

Effect of carbon ion implantation on the tribology of metal-on-metal bearings for artificial joints

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Abstract: Metal-on-metal (MoM) bearings have become popular due to a major advantage over metal-on-polymer bearings for total hip arthroplasty in that the larger femoral head and hydrodynamic lubrication of the former reduce the rate of wear. However, concerns remain regarding adverse reactions to metal debris including metallosis caused by metal wear generated at the taper-head interface and another modular junction. Our group has hypothesized that carbon ion implantation (CII) may improve metal wear properties. The purpose of this study was to investigate the wear properties and friction coefficients of CII surfaces with an aim to ultimately apply these surfaces to MoM bearings in artificial joints. CII was applied to cobalt-chromium-molybdenum (Co-Cr-Mo) alloy substrates by plasma source ion implantation. The substrates were characterized using scanning electron microscopy and a 3D measuring laser microscope. Sliding contact tests were performed with a simple geometry pin-on-plate wear tester at a load of 2.5 N, a calculated contact pressure of 38.5 MPa (max: 57.8 MPa), a reciprocating velocity of 30 mm/s, a stroke length of 60 mm, and a reciprocating cycle count of 172,800 cycles. The surfaces of the CII substrates were generally featureless with a smooth surface topography at the same level as untreated Co-Cr-Mo alloy. Compared to the untreated Co-Cr-Mo alloy, the CII-treated bearings had lower friction coefficients, higher resistance to catastrophic damage, and prevented the adhesion of wear debris. The results of this study suggest that the CII surface stabilizes the wear status due to the low friction coefficient and low infiltration of partner materials, and these properties also prevent the adhesion of wear debris and inhibit excessive wear. Carbon is considered to be biologically inert; therefore, CII is anticipated to be applicable to the bearing surfaces of MoM prostheses.

Keywords: total hip arthroplasty, metal-on-metal, carbon ion implantation

Introduction

In total hip arthroplasty (THA), large-diameter metal-on-metal (MoM) bearings have become popular as an alternative to metal-on-polymer THA.^{1,2} MoM hip prostheses readily transition into hydrodynamic lubrication mode, which results in very little wear.³⁻⁵ Although more than one million patients have received MoM THA,⁶ it is necessary to consider the effects of corrosion-induced metal ions and metal wear debris on the human body.^{2,7} The accumulation of metal wear debris produced from the bearing surface, taper-head interface, and another modular junction of the prosthesis elicits adverse reactions to metal debris (ARMD) and aseptic osteolysis, which can lead to late prosthetic loosening.^{2,7,8} A loosened prosthesis requires revision; therefore, the accumulation of wear debris is one of the major factors to determine prosthesis lifetime.

Research on a broad range of technologies has recently been focused on improvement of the physical characteristics of the original metal, particularly corrosion resistance and wear resistance, through modification of the metal surface. We have focused

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on carbon processing, which offers high biocompatibility and is also chemically inactive.^{9–11} Carbon-treated surfaces exhibit lower friction coefficients, which result in improved wear resistance and corrosion resistance.^{10–13} Fisher et al have reported that the application of a thin diamond-like carbon (DLC) film to a cobalt-chromium-molybdenum (Co-Cr-Mo) alloy inhibits the production of wear debris and the elution of metal ions.¹⁴ Furthermore, when we previously conducted friction wear testing in a high contact pressure environment to simulate local contact of the prosthesis, carbon ion implantation (CII) was observed to provide both a lower and more stable friction coefficient and less wear than that with a DLC film.¹⁵ CII is a process that was originally developed for the fabrication of DLC, although it also appears to confer improved carbon properties in its own right. However, no research has been conducted on friction and wear characteristics that result from CII.

Here, the wear properties and friction coefficients of untreated and CII-treated Co-Cr-Mo alloy surfaces were investigated with an aim to ultimately apply the CII-treated surfaces to MoM bearings in artificial joints. The surfaces were characterized using scanning electron microscopy and a 3D measuring laser microscope, and sliding contact tests were performed with a simple geometry pin-on-plate wear tester.

Materials and methods

Surface preparation

A set of flat plate specimens and pin specimens with dome-shaped tips ($r=200$ mm) were fabricated from a 0.06% low-carbon Co-Cr-Mo alloy (ASTM F1537-00). Experiments were conducted with this alloy to clearly determine the differences in durability and wear characteristics. The samples were ground and polished in steps with diamond paste. After the final polishing, the counterfaces were ultrasonically cleaned in ethanol at 50°C for 20 min and degreased in trichloroethylene. Plasma source ion implantation (PSII) was used to implant carbon atoms into the metal substrate.^{16,17} Plasma was generated by introducing a hydrocarbon gas such as methane or acetylene into the vacuum chamber using a mass-flow controller. CII was conducted at a constant pulse repetition rate of 1 kHz and a constant pulse width of 10 μ s with a -18 kV target bias for 4 h. Implantation and deposition were continued with lower plasma ion energies to achieve optimal film quality. The implant depths of the carbon atoms typically reached approximately 200 nm, and the density of carbon atoms was greater close to the surface.¹⁷ Thereby, a carbon/metal gradient layer was formed on the metal surface,

and CII with a high resistance to avulsion was achieved. Two test sample pairs were prepared from the untreated Co-Cr-Mo alloy specimen and another two sample pairs were prepared from the CII specimen.

Physical characteristics

Micrographs of the specimen surfaces were obtained using field emission scanning electron microscopy (FE-SEM; JSM 6610LV, Jeol, Tokyo, Japan). Micrographs were acquired at two randomly selected areas on each specimen. The surface morphology and roughness of the specimens were measured using a 3D measuring laser microscope (OLS4000, Shimadzu, Tokyo, Japan) with a cutoff value (λ_c) of 80 μ m at room temperature. Three readings were taken for each surface of three random samples, and the arithmetic-average height deviation from the mean plane (R_a) and maximum amplitude of summit in the unit sample area (R_z) were used to characterize the roughness of the specimens.

Pin-on-plate test

The tribological properties and friction coefficients of all the samples were examined using a standard pin-on-plate reciprocating-sliding wear-tester (Figure 1). These tests enabled the effects of different parameters to be accurately studied using a simple geometry under a constant load and speed in a well-controlled environment. The plate and pin specimens of either the untreated or CII-treated type were mounted on the apparatus. The pinheads were brought into contact with the test plates fixed in plate holders and the plates were rubbed under the pin specimen with a uniaxial reciprocating motion. The load was set at 2.5 N. The maximum Hertz contact pressure and mean contact pressure were 57.8 MPa and 38.5 MPa, respectively, as calculated based on the radius of the pin surface curvature ($r=200$ mm), Young's modulus ($E=230$ GPa), and Poisson's ratio ($\nu=0.3$) of the

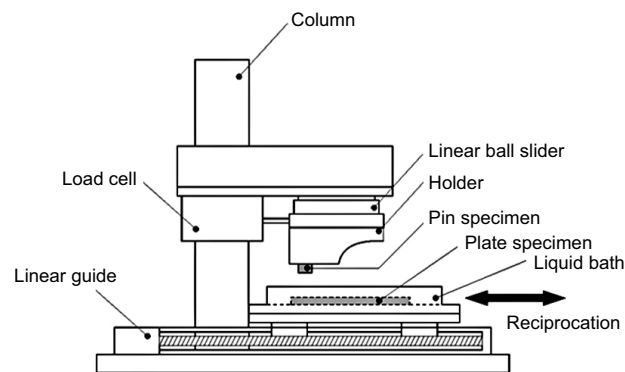


Figure 1 Schematic diagram of the reciprocating wear apparatus.

Co-Cr-Mo alloy. This contact pressure is higher than that with a typical MoM THA¹⁸ and, moreover, the pin specimen is subject to increased pressure due to continuous contact and geometrical discontinuity.¹⁹ A state of high contact pressure was applied to clarify the difference in wear characteristics for comparison. The specimens were slid together with the mean velocity of the movement path at 30 mm/s (stroke length: 60 mm, oscillation time: 2 s) and a reciprocating cycle count of 172,800 cycles (friction distance 10.4 km, 23°C±1°C). The lubricant employed was a mixed solution of 30 wt% fetal bovine serum (Qualified FBS, Gibco Laboratories, Tokyo, Japan) and 70 wt% purified water based on ISO standards and containing 0.3 wt% sodium azide as a preservative. The lubrication serum was added regularly to the liquid bath. The wear test was conducted twice and the dynamic friction coefficient value was measured using a calibrated load transducer in contact with the linear slider of the apparatus. To determine the specific wear rates of the plate specimens, the cross-sectional shapes of the wear tracks were measured at 1 mm intervals using a surface roughness tester (SE-3500K, Kosaka Laboratory, Tokyo, Japan). The wear area for each cross-section was integrated over the length of the wear track to calculate volumetric change. The worn surface of each type of pinhead was also observed using an optical microscope for industrial applications (ECLIPSE LV150, Nikon, Tokyo, Japan).

Results

Figure 2 shows SEM images of the surfaces of untreated Co-Cr-Mo and CII specimens. Although a small network-like pattern formed by carbon atom implantation was observed on the surface of the latter, both specimens were

generally featureless with a smooth surface topography. The mean surface roughness parameters for the specimens are given in Table 1. The untreated Co-Cr-Mo specimen (mean Ra =5.9 nm) had a relatively smoother surface than the CII specimen (mean Ra =9.1 nm); however, there was no significant difference between the two types of specimen. Figure 3 shows the changes in the mean value of the friction coefficient throughout the test of 172,800 running cycles. During the early stages of the tests, the friction coefficient of the Co-Cr-Mo specimen was high in the range of 0.4–0.5. This coefficient decreased temporarily after approximately 10,000 sliding cycles, then gradually rose for the remainder of the test, and reached approximately 0.55 during the final cycles. The CII specimen initially showed a low friction coefficient of 0.25–0.3, which then tended to rise gradually over time, but remained lower than that of the untreated Co-Cr-Mo specimen for the duration of the test. For both specimen types, the friction coefficient apparently increased as the surface was progressively damaged.

The mean values for specific wear in the plate test of the untreated Co-Cr-Mo and CII specimens were 5.59×10^{-8} and 4.37×10^{-8} mm³/Nm, respectively (Figure 4). There was no significant difference between these values. However, a plot of the wear track cross-sections of plate specimen showed a considerable difference in the Co-Cr-Mo specimens between minimum and maximum wear, and the minimum wear cross-sections had numerous instances of protrusions above the original surface level. In contrast, the wear tracks of the CII specimen were narrower and shallower, and the wear depth was restricted to within 200 nm (Figure 5A and B). After testing, the surface of each pin specimen was examined with

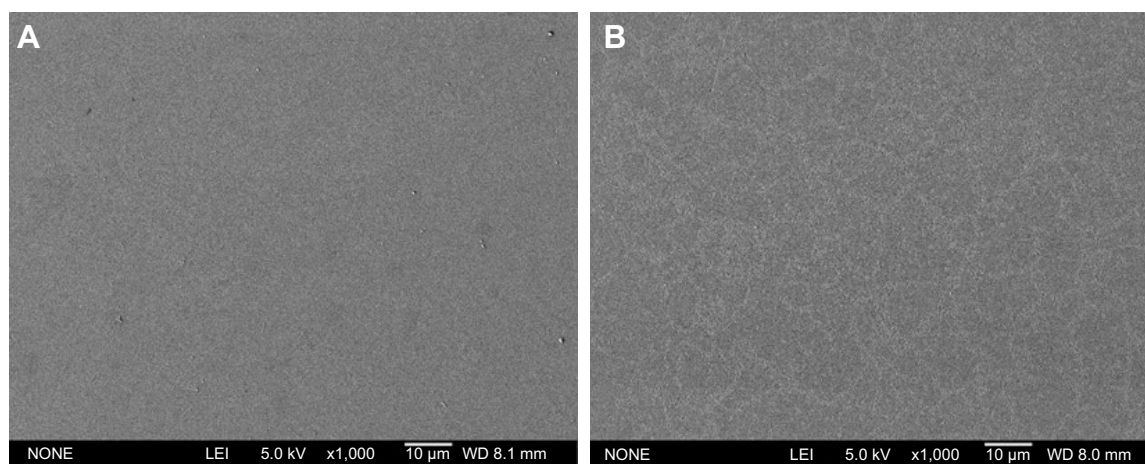


Figure 2 SEM micrographs of the (A) untreated (control) and (B) CII Co-Cr-Mo alloy surfaces.

Abbreviations: CII, carbon ion implantation; Co-Cr-Mo, cobalt-chromium-molybdenum; SEM, scanning electron microscopy.

Table 1 Surface roughness parameters for each sample

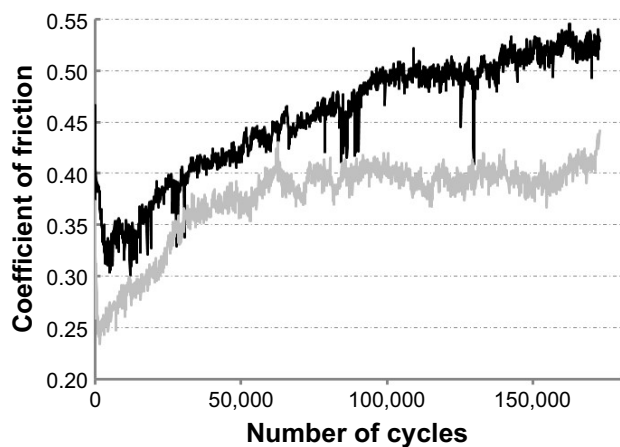
Sample	Roughness (nm), mean \pm SD	
	Ra	Rz
Co-Cr-Mo	5.9 \pm 0.4	36.8 \pm 16.3
CII	9.1 \pm 1.1	41.3 \pm 19.1

Abbreviations: CII, carbon ion implantation; Co-Cr-Mo, cobalt-chromium-molybdenum; Ra, arithmetic-average height deviation from the mean plane; Rz, maximum amplitude of the summit in the unit sample area.

an optical microscope. Surface damage and many wear tracks parallel to the direction of the sliding motion were observed, and also large protrusion areas were present near the worn area (Figure 6). The wear tracks in the bottom face indicate severe wear, principally by the occurrence of high plastic deformation. However, the large protruding areas beyond the original surface level (arrows in Figures 5A and 6) indicate the accumulation and adhesion of metal wear debris.

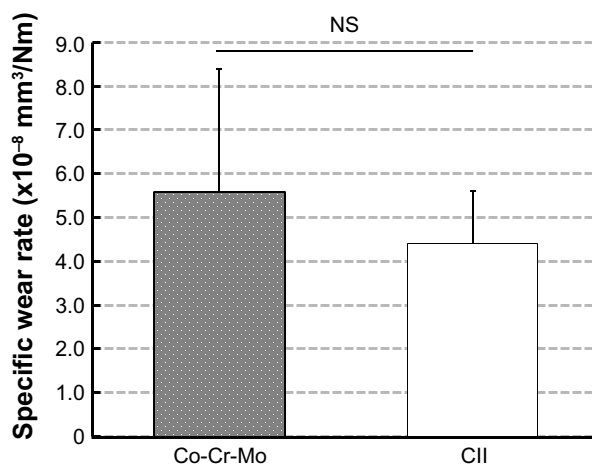
Discussion

Advances in metal processing technologies have brought improvements in femoral head sphericity and in clearance precision between the acetabulum and the femoral head. The use of second-generation MoM bearing surfaces in an artificial hip prosthesis eliminates the need for polymer inserts, which makes it feasible to design a larger femoral head and readily enables hydrodynamic lubrication.^{3–5,20,21} However, a number of problems remain to be resolved with regard to in vivo physiological toxicity, including the elution of metal ions due to corrosion and the presence of metal wear debris including ARMD.^{2,7,8} The Medical and Healthcare Products Regulatory Agency recommends annual follow-ups to

**Figure 3** Changes in friction coefficient.

Notes: The CII specimen had a lower friction coefficient than the untreated Co-Cr-Mo alloy throughout all stages of the test. Co-Cr-Mo (black) and CII (gray).

Abbreviations: CII, carbon ion implantation; Co-Cr-Mo, cobalt-chromium-molybdenum.

**Figure 4** Specific wear rate.

Note: The Co-Cr-Mo specimen tended to exhibit a higher specific wear rate than the CII specimen, although the difference was not significant.

Abbreviations: CII, carbon ion implantation; Co-Cr-Mo, cobalt-chromium-molybdenum; NS, not significant.

evaluate the life of the implant and blood metal ion sampling of MoM THA patients. Metal ion elution correlates with corrosion and wear;^{22,23} therefore, improvements in the corrosion and wear resistance of a metal surface are associated with the inhibition of metal ion elution.

Metal surface modification technologies can enhance the properties of the original material, and thereby provide improved corrosion and wear resistance. Carbon, in particular, provides excellent biocompatibility and does not interfere with osteoblast activity.^{10–13} In earlier experiments on prosthesis bearing surfaces, we created a high contact pressure environment to simulate edge contact (head-insert rim contact or polar contact within the THA), and reported that the wear resistance of CII surfaces was superior to that of DLC surfaces.¹⁵ Based on these results, the present research was conducted to evaluate the friction and wear characteristics of CII surfaces for long-term MoM sliding contact.

The surfaces of CII samples exhibited the same level of unevenness as the original untreated Co-Cr-Mo alloy. Unlike former surface engineering techniques, the PSII apparatus enables uniform ion implantation to be realized without sample manipulation or splattering of the substrates. During the early stages of the sliding test, the friction coefficient of the CII specimen was lower than that of the untreated Co-Cr-Mo specimen (Co-Cr-Mo specimen: 0.4–0.5, CII specimen: 0.25–0.3). These results reflect the characteristics of the surface layer, particularly its high carbon content. In addition, there was an almost complete absence of wear debris adhering to the CII specimen surfaces, in contrast to the Co-Cr-Mo specimen surfaces, and

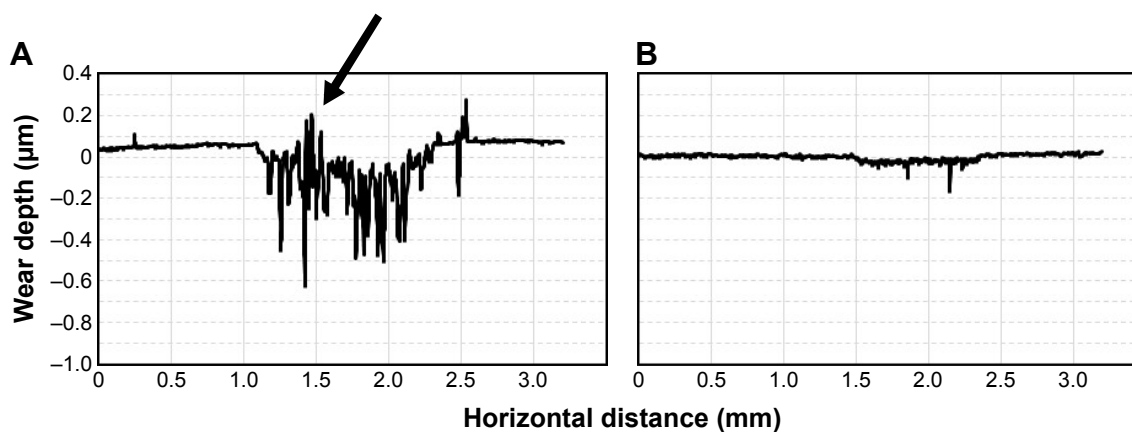


Figure 5 Cross-sectional shape of plate wear track.

Notes: The wear tracks in the Co-Cr-Mo specimen were wide and deep. The protruding areas on the surface were attributed to the accumulation and adhesion of wear debris (→) and were frequently noted only in the Co-Cr-Mo specimens. **(A)** Co-Cr-Mo and **(B)** CII.

Abbreviations: CII, carbon ion implantation; Co-Cr-Mo, cobalt-chromium-molybdenum.

the wear tracks on the CII specimen were comparatively narrow and shallow. The method used for measurement of the specific wear rate calculated from the volumetric change of the cross-sectional wear area counts any adherence of wear debris as negative wear. Therefore, the wear rate of Co-Cr-Mo specimen may have been underestimated, and it is hypothesized that the actual specific wear rate in the Co-Cr-Mo specimens may have been greater than the measured values. These results of friction and wear tests in the present study indicate that the application of CII processing to the surface of Co-Cr-Mo alloy currently used in prostheses can reduce the friction coefficient of that alloy, which would result in a lower specific wear rate. An irregular surface

that is marred by wear tracks and adhered wear debris shifts from a hydrodynamic lubrication mode to a boundary lubrication mode, which results in a higher rate of wear.^{4,24} We suspect that the wear status is stabilized in CII due to the low friction coefficient and low infiltration of partner materials, and suggest that these factors also prevent the adhesion of wear debris and inhibit excessive wear. We anticipate that CII has high potential to prolong the lifetime of MoM bearing artificial joints.

Limitations

The absolute value of the friction coefficient and specific wear rate may be high for the lubricated sliding of metallic contacts compared to other studies.^{15,25} The reason for this is attributed to the brittle low-carbon Co-Cr-Mo alloy that was used for the specimens and the high contact pressure that was applied to clarify the difference in the wear characteristics for comparison. Therefore, as the surfaces of specimens were damaged, the contact area became wide, and the friction coefficient value then gradually increased. However, because the CII layer remained in the worn area (wear depth <200 nm), the friction coefficient of CII specimen remained lower than that of the untreated Co-Cr-Mo specimen throughout the test. The results under such severe conditions should be evaluated by comparing untreated Co-Cr-Mo and CII.

Although this study has suggested the possibility of the wear debris adhesion phenomenon in Co-Cr-Mo pair tribology, the simple configuration wear test performed here may not be representative of *in vivo* conditions. Further laboratory studies are thus required to evaluate these surfaces under more sophisticated conditions, including experiments with third-body particles in hip simulators. These and other

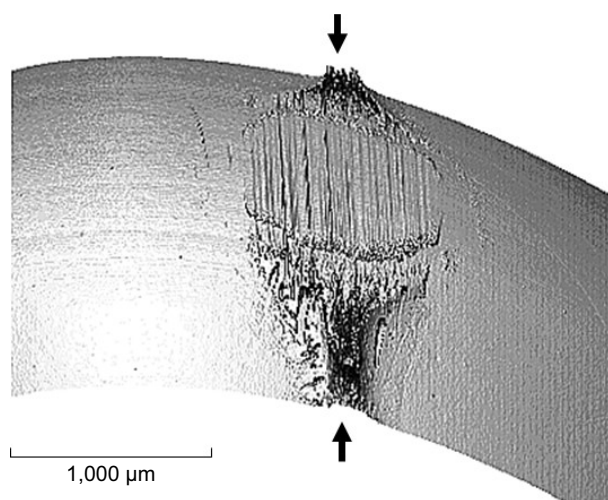


Figure 6 Image of 3D roughness measurements for a Co-Cr-Mo pinhead specimen.

Notes: Plastic deformation was observed in the area of contact. The large protrusions around the wear area (→) indicate the adhesion of wear debris.

Abbreviation: Co-Cr-Mo, cobalt-chromium-molybdenum.

future studies by our group will produce more information. The simple pin-on-plate tests enabled greater control of the experimental variables and produced fewer artifacts in the results. This approach resulted in the identification of marked differences between the materials tested. These simple configurations are particularly encouraging as tests for use in the early stages of assessment.

Conclusion

Co-Cr-Mo alloy surfaces were improved through CII processing, and the friction and wear characteristics of the resultant product were evaluated using a simple geometry wear tester. CII reduced the friction coefficient and infiltration of partner materials, which prevented the adhesion of wear debris and inhibited excessive wear.

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Disclosure

The authors report no conflicts of interest in this work.

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