Influence of Synovial Fluid Constituents on the Wear of Cobalt-Chromium-Molybdenum Alloy for Metal-on-Metal Joint Prostheses*

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The wear behavior of a cobalt-chromium-molybdenum alloy sliding against itself under a mixed or boundary lubricating condition was studied in pin-on-plate reciprocating tests with respect to metal-on-metal joint prostheses. Phospholipid L- α DPPC (dipalmitoyl phosphatidylcholine) and proteins (mixture of albumin and γ -globulin) ordinarily reduced the wear rate. However, the wear rate of the pin bearing surface which was rubbed on the same contact zone was increased by the proteins. These two contrasting results were explained by the difference in the role of the adsorbed film of proteins on the bearing surface, which served as either a protective layer to reduce wear or a blockade layer to increase wear.

Key Words: Metal-on-Metal Joint Prostheses, Synovial Fluid Constituents, Protein, Phospholipid, Boundary Lubricant, Contact Pressure, Oxidation

1. Introduction

The geometrical design with large radius and small clearance is a good design concept for hard-on-hard hip joint prostheses, because this design promotes full fluid film formation. The full fluid film produces no debris that induces tissue reaction or joint loosening⁽¹⁾. Ikeuchi et al.⁽²⁾ presented a numerical analysis of the fluid film between ceramic bearing surfaces using a Reynolds equation with the finite-difference method. Jin et al.⁽³⁾ analyzed elastohydrodynamic lubrication for hard bearing hip joints. There was fairly general agreement that full fluid film lubrication was possible during walking motion with sufficient quality of surface finish and high geometri-

cal conformity between bearing surfaces.

However, the useful clinical lifespan of joint prostheses should be evaluated in terms of the mixed or boundary lubrication property, because there exists the condition where the sliding speed is too low to generate a sufficiently thick fluid film.

In a recent study regarding the clinical wear behavior of ultra-high molecular weight polyethylene cups against metal and ceramic ball heads in comparison to metal-on-metal hip joint replacements⁽⁴⁾, the metal-on-metal articulation has taken some important steps of improvement in friction and wear mechanisms. Streicher et al.⁽⁵⁾ studied the tribological characteristics of metal-on-metal joints and concluded that serum-containing lubricant did not affect the wear rate but reduced friction. They also expected that proteins affected the tribological behavior. Walker and Erkman⁽⁶⁾ explored the lubrication property of Vitallium sliding on Vitallium (a cobalt-chromium alloy) using a sphere on flat reciprocating machine, and determined that γ -globulin was the most important constituent for lubrication. It is possible that there are other effective constituents for boundary lubrication. We^{(7),(8)} proposed a model of the

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boundary lubricating mechanism for natural synovial joints, in which the effective adsorbed film was composed of proteins, phospholipids and other conjugated constituents on articular surfaces.

The lubrication mode of the metal-on-metal hip joint which possesses both large radius and small clearance will be mixed lubrication with low contact pressure when a full fluid film is not present. This study is intended as an investigation of the mixed or boundary lubrication properties of metal-on-metal (a cobalt-chromium-molybdenum alloy) hip joints in view of the relationship between the synovial fluid constituents adsorbed onto the sliding material and the contact pressure.

2. Material and Methods

Figure 1 shows the geometries of test specimens. The cylindrical pin was 5 mm in diameter with a flat surface. The plate was 50 mm × 50 mm and 3 mm thick. The material was a cobalt-chromium-molybdenum alloy according to ASTM-F75 (Co-28Cr-6Mo). The estimated density of the alloy was 8.6×10^{-3} g/mm³. The bearing surfaces were polished to a surface finish of $R_{rms} < 0.02 \mu\text{m}$. The specimens were cleaned ultrasonically with n-hexane and distilled water prior to every test run. The Vickers hardness

Table 1 Lubricants used

Fluid Number	Solvent	Additive	Concentration (g/dl)
1	saline	synovial fluid (porcine)	35
2	saline	—	—
3	saline	albumin (human serum protein)	1.0
		γ -globulin (human serum protein)	0.3
4	saline	liposome of phospholipid L- α -DPPC (dipalmitoyl phosphatidylcholine)	0.02

Fig. 1 Geometries of test specimens made from a cobalt-chromium-molybdenum alloy. Roughness of bearing surface (R_{rms}) was $< 0.02 \mu\text{m}$

and the estimated depth of indentation for the bearing surface were measured. The stationary loading duration was 15 s.

Table 1 shows the lubricants. Synovial fluids were collected from the knees of porcine. Viscosities of the fluids are shown in Fig. 2. Human serum proteins were dissolved in saline. Albumin, whose molecular weight is 6.9×10^4 , is the most common protein in synovial fluid. γ -Globulin is the largest globular protein in synovial fluid, and its molecular weight is 1.6×10^5 . A saline solution of liposome⁽⁹⁾ of phospholipid L- α -DPPC (dipalmitoyl phosphatidylcholine, molecular weight: 735.05) was also used. DPPC was selected because it is the predominant phospholipid in synovial fluid and cartilage surface⁽⁸⁾.

Figure 3 shows a reciprocating friction machine. The lower plate was made to reciprocate with a stroke of 20 mm and a period of 1 s. A constant contact pressure (3.30, 6.74 or 15.5 MPa) was

Fig. 2 Viscosity of porcine synovial fluids divided into four groups. Normal synovial fluid ($N > 50$) was used in wear tests

Fig. 3 Reciprocating friction machine. Lower plate was made to reciprocate with a stroke of 20 mm and a period of 1 s. In some tests, a liquid bath was covered with a receptacle filled with N_2 gas in order to limit the O_2 supply

Fig. 4 Dissolved O_2 in saline solution as solvent. Lubricants were prepared immediately after dissolution of N_2 (15 min)

applied for 1.04 million cycles (41.5 km). It is obvious that the contact pressure is significantly lower than the pressure in the current joint prosthesis at the highest load in a walking cycle (2.5 kN). Following every test run, the weight loss of the test specimen was approximately converted to the wear rate ($mm^3/N \cdot m$) using the formula:

$$\text{wear rate} = (\text{calculated volumetric wear}) / ((\text{load}) \times (\text{sliding distance})).$$

Most of the wear tests were performed in air. Wear tests that limit O_2 supply in lubricants were also conducted to elucidate the influence of dissolved oxygen on the wear of Co-Cr-Mo alloy. N_2 gas was dissolved in saline solution for 15 min (Fig. 4). The liquid bath was covered with a receptacle filled with N_2 gas.

3. Results

Figure 5 shows the Vickers hardness and the estimated depth of indentation for the bearing surface. The hardness decreases gradually with the load, and remains constant in the deeper zone of the bearing material.

Figure 6 shows the wear rates of pin and plate in synovial fluid. The wear rates of plates increased with contact pressure. In contrast, the wear rates of pins were not significantly affected by the variation in contact pressure. The highest wear rate of pins was recorded at the lowest contact pressure of 3.30 MPa.

The wear rates in saline solution of synovial fluid constituents (proteins or DPPC) are shown in Figs. 7 and 8. Tests with saline solution recorded a much higher wear rates than those with synovial fluid except at 15.5 MPa. The wear rates of pins (Fig. 7) increased with a decrease in contact pressure. Proteins, in particular, show marked wear characteristics. The wear rate of plates (Fig. 8) also increased with a decrease in contact pressure. However, pro-

Fig. 5 Vickers hardness and the estimated depth of indentation for the bearing material, $N=8$, Error bars indicate S.D.

Fig. 6 Wear rate in saline solution of synovial fluid

teins reduced the wear rates over a wide range of contact pressure. The wear rate in DPPC solution was also lower than that in saline solution at both 3.30 MPa and 6.74 MPa.

Figure 9 shows the wear rates with and without dissolution of N_2 in lubricants, when the contact pressure was 3.30 MPa. Dissolution of N_2 increased wear rates; this was evident in the wear rates of plates in saline solution. For the pin, the increase in the wear rate by proteins was restricted by the

Fig. 7 Wear rate of pins in saline solution of either proteins or DPPC

Fig. 8 Wear rate of plates in saline solution of either proteins or DPPC

dissolution of N_2 . By contrast, proteins reduced wear rate of plate even with the dissolution of N_2 .

Lu and McKellop⁽¹⁰⁾ reported that the heat generated by ball-cup friction might cause precipitation of the proteins from bovine serum as a lubricant and that the resultant accumulation of a solid layer of precipitated protein between the ball and cup could artificially protect the bearing surface from wear. In this series of the wear tests, the accumulation of precipitate including wear particles onto the worn bearing surfaces was not observed; all the worn bearing surfaces after the wear tests were glossy and metallic, and traces owing to third-body wear were not obvious.

4. Discussion

In general, the wear rate at a steady state is constant under adhesive wear conditions at different contact pressures. However, there are some exceptions to the rule. Burwell⁽¹¹⁾ showed that the specific wear in a steel sliding on a steel rose sharply above a

Fig. 9 Influence of limitation of O_2 supply on wear rate of pin and plate, with a contact pressure of 3.30 MPa

critical contact pressure, which was approximately equal to one-third of the indentation hardness. Although the contact pressures in the present study were very low, the wear rate was affected by the contact pressure ranging from 3.30 MPa to 15.5 MPa. At the contact pressure of 3.30 or 6.74 MPa, the synovial fluid (Fig. 6) reduced the wear rates more than three other lubricants (Figs. 7 and 8) did. Walker and Erkman⁽⁶⁾ showed approximately the same result and discussed the influence of synovial fluid constituents. However, it is possible that the viscous effect affected the wear characteristics, because the synovial fluid has considerable viscosity. As shown in Fig. 6, even if the contact pressure was the same, the difference in the wear rate between the pin and the plate was observed. This indicates that the difference would be caused by the difference in rubbing situation. The upper pin surface was continuously rubbed on the same contact zone. On the other hand, the contact zone of the lower plate surface was continuously sifted in one stroke, so that the rubbed area appeared to be replenished with the provided lubricant. Therefore, the rubbing situation of the pin is more severe than that of the plate.

The wear tests presented in Figs. 7 and 8 were

carried out to specify the most important constituent for an effective boundary lubricant. Proteins and DPPC were chosen for use in this study, because these two constituents may act as a protective film for bearing surfaces. The artificial joint within the human body has no lubricant supply except for synovial fluid or exudate. The synovial fluid is a kind of water-based lubricant. Proteins are amphiphilic molecules. In other words, proteins have a more or less hydrophobic character⁽⁷⁾. Bearing surfaces of a Co-Cr-Mo alloy are hydrophobic. Therefore, it is reasonable to assume that the amphiphilic molecules of proteins easily adsorb onto the bearing surfaces owing to the good affinity between a protein constituent and a support⁽¹²⁾. DPPC is also easily adsorbed onto the bearing surfaces because it has a hydrophobic group.

The wear results of plates (Fig. 8) indicated that proteins and DPPC acted as effective boundary lubricants. Proteins appeared to be more effective. The reason may be that the molecular weight of proteins is more than a 100-fold as high as that of DPPC.

The proteins that exhibited a boundary lubricating ability for plates (Fig. 8) increased the wear rates of pins. The increase in wear of pins was observed in the wear tests of a stainless steel (SUS316) sliding against itself at a low contact pressure⁽¹³⁾. These results suggest that there was another effect by the proteins adsorbed onto the bearing surface. The Vickers hardness for the bearing surface (Fig. 5) and N_2 -dissolution tests (Fig. 9) support the results. Metallic surfaces such as a Co-Cr-Mo alloy surface form oxidized layers that ordinarily reduce friction and wear⁽¹⁴⁾. The degradation of such layers, which is caused by rubbing motion, leads to an increase in wear. The phenomenon is liable to occur at the pin bearing surface. A blockade layer model (Fig. 10) was proposed to explain the influence of proteins on the wear of pins (Fig. 7). If sufficient oxygen were supplied from the environment, the metallic surface would form an oxidized layer (Fig. 10(a-1)). However, the rubbing motion seems to break up the oxidized layer (Fig. 10(a-2)). Although the pin surface is

continuously rubbed on the same contact zone, the exposed base metal surface is reoxidized when sufficient oxygen is supplied (Fig. 10(a-1)). This leads to the low wear rate of the pins. If there were proteins in the water-based lubricant, the proteins would adsorb onto the bearing surface (Fig. 10(b-1)). As the exposed base metal surface is chemically active, proteins also adsorb onto that surface (Fig. 10(b-2)). The adsorbed layer of proteins increases the wear rate because it seems to block the oxygen supply from the lubricant to the exposed base metal. The results shown in Fig. 9 appear to support the blockade layer mechanism, because the reduction in the amount of dissolved oxygen in the lubricant reduced the protein effect on the pin. However the blockade layer model seems to be inapplicable to the adsorbed layer of DPPC, because the molecular weight of DPPC is so low that no thick layer can be formed.

These findings indicate that proteins are one of the important factors as regards the wear mechanism in metal-on-metal joint prostheses. For the design of the joints, it is preferable that continuous sliding on the same zone be avoided.

5. Conclusions

The experimental investigations of the wear characteristics of a cobalt-chromium-molybdenum alloy with respect to the new generation of metal-on-metal joint prostheses have been conducted under simplified sliding conditions. Important features are summarized below:

1. Proteins in lubricant usually acted as an effective boundary lubricant, in which the adsorbed film protected the bearing surface. However, the wear rate of the bearing surface which was rubbed on the same contact zone was increased by the proteins. The reason was that the adsorbed film obstructed the oxidation of the worn and exposed base metal. These two effects of proteins varied depending on the contact pressure.
2. Although DPPC acted as a protective film of the bearing surface, the influence of DPPC on the wear characteristic was smaller than that of proteins.

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Fig. 10 "Blockade layer model" of metallic surface

References

- (1) Revell, P.A., AL-Saffar, N. and Kobayashi, A., Biological Reaction to Debris in Relation to Joint Prostheses, *Proc. Instn. Mech. Engrs.*, Vol. 211, Part H (1997), p. 187-197.
- (2) Ikeuchi, K., Ohashi, M., Tomita, N. and Oka, M., The Lubrication in Ceramic-Ceramic Prostheses, *J. Japanese Soc. for Clinical Biomech. and Related Res.*, (in Japanese), Vol. 16 (1995), p. 381-383.
- (3) Jin, Z.M., Dowson, D. and Fisher, J., Analysis of Fluid Film Lubrication in Artificial Hip Joint Replacements with Surfaces of High Elastic Modulus, *Proc. Instn. Mech. Engrs.*, Vol. 211, Part H (1997), p. 247-256.
- (4) Semlitsch, M. and Willert, H.G., Clinical Wear Behaviour of Ultra-high Molecular Weight Polyethylene Cups Paired with Metal and Ceramic Ball Heads in Comparison to Metal-on-Metal Pairings of Hip Joint Replacements, *Proc. Instn. Mech. Engrs.*, Vol. 211, Part H (1997), p. 73-88.
- (5) Streicher, R.M., Semlitsch, M., Schon, R., Weber, H. and Rieker, C., Metal-on-Metal Articulation for Artificial Hip Joints: Laboratory Study and Clinical Results, *Proc. Instn. Mech. Engrs.*, Vol. 210, Part H (1996), p. 223-232.
- (6) Walker, P.S. and Erkman, M.J., Metal-on-Metal Lubrication in Artificial Human Joints, *Wear*, 21 (1972), p. 377-392.
- (7) Higaki, H., Murakami, T. and Nakanishi, Y., Lubricating Ability of Langmuir-Blodgett Films as Boundary Lubricating Films on Articular Surfaces, *JSME Int. J., Series C*, Vol. 40, No. 4 (1997), p. 776-781.
- (8) Murakami, T., Higaki, H., Sawae, Y., Ohtsuki, N., Moriyama, S. and Nakanishi, Y., Adaptive Multimode Lubrication in Natural Synovial Joints and Artificial Joints, *Proc. Instn. Mech. Engrs.*, Vol. 212, Part H (1998), p. 23-35.
- (9) Murakami, T., Sawae, Y., Higaki, H., Ohtsuki, N. and Moriyama, S., The Adaptive Multimode Lubrication in Knee Prostheses with Artificial Cartilage during Walking, *Elastohydrodynamics-'96: Fundamentals and Applications in Lubrication and Traction*, (1997), p. 371-382, Elsevier.
- (10) Lu, Z. and McKellop, H., Frictional Heating of Bearing Materials Tested in a Hip Joint Wear Simulator, *Proc. Instn. Mech. Engrs.*, Vol. 211, Part H (1997), p. 101-107.
- (11) Burwell, Jr.J.T., Survey of Possible Wear Mechanisms, *Wear*, 1 (1957/58), p. 119-141.
- (12) Nakanishi, Y., Murakami, T. and Higaki, H., Lubrication Property of Metal-on-Metal Hip Joints, *Proc. Int. Conf. New Frontiers in Biomech. Eng.*, (1997), p. 443-446, JSME.
- (13) Nakanishi, Y., Murakami, T. and Higaki, H., Improvement of Wear Characteristic of Metal-on-Metal Artificial Hip Joint by means of Magnetic Field: 1st Report, Influence of Alternating Current Magnetic Field on Wear Characteristic of Stainless Steel, *JSME Int. J., Series C*, Vol. 42, No. 3 (1999), p. 552-559.
- (14) Bowden, F.P. and Tabor, D., *Friction and Lubrication of Solids*, (1954), Oxford.