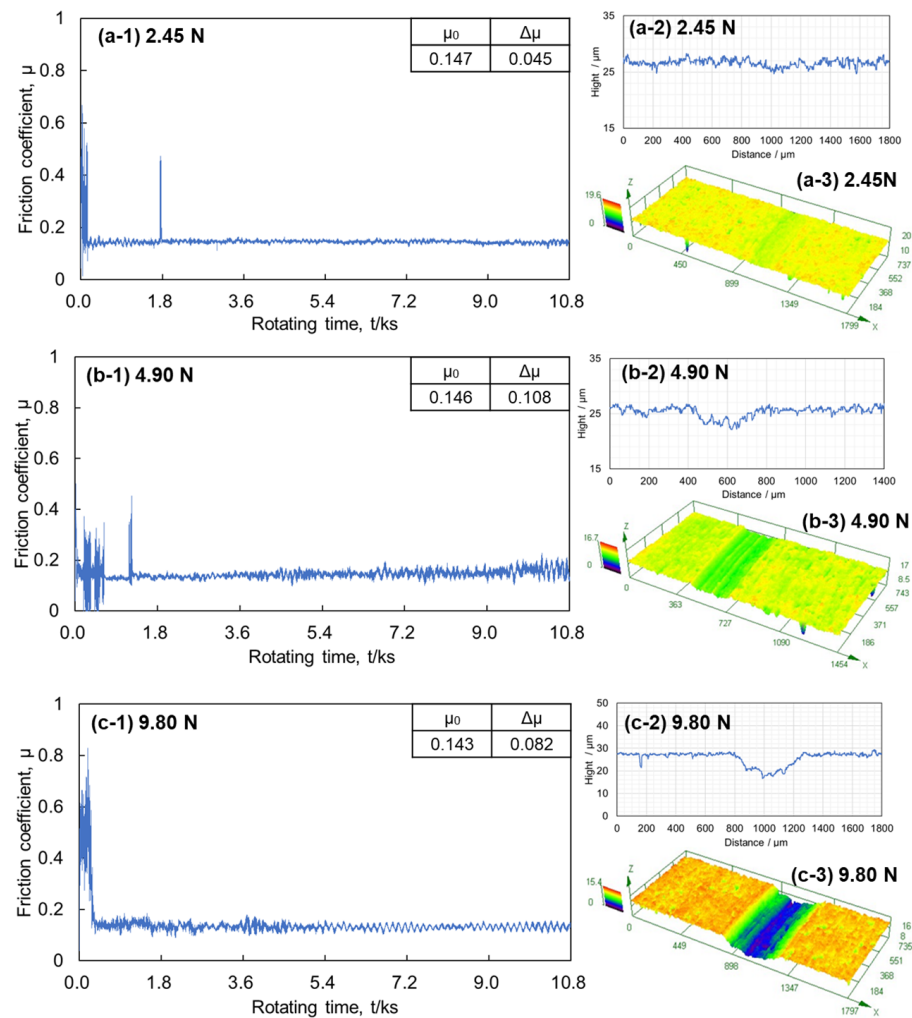


Figure 8. Changes in the friction coefficient and sliding surface profile of Ti–20%Ti(N) using SUS440C ball under an applied load of (a) 2.45 N, (b) 4.90 N, and (c) 9.80 N.

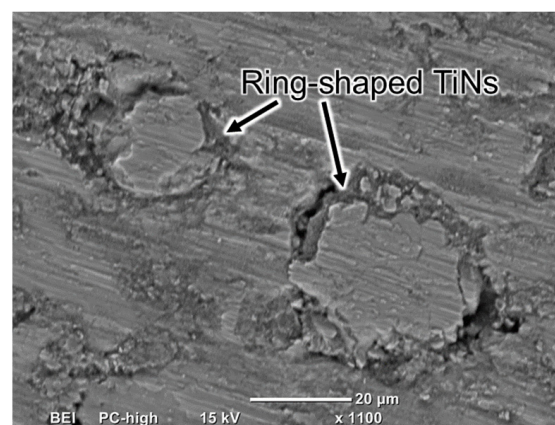


Figure 9. SEM observation results of ring-shaped TiN dispersoids on sliding surface of Ti–20%Ti(N) disk specimen after wear test under applied load of 2.45 N.

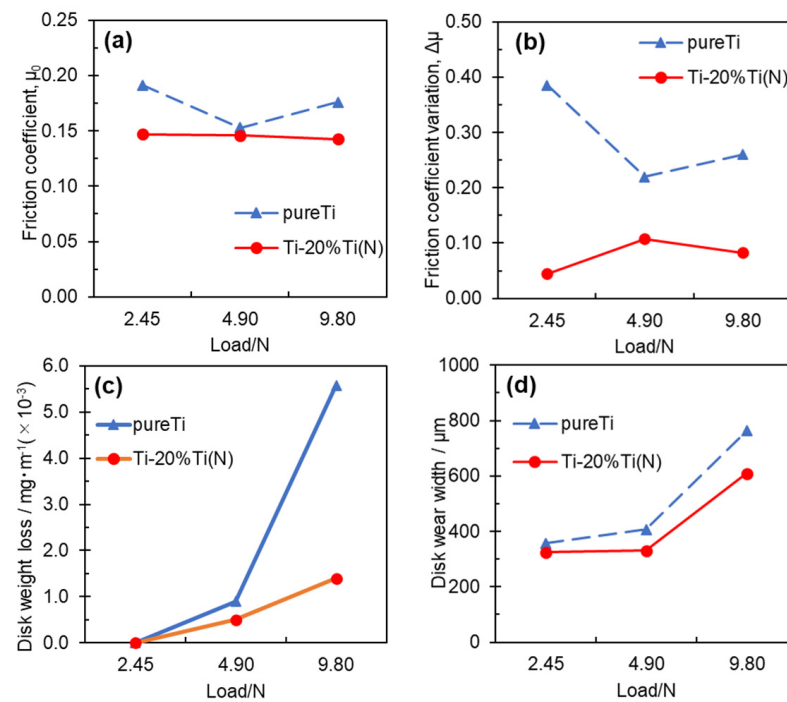


Figure 10. Dependence of (a) friction coefficient value; (b) friction coefficient variation value; (c) disk weight loss value; (d) disk wear width value on applied loads of pure Ti and Ti-20%Ti(N).

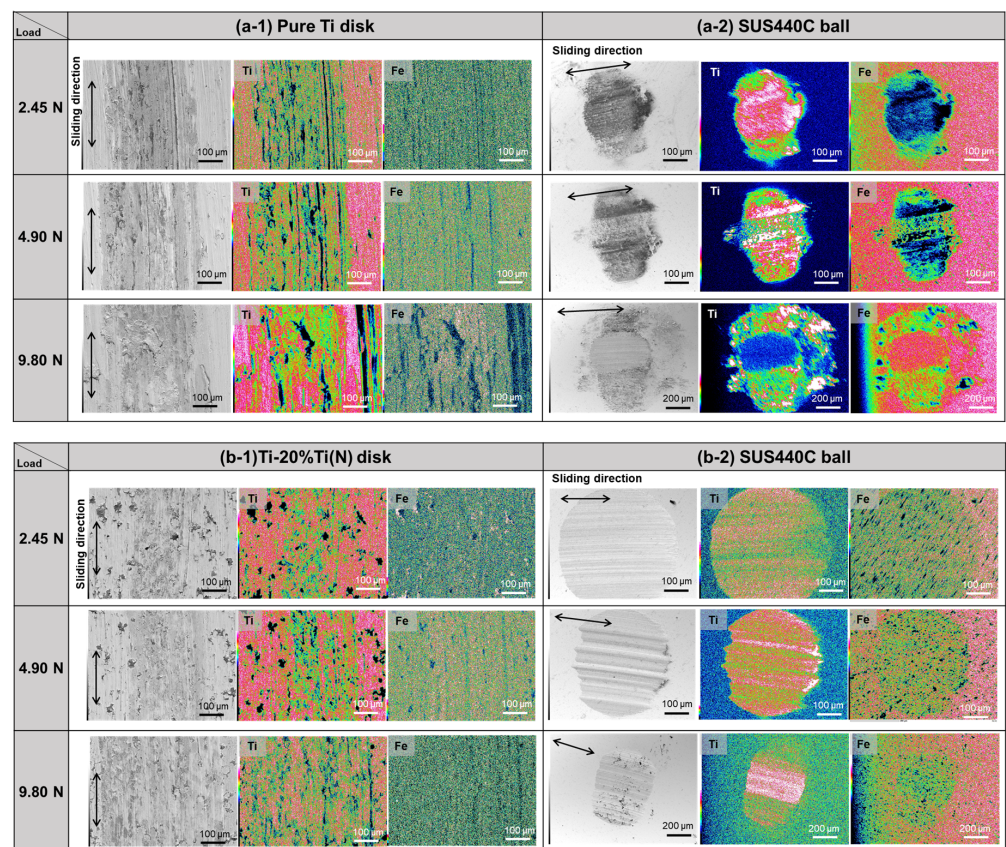


Figure 11. SEM-EDS analysis on the wear surface of the pure Ti specimen, Ti-20%TiN specimen, and SUS440C ball as the counter material under applied loads of 2.45, 4.90, and 9.80 N.

4. Conclusions

In this study, Ti matrix composites with ring-shaped hard TiN dispersoids were fabricated by consolidating pre-mixed pure Ti and core-shell structured Ti-(N) powders by a PM route with SPS. The ball-on-disk wear test under oil lubrication conditions clarified the improved tribological properties and wear resistance of these composites, compared to monolithic pure Ti material. The main results of this study are summarized as follow:

1. Core-shell structured Ti-(N) powder, nitrogen content of 10.51 wt%, was obtained by heat treatment at 1273 K for 10 min under N₂ gas, which is significantly higher than that of 0.003 wt% raw CP-Ti powder. It consisted of (i) the Ti₂N/TiN region as shells with a thickness of 4–6 µm (ii) N elements dissolved in the matrix, and (iii) the raw Ti powder.
2. The initial familiarity period of the Ti-TiN composites was shortened, and subsequently, low and stable friction coefficients were achieved, compared to the pure Ti specimen employed as a reference material. The average value of the friction coefficient and its mean variation were 0.143–0.147 and 0.045–0.108 of the Ti-TiN composites; in contrast, those values of the pure Ti sample were 0.153–0.191 and 0.220–0.385. SEM-EDS analysis clarified that the pure Ti disk specimen had numerous abrasive wear scratches and Fe adhesion from the SUS440C ball. The percentage of the weight loss was drastically decreased by 74% when a load of 9.8 N was applied to the Ti-TiN composites, in comparison with the pure titanium disk.
3. These improved properties were mainly ascribed to two factors: the ring-shaped hard TiN dispersoids effectively prevented the adhesion phenomenon and improved the oil film formability, and the N solid solution in the core region increased the microhardness and abrasive wear resistance. The understanding of the amount and morphology of the ring-shaped hard TiN dispersoids in a Ti matrix will be addressed in our future work.

Author Contributions: J.U.: conceptualization, investigation, writing—original draft, writing—review and editing, and visualization; H.F.: investigation and visualization; R.T.: investigation; T.T.: visualization; A.I.: methodology and investigation; S.K.: investigation and visualization; Y.Y.: methodology; S.L.: methodology; and K.K.: supervision. All authors have read and agreed to the published version of the manuscript.

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