Differences in Wear Behaviors at Sliding Contacts for β -Type and ($\alpha + \beta$)-Type Titanium Alloys in Ringer's Solution and Air

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The wear behaviors of combinations comprised of a new titanium alloy, Ti-29Nb-13Ta-4.6Zr (TNTZ) and a conventional titanium alloy, Ti-6Al-4V extra-low interstitial (Ti64) were investigated using ball-on-disc type configuration in Ringer's solution for metal-to-metal contacting biomedical implant applications. The worn surfaces, wear debris, and subsurface damage were analyzed using a scanning electron microscopy combined with energy-dispersive spectroscopy and an electron probe microanalysis. Moreover these wear characteristics are compared to the results obtained from the wear tests in air. Volume loss of both the disc and ball primarily increases for the TNTZ disc/TNTZ ball combination in Ringer's solution compared to that in air. This increase can be explained by the ejection of debris from the contact region induced by the presence of Ringer's solution. Subsequently, this increases the number of areas with asperity junctions between the disc and ball, thereby leading to severe delamination wear. In contrast, the volume loss of both the disc and ball decrease for the Ti64 disc/Ti64 ball combination in Ringer's solution compared to that in air. It is believed that the predominately abrasive wear associated with Ti64 is effectively suppressed by the use of Ringer's solution. [doi:10.2320/matertrans.M2014365]

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1. Introduction

Pure titanium (Ti) and its alloys are currently attracting attention as biomedical materials because of their high specific strength, good biocompatibility, and good corrosion resistance. Although their wear resistance is generally poor,¹⁾ they are often used for biomedical applications including in devices with parts in metal-to-metal contact. Wear resistance is one of the most important material properties for these types of applications because the devices often contain many mechanical joints.

The poor wear resistance of Ti and its alloys is attributed to a few main factors.²⁾ First, Ti and its alloys have low resistance to plastic shearing and low work hardening. In addition, only minimal protection is provided by the surface oxide formed because of the high temperature induced from the friction that occurs during dry sliding. To overcome these limitations, many different surface treatments have been applied to Ti and its alloys.^{1,3,4)} However, with the exception of wear resistance, such surface treatments are sometimes detrimental to other material properties; for example, gas nitriding enhances wear resistance of titanium alloys, whereas deteriorating its fatigue strength.⁴⁾ In order to improve the wear resistance without any trade-off, it is necessary to study the wear mechanisms of the untreated alloy.

When titanium alloys are used for the heads of artificial hip joints or the rods and screws of spinal fixation devices, it is possible for their performance to degrade because of frictional wear from sliding or movement that induces small amplitude changes.⁵⁾ Consequently, failure can easily occur because of the excessive wear experienced by the components during performance of the applications. This wear

behavior of the sliding system is dependent upon many factors, including the properties of the specimen and counterface materials, their interaction with the environment, and the experimental conditions.⁶⁾ Two types of titanium alloys were tested in this study. The first is the conventional ($\alpha + \beta$)-type Ti-6Al-4V extra low interstitial (Ti64) alloy, which accounts for approximately 45–60% of the total titanium alloys produced globally,⁷⁾ and the second is a newly developed β -type Ti alloy for biomedical applications, Ti-29Nb-13Ta-4.6Zr (TNTZ). It has been reported that the vanadium in Ti64 is toxic to the human body,⁸⁾ and stress shielding can occur because the Young's modulus of Ti64 (approximately 110 GPa) is higher than that of the cortical bone (approximately 10–30 GPa).⁹⁾ Conversely, TNTZ exhibits good biocompatibility because it is nontoxic, and has a lower Young's modulus (approximately 60 GPa) than that of Ti64.¹⁰⁾

It is well known that low wear resistance results in implant loosening and that the presence of wear debris causes inflammatory reactions that result in the patient with the implant experiencing pain.^{11,12)} Thus, a better understanding of the mechanisms involved in the friction and wear of Ti alloys is required to improve their wear properties. The wear behaviors and mechanisms of untreated Ti64 and TNTZ in air have been analyzed and compared by Lee *et al.*¹³⁾ on comparing between untreated Ti64 and TNTZ in air. From the results, it is concluded that volume losses (V_{loss}) of the TNTZ discs and balls is larger than that of the respective Ti64 discs and balls. Further, when the TNTZ disc slides against the TNTZ ball, V_{loss} of both the disc and ball exhibits the maximum values. This result is related to severe subsurface deformation of TNTZ, which is caused by lower resistance to plastic shearing of TNTZ than that of Ti64 induces delamination, resulting in higher wear rate. However, the wear behaviors of Ti alloys in the human body differ from those in air.¹⁴⁾ Therefore, the wear properties of TNTZ/

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TNTZ, Ti64/Ti64, and Ti64/TNTZ combinations were examined using a frictional wear-testing machine in a simulated body environment (Ringer's solution) at 310 K. Moreover, the wear characteristics of TNTZ/TNTZ, Ti64/Ti64, and Ti64/TNTZ combinations in air were also examined once more from the previous results¹³⁾ and newly obtained some results in this study, to compare to the results obtained in Ringer's solution.

2. Experimental Procedure

2.1 Materials

Wear tests were performed using a ball-on-disc configuration. The balls and discs used in this study were same as those used previously.¹³⁾ Hot-rolled plates of Ti64 with a thickness of 4 mm (Ti: bal., Al: 6.00, V: 3.99, O: 0.14, C: 0.01, N: 0.002 mass%) were annealed at 1023 K for 3.6 ks in vacuum followed by air-cooling. In addition, hot-forged bars of TNTZ with a diameter of 25 mm (Ti: bal., Nb: 29.4, Ta: 13.0, Zr: 4.64, O: 0.06, C: 0.01, N: 0.008 mass%) were hot-rolled at 1373 K to form plates with a thickness of 3 mm, followed by air-cooling. Then, the TNTZ plates were subjected to a solution treatment at 1063 K (β transus temperature + 50 K) for 3.6 ks in an Ar atmosphere followed by water quenching. The Ti64 and TNTZ discs (20 mm $\times$ 20 mm $\times$ 2 mm) were machined from the aforementioned Ti64 and TNTZ plates, respectively.

On the other hand, the 4.8 mm diameter Ti64 and TNTZ balls were machined using an annealed 6 mm diameter Ti64 bar (Ti: bal., Al: 6.25, V: 3.98, O: 0.13, C: 0.18, N: 0.007 mass%), and a hot-forged 7 mm diameter TNTZ bar (Ti: bal., Nb: 29.4, Ta: 13.0, Zr: 4.64, O: 0.06, C: 0.01, N: 0.008 mass%), respectively. The microstructure of the Ti64 disc exhibits an equiaxed α structure composed of a small amount of primary α phase and a large amount of (secondary $\alpha + \beta$ phase), whereas the microstructure of the TNTZ disc exhibits single equiaxed β grains. The microstructure of the Ti64 and TNTZ balls display a hot-forged ($\alpha + \beta$)-type structure and single equiaxed β grains, respectively. The grain sizes of the balls are smaller compared to those of the discs because of a high reduction ratio developed during hot forging.

The hardness of these balls and discs has also been reported previously.¹³⁾ The hardness (Hv) of the Ti64 discs (318.2 ± 2.50) is higher than that of the TNTZ discs (182.2 ± 3.53). Moreover, the hardness of the Ti64 balls (344.8 ± 2.44) is also higher than that of the TNTZ balls (217.4 ± 3.60). Further, the hardness of the Ti64 and TNTZ discs is almost similar to, but slightly higher than that of the Ti64 and TNTZ balls, respectively. This result can be explained because the grain diameters of the Ti64 and TNTZ ball are smaller than those of the Ti64 and TNTZ disc, respectively.

2.2 Frictional wear test

Figure 1 shows the schematic drawing of the frictional wear testing machine used in this study. Frictional wear tests were carried out with a load of 4.9 N in Ringer's solution at 310 K using a ball-on-disc frictional wear-testing system. The wear tests were performed for up to 1.2×10^4 cycles at

Fig. 1 Schematic drawing of friction wear testing machine.

60 rpm for a test duration of 1.2×10^4 s. The sliding speed for each wear test was 31.4 mm/s and the diameter of the wear track was 10 mm. Before and after each wear test, both the discs and balls were cleaned with acetone and dried in air at room temperature for 21.6 ks to avoid contamination. The weight of each disc and ball before and after the wear test were W_1 and W_2 , respectively; these weights were measured using a precise electric balance (± 0.0001 g). The wear weight loss (W_{loss}) was obtained from the following equation:

$$W_{\text{loss}} = W_2 - W_1. \quad (1)$$

To measure the amount of wear debris generated during the wear tests, W_{loss} was converted into V_{loss} using the following equation:

$$V_{\text{loss}} = \frac{W_{\text{loss}}}{D_{\text{alloy}}}. \quad (2)$$

D_{alloy} is the mass per unit volume, i.e., the density of each alloy (Ti64 = 4.4 mg/mm³ and TNTZ = 6.0 mg/mm³), respectively. Moreover, the frictional coefficients of the sliding couple were also recorded continuously throughout testing using a computer data-acquisition system. For comparison, the wear characteristics in air examined at room temperature under the condition same as the previous study.¹³⁾

2.3 Metallurgical analysis of worn surfaces and wear debris

The wear debris was analyzed using a scanning electron microscopy (SEM) combined with energy dispersive spectroscopy (EDS), and the wear mechanisms were investigated by analyzing the worn surfaces and wear debris. Moreover, some of the discs were sectioned parallel to the wear track (sliding direction) by a wire-cutting electric discharge machine to enable SEM observation of the subsurface damage incurred as the result of the wear testing. The cut surfaces were first metallographically polished using up to a 2400 grit-sized silicon carbide papers and were subsequently buff-polished using an Al₂O₃ powder with an average diameter of 1 μ m and a colloidal SiO₂ solution. Electron probe micro-analyzer (EPMA) observations were also made to enable the analysis of the oxygen (O) content within the wear track of the discs.

3. Results

3.1 Wear properties

V_{loss} was calculated to compare the amount of wear debris generated during the wear tests in Ringer's solution. Figure 2(a) represents the V_{loss} of discs and balls made of

Fig. 2 Volume losses of Ti64 and TNTZ discs and balls obtained from the frictional wear tests in (a) Ringer's solution and (b) air (from Ref. 13).

Fig. 3 Frictional coefficient of (a) Ti64 disc against Ti64 ball, (b) Ti64 disc against TNTZ ball, (c) TNTZ disc against Ti64 ball, and (d) TNTZ disc against TNTZ ball combinations, respectively in Ringer's solution and air as a function of sliding distance obtained in this study.

Ti64 and TNTZ subjected to the frictional wear tests in Ringer's solution at 310 K. The V_{loss} of discs and balls made of TNTZ tend to be larger than those of Ti64, regardless of the mating alloys. Further, when the TNTZ disc slides against the TNTZ ball, V_{loss} of both the disc and ball exhibits the maximum values. This V_{loss} trend, dependent upon the type of alloys used, corresponds to the results obtained previously in air (Fig. 2(b)¹³). Thus, it can be presumed that TNTZ has lower resistance to plastic shearing, and that consequently, a large amount of shear strain could be stored during sliding as reported in the previous study.¹³

In addition, interestingly, V_{loss} in Ringer's solution increases for some components in combinations compared to that in air. Specifically, V_{loss} of both disc and ball increases considerably for the TNTZ disc/TNTZ ball combination

(TNTZ combination) in Ringer's solution compared to air. V_{loss} generally decreases in Ringer's solution compared to air because Ringer's solution can act as a liquid lubricant during sliding.^{15–17} In this study, however, decreases in V_{loss} of both disc and ball during immersion in Ringer's solution during wear testing is observed for only the Ti64 disc/Ti64 ball combination (Ti64 combination). Detailed discussion of the wear analysis will be presented in the following section.

The frictional coefficient variations of each material combination of discs and balls with sliding distance in Ringer's solution and air are presented in Fig. 3. The frictional coefficient behaviors of the combinations including Ti64 components are lower than that of the TNTZ combinations in both Ringer's solution and air, indicating that TNTZ exhibits more severe wear compared to Ti64 in

Fig. 4 SEM micrographs showing wear scars on mating balls and corresponding EDS analysis; SEM micrographs of (a) Ti64 ball against Ti64 disc, (b) Ti64 ball against TNTZ disc, (c) TNTZ ball against Ti64 disc, and (d) TNTZ ball against TNTZ disc obtained from frictional wear tests in Ringer's solution and (e) Ti64 ball against Ti64 disc, (f) Ti64 ball against TNTZ disc, (g) TNTZ ball against Ti64 disc, and (h) TNTZ ball against TNTZ disc obtained from frictional wear tests in air, and EDS patterns for (i) point A, (j) point B, (k) point C, and (l) point D obtained in this study.

both Ringer's solution and air. Moreover, the average friction coefficients over the total distance of the combinations including Ti64 components do not exceed 0.5 both in air and Ringer's solution. This is because hexagonal close-packed (hcp) lattice-structured metals such as Ti are not likely to generate frictional coefficient values above 0.5 even when unlubricated because of the limited number of slip planes.¹⁸⁾ In contrast, the average frictional coefficients for the TNTZ combination increase considerably in Ringer's solution compared to air and this signifies that the TNTZ combination experiences more severe wear in Ringer's solution than in air.

3.2 Morphologies of worn surfaces and debris

The morphologies of the worn specimen surfaces and the wear debris generated during wear testing in Ringer's solution and air were examined using an SEM equipped with EDS. As shown in Fig. 4, wear scars are produced on the

surface of the Ti64 and TNTZ balls during the wear tests. The scars created on the TNTZ balls following contact with both the Ti64 and TNTZ discs exhibit more severe wear than those of the Ti64 balls following contact with discs from both alloys in Ringer's solution as shown in Figs. 4(a)–(d). This trend corresponds well with the results in Figs. 4(e)–(h) obtained in air.

The corresponding EDS analysis of the adhered material within the Ti64 ball scar tested in Ringer's solution, marked as point A in Fig. 4(b), demonstrates that it contains niobium (Nb) and tantalum (Ta) (Fig. 4(i)). The EDS analysis of the adhered material within the Ti64 ball scar tested in air in this study, marked as point C in Fig. 4(f), also demonstrates that it contains niobium (Nb) and tantalum (Ta) (Fig. 4(k)). In the cases of the TNTZ balls, within the wear scar, aluminum (Al) is detected as shown in Fig. 4(j) and the Ti64 adhesion is clearly observed on the wear scar of the TNTZ ball at point B

Fig. 5 SEM micrographs of wear tracks on (a) Ti64 disc against Ti64 ball, (b) Ti64 disc against TNTZ ball, (c) TNTZ disc against Ti64 ball, and (d) TNTZ disc against TNTZ ball obtained from frictional wear tests in Ringer's solution and (e) Ti64 disc against Ti64 ball, (f) Ti64 disc against TNTZ ball, (g) TNTZ disc against Ti64 ball, and (h) TNTZ disc against TNTZ ball obtained from frictional wear tests in air obtained in this study.

in Fig. 4(c) in Ringer's solution. However, no adhesion material was observed within the wear scar of the TNTZ ball against the Ti64 disc tested in air (Fig. 4(g)) according to the EDS results (Fig. 4(l)) obtained in this study. Moreover, the morphology of wear scar of the TNTZ combination exhibits more severe wear with large plastic deformation in Ringer's solution than in air as shown in Figs. 4(d) and (h), respectively.

Figures 5(a)–(d) represents the wear tracks on the Ti64 and TNTZ discs observed after the friction wear tests in Ringer's solution. The wear track of the Ti64 combination are characterized by small extent of surface deformation with the presence of continuous uniform grooves, all indicative of mild wear, as shown in Fig. 5(a). These characteristics of the wear tracks are similar to those obtained in air that exhibits oxidative and abrasive wear, as shown in Fig. 5(e). On the other hand, the wear track of the Ti64 disc also exhibits small extent of surface deformation with the presence of continuous uniform grooves when the mating ball material is TNTZ in air (Fig. 5(f)). While, the wear track of the Ti64 disc exhibits slightly more severe surface deformation when the mating ball material is TNTZ (Fig. 5(b)) compared to that when the mating ball material is Ti64 in Ringer's solution (Fig. 5(a)).

Conversely, the wear tracks of the TNTZ discs exhibit a galling wear-like appearance, with greater surface deformation and damage in Ringer's solution, as shown in Figs. 5(c) and (d). These features corresponds with the results obtained in air (Figs. 5(g) and (h)), indicating that the wear occurs predominantly by adhesion and delamination.¹³⁾ Furthermore, it is observed that the TNTZ disc has considerably more severe plastic deformation with large adhesion material when the mating ball material is TNTZ in Ringer's solution rather than in air, as shown in Figs. 5(d) and (h), respectively.

The morphological analysis of the wear debris collected from the discs and balls at the end of frictional wear tests in Ringer's solution is shown in Figs. 6(a)–(d). The cutting chip-like wear debris can be clearly observed in the combinations containing the Ti64 discs, as shown in Figs. 6(a) and (b), indicating that a microcutting action occurs during sliding. The corresponding EDS analysis of the cutting chip-like wear debris, marked as point A (Fig. 6(b)),

shows that it comprises of Ti and Al (Fig. 6(i)). This result suggests that the abrasive wear also occurs^{19,20)} in Ringer's solution during the sliding of the Ti64 disc in same manner as the results obtained in air (Figs. 6(e) and (f)), regardless of the mating ball material. The corresponding EDS analysis of the cutting chip-like wear debris generated from the Ti64 disc/TNTZ ball combination tested in air, marked as point D (Fig. 6(f)), shows that it comprises of Ti and Al (Fig. 6(l)).

In contrast, a large amount of flake-like wear debris are observed in the ball-on-disc combinations utilizing the TNTZ discs, as shown in Figs. 6(c) and (d) indicating that delamination wear occurs.^{21–23)} The corresponding EDS analysis of the flake-like wear debris generated from the Ti64 disc/TNTZ ball tested in both Ringer's solution and air, marked as point C (Fig. 6(c)) and point E (Fig. 6(g)), shows that it comprises of Ti, Nb, and Ta (Figs. 6(k) and (m)). Particularly, the flake-like debris generated from the TNTZ combination collected from the test in Ringer's solution (Fig. 6(d)), is larger than that from the TNTZ combination tested in air (Fig. 6(h)). This signifies that the TNTZ combination suffers more severe plastic deformation at the contact region between the disc and ball in Ringer's solution compared to air.

Specifically, the corresponding EDS analysis of the flake-like debris in Fig. 6(b), marked as point A, denotes that it is composed of Ti and Al (Fig. 6(i)). Thus, it is believed that delamination wear occurs for the Ti64 disc against the TNTZ ball in Ringer's solution, in contrast to the behavior observed in air. Therefore, V_{loss} of the Ti64 disc increase in Ringer's solution when the mating ball material is TNTZ compared to in air, since the wear mechanism transition occurs from the abrasive wear to the delamination wear.

Figure 7 also represents the morphological analysis of the wear debris collected from the discs and balls at the end of frictional wear tests for the TNTZ combination in Ringer's solution and air. According to the model of debris formation in adhesive wear,²⁴⁾ the formation of a debris fragment by asperity rupture is followed by its adhesive transfer to the counterface, to form a new asperity on that surface. Consequently, further sliding causes more fragments to be formed, which adhere to the original fragment until a much

Fig. 6 SEM morphologies of debris collected at the end of frictional wear tests in Ringer's solution and air for (a) Ti64 disc against Ti64 ball, (b) Ti64 disc against TNTZ ball, (c) TNTZ disc against Ti64 ball and (d) TNTZ disc against TNTZ ball obtained from frictional wear tests in Ringer's solution, and (e) Ti64 disc against Ti64 ball, (f) Ti64 disc against TNTZ ball, (g) TNTZ disc against Ti64 ball and (h) TNTZ disc against TNTZ ball obtained from frictional wear tests in air, and EDS patterns for (i) point A, (j) point B, (k) point C, (l) point D, and (m) point E obtained in this study.

Fig. 7 SEM morphologies of debris collected at the end of frictional wear tests for TNTZ disc against TNTZ ball in (a) Ringer's solution and (b) air obtained in this study.

larger conglomerate debris eventually becomes detached. This debris may be flattened and elongated in the direction of sliding by further plastic deformation. The morphologies of the debris for the TNTZ combinations in both Ringer's

solution and air exhibit multi-layered and flattened structures, as shown in Figs. 7(a) and (b). This result also strongly suggests that the TNTZ combinations experience strong adhesion as aforementioned above.

Fig. 8 SEM morphologies of debris collected at the end of frictional wear tests for TNTZ disc against TNTZ ball in (a) Ringer's solution and (b) air obtained in this study.

Fig. 9 SEM micrographs of longitudinal sections of wear tracks for (a) Ti64 disc against Ti64 ball, (b) Ti64 disc against TNTZ ball, (c) TNTZ disc against Ti64 ball, and (d) TNTZ disc against TNTZ ball obtained from frictional wear tests in Ringer's solution and (e) Ti64 disc against Ti64 ball, (f) Ti64 disc against TNTZ ball, (g) TNTZ disc against Ti64 ball, and (h) TNTZ disc against TNTZ ball obtained from frictional wear tests in air obtained in this study.

A large amount of blocky debris is also observed from all combinations in both Ringer's solution and air. It is believed that the blocky debris is generated from the abrasion of the disc or ball, or the fragmentation of large debris such as flake-like debris. The shape of blocky debris is roughly round because they are abraded or deformed during sliding. The morphological analysis of the blocky debris collected from the discs and balls at the end of frictional wear tests for the TNTZ combination in Ringer's solution and air is also shown in Fig. 8. It is believed that the blocky debris is generated from the abrasion of the disc or ball, or the fragmentation of large debris such as flake-like debris. The average dimension of the blocky debris is clearly larger in Ringer's solution ($10.5\ \mu\text{m}$) than in air ($2.9\ \mu\text{m}$).

Figures 9(a)–(d) show the longitudinal cross-sections of wear tracks of the Ti64 and TNTZ discs obtained from the frictional wear tests performed in Ringer's solution. The subsurface crack formation in the disc occurs when the asperity of the mating ball plows into the surface of the disc and the normal and tangential loads are transmitted through the contact points. As shown in Fig. 9, the subsurface cracks are clearly visible beneath the wear tracks in the cross-section

of all discs, with the exception of the Ti64 combination (Fig. 9(a)). It is presumed that Ringer's solution does not act as a lubricant and thereby cannot reduce strain accumulation in those discs during sliding. Specifically, the subsurface crack can be observed in the cross-section of the wear tracks of the Ti64 disc/TNTZ ball combination that was tested only in Ringer's solution, as shown in Fig. 9(b). This finding corresponds to the aforementioned results from both V_{loss} (Fig. 2) and morphological analysis of the wear debris (Fig. 6) that indicate that the severity of wear increases in Ringer's solution owing to the delamination of the Ti64 disc.

Oxidation phenomena are also important in sliding wear because all Ti alloys form oxide films in air. It is well known that some local temperatures at the sliding interface are considerably higher than those of the surroundings and that these temperature differences may be enhanced at the asperity contacts by transient "flashes".²⁵⁾ Flash temperatures of several hundred degrees can readily be generated during sliding. Therefore, only moderate sliding speeds are needed with most metals for these flash temperatures to become sufficiently high to cause extensive surface oxidation.²⁵⁾ Results of the EPMA assessment of the O intensity maps

Fig. 10 SEM micrographs and corresponding EPMA maps of oxygen on wear tracks of discs against TNTZ ball obtained from frictional wear tests in Ringer's solution and air; (a) and (e) Ti64 disc tested in Ringer's solution, (b) and (f) Ti64 disc tested in air, (c) and (g) TNTZ disc tested in Ringer's solution, and (d) and (h) TNTZ disc tested in air obtained in this study.

Fig. 11 Schematic drawing of the differences between (a) two-body abrasion and (b) three-body abrasion.

for both the Ti64 and TNTZ disc tracks against the TNTZ ball are presented with corresponding SEM micrographs in Fig. 10. It is clearly observed that the Ti64 discs exhibits a higher O intensity compared to the TNTZ discs in both Ringer's solution and air. In addition, evaluation demonstrates partial oxidation of the wear track of the Ti64 discs. This result can be explained because the extensive oxidation occurs only at the asperity contact and is associated with the flash temperatures at low ambient temperatures.²⁵⁾

4. Discussion

4.1 Debris characteristics in abrasive and delamination wear

Material is removed from a surface by hard debris or hard protuberances during abrasive wear. A distinction can be made between two-body abrasive wear and three-body abrasive wear with regard to the debris effects at the contact region, as presented in Fig. 11. When debris is initially present in the space between the disc and ball, it remains in the contact region between the disc and ball during the wear tests. In this case, the debris can act as a third-body so that its effects on abrasion at the contact region in three-body wear should be considered. However, if a large amount of the blocky debris generates, the debris is likely to roll or tumble at the contact region. In addition, when rounded debris pressed against a flat surface, rounded debris of hardness H_a will cause plastic scratching such as an abrasive groove in a surface of hardness H_s only if $H_a/H_s > 1.2$.²⁵⁾

In general, the oxide debris can easily act as third-body abrasive particles during sliding because it has a higher hardness than the matrix by oxidation.²⁶⁾ While, in the case of the TNTZ combination, the blocky debris is primarily metallic because the debris generated by delamination is almost wholly composed of metallic particles.^{2,27)} Thus, the hardness of the metallic blocky debris is considered to be similar to the TNTZ disc or ball, in contrast with that of the oxide debris, since they are same TNTZ material. Therefore, it may be concluded that the abrasion by blocky debris is negligible in three-body abrasion for the TNTZ combination. This entrapped debris can act as a solid lubricant rather than a third-body, leading to the reduction of the real area of contact (A_r) and frictional coefficient during the wear tests.

In the theory of delamination, firstly proposed by Suh²¹⁾ and successively discussed and implemented by numerous authors.^{2,27)} It is supposed that the contacting asperities experience an incremental plastic deformation during sliding, which accumulates during repeated contacts. At a critical level of accumulated strain, the subsurface cracks are nucleated below the wear track, as shown in Fig. 9. When the crack becomes sufficiently large, it fractures to yield flake-like debris (delamination). According to the results, the TNTZ combinations have the most severe delamination wear in both Ringer's solution and air, respectively. For the TNTZ combination, the flake-debris is likely to be fragmented into blocky debris during sliding, since the dimensions of the flake-like debris are larger than those of the abrasion debris.

4.2 Debris characteristics in oxidative wear

The analysis presented in a previous study¹³⁾ demonstrates that the oxide films on the worn surfaces are not sufficiently supported by the underlying TNTZ material. Consequently, the oxide films tend to be continuously fragmented. Specifically, they are not protective and the resulting frictional coefficient is high, thereby leading to severe delamination wear for the TNTZ combination.

On the other hand, oxide thickness that would take a year to grow under static conditions can develop in hours or even minutes during sliding wear. This strong enhancement of

oxidation by sliding results from the increased diffusion rates of ions through a growing oxide layer by the flash temperatures.²⁵⁾ Furthermore, in the case of Ti64, when a Ti atom presented as Ti^{4+} in oxide films (TiO_2 layer) is substituted with Al^{3+} , an oxygen vacancy is generated in order to satisfy the electroneutrality according to the point defect theory.²⁸⁾ Thus, O diffusion increased because of Al in the TiO_2 layer for Ti64. Auger electron spectroscopy analysis given by Nakai *et al.*²⁹⁾ also reveals that O exists at a greater depth in Ti64 in comparison with TNTZ after gas nitriding. Therefore, it can be concluded that the oxidation of Ti64 is more strongly enhanced than that of TNTZ due to Al component in Ti64. Results of the EPMA evaluation of the O intensity maps (Fig. 9) also demonstrate that Ti64 is more strongly oxidized compared to TNTZ during the wear tests, in both air and Ringer's solution.

In addition, the average frictional coefficients over the total distance do not increase for the combinations including Ti64 components in Ringer's solution in contrast to the TNTZ combination, as shown in Fig. 3. This is because oxide films partially formed on the contact surfaces reduce the metal-to-metal contacts between the discs and balls. Particularly, the solid lubricant effects of debris are not especially remarkable for the Ti64 combination in air because the generated wear debris consists primarily of very fine oxide debris (approximately 1 μm in diameter), as shown in Fig. 6(a). Conversely, the oxide debris can act as a third-body in abrasive wear for this combination because it is considered that it has a higher hardness than the matrix.²⁶⁾

4.3 Differences of the effects of debris to the wear behaviors between Ringer's solution and air

The wear rate and frictional coefficient generally increase when the wear test is conducted in air as compared to in Ringer's solution.^{15–17)} In this study, however, they largely decrease in air for the TNTZ combination. This wear behavior occurs because of the functional roles of debris at the contact region between the TNTZ disc and ball. Ti alloys, which are well known that they have poor wear resistance, were used as both discs and balls in this study. Specifically, TNTZ demonstrates poorer wear resistance than Ti64 in air.¹³⁾ Consequently, a large amount of metallic debris are generated from the TNTZ combination during the wear tests both in Ringer's solution and air, as shown in Figs. 6(d) and (h).

In addition, the amount of the blocky debris remaining at the contact region is considerably smaller following the wear tests in Ringer's solution. This is because minimal effort is required to eject debris from the contact region using Ringer's solution. In this case, the contributions of the debris effects as a solid lubricant at the contact region are negligible compared to those in air.

On the other hand, the average dimension of the blocky debris is also larger in Ringer's solution (10.5 μm) than in air (2.9 μm), as shown in Fig. 8. These results indicate that the retention time of the blocky debris at the contact region is longer in air than in Ringer's solution. It is believed that the flake-like debris generated by delamination is kept fragmented during sliding in air.

In a fluid-lubricated system, the ratio between the thickness of the lubricant film and the asperity height of the worn

surfaces (λ) determines the lubricant effects.^{25,30)} When the entrapped debris acts as a solid lubricant during sliding in air, the dimension of the debris can be incorporated as the thickness of the lubricant film. When λ is above approximately 1 for metals, then the asperities on the opposing surfaces do not come into contact with one another and the wear rate will be reduced.³⁰⁾ This is because the wear rate depends on A_r that is the total sizes of the asperity junctions.²⁵⁾ Specifically, A_r is one of the most important factors for determining the extent of the delamination wear because the average surface area of each delaminated sheet can be assumed to be proportional to A_r .²¹⁾ It is believed that the dimensions of the blocky debris are larger than the asperity height for the TNTZ combination, resulting in a $\lambda > 1$. Thus, this is the reason why V_{loss} of the TNTZ combination in air does not exhibit definitive differences from those of other combinations, although TNTZ has low plastic shear resistance that can cause severe delamination wear. From the aforementioned results, it is concluded that the blocky debris acts as a solid lubricant for the TNTZ combination in air.

5. Summary

In this study, the frictional wear characteristics of Ti64 and TNTZ discs sliding against Ti64 and TNTZ balls in Ringer's solution were examined, and compared to those in air. The primary findings of this study are the following:

- (1) The V_{loss} of some components in the disc/ball combinations changes in Ringer's solution compared to in air. Particularly, V_{loss} of both the disc and ball more largely increases in Ringer's solution than in air for the TNTZ combination in air. It is believed that it suffers more severe delamination wear owing to the ejection of debris from the contact region by Ringer's solution compared to air, effectively increasing A_r between the disc and ball.
- (2) The V_{loss} of both the disc and ball slightly decreases for the Ti64 combination in Ringer's solution compared to air. This suggests that the debris effects are not large for the Ti64 combination in air because oxidative and abrasive wear is dominant for this combination. This different change of the V_{loss} trend in between Ringer's solution and air, compared to the TNTZ combination, results from the different predominant wear mechanisms.

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