

provides passivation by surface oxidation and can dissolve certain foreign materials that may remain from the previous procedure. Moreover, a previous study reported that the Cr concentration of dry-polished stainless steel was lower at the surface than in the bulk [39]. We therefore treated the surface with nitric acid with the aim of increasing the Cr concentration by “re-surfacing.”

After the nitric acid treatment, the Co-Cr-Mo samples were irradiated with O₂ plasma at 500-W high-frequency output and 150 mL/min O₂ gas flow for 5 min by using O₂ plasma etcher (PR500, Yamato Scientific Co., Ltd., Tokyo, Japan). The O₂ plasma treatment increased the thickness of the surface oxide layer.

2.2. *4-Methacryloxyethyl trimellitate anhydride coating on Co-Cr-Mo alloy and MPC graft polymerization*

4-Methacryloxyethyl trimellitate anhydride (4-META) and acetone were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). The previous studies suggested that 4-META and methacrylates were applicable as photocurable bonding liners that can bind a resin composite to a metal substrate [40–42]. MPC was synthesized industrially by using the method developed by Ishihara et al. [25] and was supplied by AI Bio-Chips Co., Ltd. (Tokyo, Japan). 2-Hydroxy-1-[4-(hydroxyethoxy)phenyl]-2-methyl-propanone (DAROCUR[®] 2959, D2959) was purchased from Ciba Specialty Chemicals Holding Inc. (Basel, Switzerland). D2959 is a highly efficient radical photoinitiator for ultraviolet (UV) curing of the systems containing unsaturated monomers and prepolymers. It is particularly well known as a cytocompatible UV photoinitiator

with UV intensities of $<6 \text{ mW/cm}^2$ that can perform polymerization for up to 10 min with a UV light of 365 nm [43].

The synthesis of Co-Cr-Mo-g-MPC is schematically illustrated in Fig. 1. The various pretreated Co-Cr-Mo samples were coated with an acetone solution containing 10mass% 4-META by using a spin coater (K-359 S-1, Kyowariken Inc., Tokyo, Japan) and then dried in the dark at 40°C for 3 h to remove the acetone. MPC and D2959 were dissolved in degassed ethanol to a concentration of 2mass% and 0.1mass%, respectively. The Co-Cr-Mo samples coated with 4-META after various pretreatments were immersed in the MPC-ethanol solution containing D2959. Photo-induced graft polymerization on the Co-Cr-Mo surface was carried out using UV irradiation (UVL-400HA ultra-high pressure mercury lamp, Riko-Kagaku Sangyo Co., Ltd., Finabashi, Japan) with an intensity of 5 mW/cm^2 at 60°C for 10 min with a Toshiba D-35 filter to allow the passage of UV light of only $350 \pm 50 \text{ nm}$ wavelength. After the polymerization, the Co-Cr-Mo-g-MPC samples were removed from the solution, washed with ethanol, and dried at room temperature.

2.3. MPC graft polymerization on cross-linked polyethylene

Compression-molded UHMWPE (GUR1020 resin, Poly Hi Solidur Inc., IN, USA) bar stock was gamma irradiated at 50 kGy in N_2 gas and annealed at 120°C in N_2 gas for crosslinking. After cooling, the cross-linked polyethylene (CLPE) specimens were machined from this bar stock.

MPC grafting onto the CLPE surface was performed as described in previous studies [23,24]. They were immersed in an acetone solution containing 10 mg/mL benzophenone for 30 s and then

dried in the dark at room temperature to remove the acetone. MPC was dissolved in degassed pure water to a concentration of 0.5 mol/L. The benzophenone-coated CLPE samples were immersed in the aqueous MPC solution. Photo-induced graft polymerization on the CLPE surface was carried out using UV irradiation with an intensity of 5 mW/cm² at 60°C for 90 min. After the polymerization, the CLPE-g-MPC samples were removed from the solution, washed with pure water and ethanol, and dried.

2.4. Surface analysis by Fourier-transform infrared spectroscopy, X-ray photoelectron spectroscopy and water-contact angle measurement

The functional group vibrations of the Co-Cr-Mo alloy surfaces before and after the MPC grafting were examined by Fourier-transform infrared (FT-IR) spectroscopy with attenuated total reflection (ATR) equipment. The FT-IR/ATR spectra were obtained using an FT-IR analyzer (FT/IR615, JASCO Co. Ltd., Tokyo, Japan) for 32 scans (1.2 sec/scan) over the range of 800 to 2000 cm⁻¹ at a resolution of 4.0 cm⁻¹.

The surface elemental conditions of the Co-Cr-Mo alloy before and after the MPC grafting were analyzed using X-ray photoelectron spectroscopy (XPS). The XPS spectra were obtained using an XPS spectrophotometer (AXIS-HSi165, Kratos Analytical Ltd., UK) equipped with a 15-kV Mg-K α radiation source at the anode. The take-off angle of the photoelectrons was maintained at 90°. Five scans (approximately 260 to 425 sec/scan depending on the atomic signal strength) were taken for each sample.

The static water contact angles on the Co-Cr-Mo surfaces that were subjected to different types of pretreatments before and after the MPC grafting were measured using the sessile drop method with an optical bench-type contact angle goniometer (Model DM300, Kyowa Interface Science Co., Ltd., Saitama, Japan). Drops of purified water (1 μ L) were deposited on the Co-Cr-Mo-g-MPC surface, and the contact angles were directly measured with a microscope after 60 s of dropping, according to the ISO 15989 standard [44]. Measurements were repeated six times for each sample, and the average values were considered as the contact angles.

2.5. *Surface observation by fluorescence microscopy*

We used rhodamine 6G (Wako Pure Chemical Industries, Ltd., Osaka, Japan) that can be applied simply and rapidly to a polymer coating and imaged using fluorescence microscopy (FM). Wang et al. found that rhodamine 6G effectively stains poly(MPC) that possesses great structural similarity to lipids [45]. This simple staining technique enables the evaluation of the coated area by FM.

An aqueous solution of 200 mass ppm rhodamine 6G was used for all the staining experiments. All the samples were stained by following a two-step procedure: (1) The samples were immersed in the rhodamine 6G solution for 30 s and then removed. (2) Next, they were washed two times consecutively in distilled water for 30 s and then dried.

A fluorescence microscope (Axioskop 2 Plus, Carl Zeiss AG, Oberkochen, Germany) was used for FM imaging and examination of all samples. Pseudo-color images were obtained using a CCD camera (VB-7010, Keyence Co., Osaka, Japan) and imaging software (VH analyzer 2.51, Keyence

Co., Osaka, Japan). Lenses with $\times 10$ magnification and appropriate exposure time (approximately 1/10 s) were employed to obtain best image quality of the various samples.

It is known that most fluorescent dyes undergo a process called photobleaching under normal imaging conditions, with subsequent deterioration during fluorescence [45]. In general, the fluorescence intensity decreases with time during imaging [45]. In the present study, the Co-Cr-Mo-g-MPC samples were stained with rhodamine 6G, and they were illuminated within 5 min of staining. The time required for appropriate exposure was within 1 to 2 min. It was therefore assumed that the effect of photobleaching of rhodamine 6G was not very significant under these experimental conditions.

2.6. Friction test

The friction coefficients between the pins fabricated from various materials and the untreated Co-Cr-Mo ($n = 2$) or Co-Cr-Mo-g-MPC (pretreated with nitric acid and O_2 plasma, $n = 3$) plates were measured using a custom-made pin-on-plate machine [46]. Each pin was a cylinder measuring 5 mm in height and 9 mm in diameter. Friction tests were carried out at a temperature of 37°C , a contact stress of 2.4 MPa, and a swing distance of 25 mm with a frequency of 1 Hz [47]. The lubricant used was a mixture of 27vol% bovine serum, 20 mM/L of ethylene diamine tetraacetic acid (EDTA), and 0.2mass% sodium azide [48]. The friction tests were performed up to maximum 5.0×10^4 cycles (preliminary test, $n = 1$), and the lubricant was not changed during the tests.

3. Results

Fig. 2 shows the FT-IR/ATR spectra of the untreated Co-Cr-Mo sample and the nitric acid- and O₂ plasma-pretreated Co-Cr-Mo-g-MPC sample. Absorption peaks were not observed for the Co-Cr-Mo sample before the MPC grafting and for either the nitric acid- or O₂ plasma-pretreated Co-Cr-Mo-g-MPC samples (data not shown). In contrast, new absorption peaks were observed only for the Co-Cr-Mo-g-MPC samples pretreated with both nitric acid and O₂ plasma. The peaks at 1720, 1550, and 1460 cm⁻¹ are attributed to the aromatic ring C=O and -CH₂- in the 4-META and MPC graft polymer. The peaks at 1080 and 970 cm⁻¹ are due to the phosphate group in the MPC unit [25].

Table 2 summarizes the elemental compositions of the Co-Cr-Mo surfaces that were subjected to the different types of pretreatments. After the nitric acid pretreatment, the O₂ and Co compositions decreased and the Cr and Mo compositions increased. After O₂ plasma pretreatment, the O₂ composition increased to approximately 53% due to the formation of the surface oxide layer. After the combined nitric acid and O₂ plasma pretreatment, the compositions of O₂, Co, and Cr were higher than those before the pretreatment.

The XPS spectra of the binding energy region of the Co_{2p}, Cr_{2p}, and Mo_{3d} electrons obtained from the nitric acid- and O₂ plasma-pretreated Co-Cr-Mo sample before and after the 4-META coating are shown in Fig. 3. Prior to the 4-META coating, the Co oxide (Co²⁺), Cr oxide (Cr³⁺), and Mo oxide (Mo⁴⁺ and Mo⁶⁺) peaks were observed in the Co_{2p}, Cr_{2p}, and Mo_{3d} spectra, respectively. After the 4-META coating, Co_{2p} and Mo_{3d} were depleted but Cr_{2p} was almost unchanged.

Fig. 4 shows the XPS spectra (N_{1s} and P_{2p}) of the untreated Co-Cr-Mo sample and the nitric acid- and O_2 plasma-pretreated Co-Cr-Mo-g-MPC sample. In both N_{1s} and P_{2p} spectra, the peaks appeared only for Co-Cr-Mo-g-MPC. The peaks at 403 and 134 eV were assigned to the $-N^+(CH_3)_3$ and phosphate groups, respectively. These peaks are the characteristic of the phosphorylcholine present in the MPC units.

Table 3 summarizes the elemental compositions of the Co-Cr-Mo-g-MPC surfaces that were subjected to different types of pretreatments. The surface nitrogen (N) and phosphorous (P) compositions in the Co-Cr-Mo-g-MPC samples were higher than those in the untreated Co-Cr-Mo samples. It should be noted that in the Co-Cr-Mo-g-MPC samples pretreated with both nitric acid and O_2 plasma, the measured N and P compositions increased to 3.0 and 2.9, respectively, and the Co, Cr, and Mo from the Co-Cr-Mo substrate were not detected.

Fig. 5 shows the static water contact angle on the Co-Cr-Mo surfaces subjected to different types of pretreatments before and after the MPC grafting. The static water contact angle on the Co-Cr-Mo surface before the MPC grafting was approximately 70° to 90° ; however, among the three differently pretreated surfaces, the nitric acid- and O_2 plasma-pretreated Co-Cr-Mo-g-MPC surface showed the lowest angle. The static water contact angle on the nitric acid- and O_2 plasma-pretreated Co-Cr-MO-g-MPC surface was as low as 15° . On the other hand, compared to the angle on the untreated Co-Cr-Mo surface, the angle on the only nitric acid-pretreated Co-Cr-Mo-g-MPC surface was almost unchanged (approximately 65°) and that on the only O_2 plasma-pretreated Co-Cr-Mo-g-MPC surface was slightly decreased to 45° .

Fig. 6 shows the FM images of the untreated Co-Cr-Mo surface and the nitric acid- and O₂ plasma-pretreated Co-Cr-Mo-g-MPC surface. On the Co-Cr-Mo-g-MPC surface, rhodamine 6G stained poly(MPC) selectively (Fig. 6(b)). This resulted in a large contrast in the fluorescence intensity between the MPC-grafted layer (green to yellow) and the non-grafted substrates (blue) (Fig. 6(d)). The poly(MPC) layer stained with rhodamine 6G was more clearly visible but the staining was not uniform. It therefore indicates that the grafting of the poly(MPC) layer on the Co-Cr-Mo surface is not uniform. On the untreated Co-Cr-Mo surface, such a contrast was not observed (Fig. 6(a, c)).

Fig. 7 shows the friction coefficients of the sliding couples, namely, Co-Cr-Mo-g-MPC, CLPE, CLPE-g-MPC, and untreated Co-Cr-Mo pins sliding against the Co-Cr-Mo-g-MPC and untreated Co-Cr-Mo plates. The Co-Cr-Mo/Co-Cr-Mo couple showed a high friction coefficient of approximately 0.24 in the initial 10 cycles; the value increased gradually and reached approximately 0.38 after 5.0×10^4 cycles. The CLPE/Co-Cr-Mo-g-MPC and Co-Cr-Mo/Co-Cr-Mo-g-MPC couples showed a lower friction coefficient than the CLPE/untreated Co-Cr-Mo and Co-Cr-Mo/untreated Co-Cr-Mo couples, respectively. The CLPE/Co-Cr-Mo-g-MPC couple showed the lowest friction coefficient of approximately 0.05, and this value was almost steady during the experiment. In both CLPE-g-MPC/Co-Cr-Mo-g-MPC and Co-Cr-Mo-g-MPC/Co-Cr-Mo-g-MPC couples, the poly(MPC) layer sliding against the MPC polymer layer showed almost the same friction coefficient of approximately 0.12 up to the initial 100 cycles. After 5.0×10^4 cycles, the friction coefficients of the Co-Cr-Mo/Co-Cr-Mo-g-MPC

and Co-Cr-Mo-g-MPC/Co-Cr-Mo-g-MPC couples increased, whereas that of the CLPE-g-MPC/Co-Cr-Mo-g-MPC couple decreased.

4. Discussion

In this study, with the aim of reducing wear, we synthesized a high lubricious Co-Cr-Mo alloy surface by poly(MPC) grafting for its application in artificial joints. To ensure the *in vivo* long-term retention of this poly(MPC) graft on the Co-Cr-Mo alloy, we used the 4-META intermediate layer and the photo-induced radical graft polymerization technique to create a strong bonding between the Co-Cr-Mo substrate and the poly(MPC) chain via the 4-META layer. 4-META has already been known as a binder used in dental resin, and it can strongly bind resin to metal in dental implants [41,42]. Suzuki et al. reported a strong evidence that the carboxylate anions were formed due to an ionic interaction between the carboxyl group of poly(carbonic acid) and the surface hydroxyl group on the oxide layer of stainless steel [49]. Yamabe et al. reported that an ionic bond was formed between the carboxyl group and Cr on the surface of stainless steel [50]. The various pretreatments performed in this study aimed at an efficient interaction between the carboxyl group of the 4-META layer and the surface hydroxyl group on the Cr oxide layer of the Co-Cr-Mo alloy.

As presented in Table 2, the surface Cr content in the Co-Cr-Mo alloy after the nitric acid pretreatment was higher than that of the untreated Co-Cr-Mo alloy. Seo et al. reported that a dry-polished stainless steel lacked in the surface Cr content [39]. Accordingly, the as-polished

Co-Cr-Mo alloy in this study may also lack the surface Cr content, and the surface etching by nitric acid treatment would have produced the Cr-rich surface layer.

Exposure of the Co-Cr-Mo alloy to O₂ plasma formed an oxide layer on the Co-Cr-Mo surface (Table 2 and Fig. 3(a)). The static water contact angle on the nitric acid-pretreated Co-Cr-Mo-g-MPC surface was higher than that on the nitric acid- and O₂ plasma-pretreated Co-Cr-Mo-g-MPC surface (Fig. 5). Additionally, the measured compositions of N and P in the only nitric acid-pretreated Co-Cr-Mo-g-MPC samples were lower than those in the nitric acid- and O₂ plasma-pretreated Co-Cr-Mo-g-MPC samples (Table 3). It was considered that washing with ethanol removed the 4-META-MPC graft copolymer (4-META-*co*-MPC) from the only nitric acid-pretreated Co-Cr-Mo surface because there was an inadequate ionic bonding between 4-META and the only nitric acid-pretreated Co-Cr-Mo surface without an oxide layer.

The peaks at 780, 236, and 232 eV in the XPS spectra were assigned to Co²⁺, Mo⁴⁺, and Mo⁶⁺, respectively, as shown in Fig. 3. After the 4-META coating, these peaks disappeared from the Co-Cr-Mo surface. The peaks at 586 and 576 eV in the XPS spectra were assigned to Cr³⁺ (Fig. 3), indicating that Cr³⁺ persisted on the Co-Cr-Mo surface even after the 4-META coating. These results suggest that compared to other metallic oxides, Cr³⁺ predominantly binds to the carboxyl group of 4-META with a stronger ionic interaction [50]. This can be explained by the Lewis acid-base interaction model of a previous study [50]. It is assumed that the proton exchange between the carboxyl groups and active electrophilic metallic ions existing in the surface hydrated oxide resulted in the formation of carboxylate anions; these carboxyl species that diffused into the

hydrated oxide layer could easily undergo strong ionic interactions with the polar hydroxyl groups of hydrated Cr^{3+} . The binding between 4-META-co-MPC and the Co-Cr-Mo substrate might contribute to the stable polymer/metal interface.

Friction coefficients of various bearing couples in the previous studies are summarized in Table 4.

In Fig. 7, the Co-Cr-Mo/Co-Cr-Mo couple showed a friction coefficient of approximately 0.24 as high as the previous studies. The CLPE/Co-Cr-Mo couple also showed a friction coefficient of approximately 0.09 as high as the previous studies. In contrast, it was confirmed that compared to the untreated Co-Cr-Mo surface, the Co-Cr-Mo-g-MPC (excluding the CLPE-g-MPC/Co-Cr-Mo-g-MPC bearing couple) surface showed an extremely low friction coefficient. Since MPC is highly hydrophilic and poly(MPC) is water soluble, the water wettability of the Co-Cr-Mo-g-MPC surface was greater than that of the untreated Co-Cr-Mo surface, as shown in Fig. 5. Consequently, the grafted poly(MPC) layer successfully provided high lubricity to the Co-Cr-Mo surface (Fig. 7). The reduction in the friction may contribute to the improvement in the anti-wear properties [22]. From the viewpoint of tribological advantage, a highly lubricious metal bearing material will enable the development of a novel biocompatible artificial hip joint system.

Various factors such as the type of bearing material, surface roughness, homogeneity of the surface, and chemical composition affect the lubricity of artificial joints [54]. In the case of Co-Cr-Mo-g-MPC, the lubricity would change depending on the ambient *in vitro* and *in vivo* conditions. The bearing surface with poly(MPC) in artificial hip joints is assumed to have a

structure similar to an artificial cell membrane. The Co-Cr-Mo-g-MPC/Co-Cr-Mo-g-MPC or CLPE-g-MPC/Co-Cr-Mo-g-MPC bearing couples therefore mimic the natural joint cartilage *in vivo*. A friction coefficient of cartilage/SUS pin-on-plate was 0.01 to 0.05 [55], and that of cartilage/cartilage pin-on-plate was 0.02 [56], as shown in Table 4. In contrast, the Co-Cr-Mo-g-MPC/Co-Cr-Mo-g-MPC or CLPE-g-MPC/Co-Cr-Mo-g-MPC bearing couples mimicking the natural joint, showed high friction (friction coefficient = 0.12) in this study. Images of grafted non-grafted poly(MPC) /grafted poly(MPC) and poly(MPC)/grafted poly(MPC) bearing interfaces are shown in Fig. 8. The grafted poly(MPC)/non-grafted poly(MPC) bearing interface in the CLPE/Co-Cr-Mo-g-MPC couple showed a low friction coefficient with the water wettability of poly(MPC) (Fig.8(a)). The grafted poly(MPC)/grafted poly(MPC) bearing interface in the CLPE-g-MPC/Co-Cr-Mo-g-MPC couple showed slightly higher friction than the grafted poly(MPC)/non-grafted poly(MPC) bearing interface. The MPC graft polymer on Co-Cr-Mo might have low density because the polymerization method used was “grafting to” [57]. Fukuda et al. reported that the friction was higher in a bearing couple with low-density polymer brushes than in a bearing couple with high-density polymer brushes [58]. Therefore, it is assumed that a bearing couple with low-density poly(MPC) brushes may cause high friction with interpenetration as shown in Fig. 8(b) [59]. High-density poly(MPC) by “grafting from” might be possible to resist the interpenetration by its volume effects arising from chain mobility.

5. Conclusions

We created a highly lubricious metal bearing material for its application as a novel artificial hip joint system: The MPC polymer was grafted onto the surface of the Co-Cr-Mo alloy by employing the 4-META intermediate layer and using the photo-induced radical graft polymerization technique and the nitric acid and O₂ plasma pretreatments of the Co-Cr-Mo alloy. In conclusion, the grafted poly(MPC) layer successfully provided high lubricity to the Co-Cr-Mo surface. The grafted poly(MPC)/non-grafted poly(MPC) bearing interface had a lower friction value than that of the grafted poly(MPC)/grafted poly(MPC) bearing interface.

References

- [1] Kurtz S, Mowat F, Ong K, Chan N, Lau E, Halpern M. Prevalence of primary and revision total hip and knee arthroplasty in the United States from 1990 through 2002. *J Bone Joint Surg Am* 2005;87(7):1487–97.
- [2] Harris WH. The problem is osteolysis. *Clin Orthop* 1995;311:46–53.
- [3] Kobayashi A, Freeman MA, Bonfield W, Kadoya Y, Yamac T, Al-Saffar N, et al. Number of polyethylene particles and osteolysis in total joint replacements. A quantitative study using a tissue-digestion method. *J Bone Joint Surg Br* 1997;79(5):844–8.
- [4] Sochart DH. Relationship of acetabular wear to osteolysis and loosening in total hip arthroplasty. *Clin Orthop* 1999;363:135–50.
- [5] McKellop H, Shen FW, Lu B, Campbell P, Salovey R. Development of an extremely wear-resistant ultra high molecular weight polyethylene for total hip replacements. *J Orthop Res* 1999;17(2):157–67.
- [6] Muratoglu OK, Bragdon CR, O'Connor DO, Jasty M, Harris WH. A novel method of crosslinking ultra-high-molecular-weight polyethylene to improve wear, reduce oxidation, and retain mechanical properties: Recipient of the 1999 HAP Paul Award. *J Arthroplasty* 2001;16(2):149–60.
- [7] Urban JA, Garvin KL, Boese CK, Bryson L, Pedersen DR, Callaghan JJ, et al. Ceramic-on-polyethylene bearing surfaces in total hip arthroplasty. Seventeen to

- twenty-one-year results. *J Bone Joint Surg Am* 2001;83(11):1688–94.
- [8] St John KR, Zardiackas LD, Poggie RA. Wear evaluation of cobalt-chromium alloy for use in a metal-on-metal hip prosthesis. *J Biomed Mater Res B Appl Biomater* 2004;68(1):1–14.
- [9] McMinn DJ, Daniel J, Pynsent PB, Pradhan C. Mini-incision resurfacing arthroplasty of hip through the posterior approach. *Clin Orthop Relat Res* 2005;441:91–8.
- [10] Clarke IC, Good V, Williams P, Schroeder D, Anissian L, Stark A, et al. Ultra-low wear rates for rigid-on-rigid bearings in total hip replacements. *Proc Inst Mech Eng [H]* 2000;214(4):331–47.
- [11] Fisher J, Hu XQ, Stewart TD, Williams S, Tipper JL, Ingham E, et al. Wear of surface engineered metal-on-metal hip prostheses. *J Mater Sci Mater Med* 2004;15(3):225–35.
- [12] Keel JB, Kuster MS. Massive wear of an incompatible metal-on-metal articulation in total hip arthroplasty. *J Arthroplasty* 2004;19(5):638–42.
- [13] Korovessis P, Petsinis G, Repanti M, Repantis T. Metallosis after contemporary metal-on-metal total hip arthroplasty. Five to nine-year follow-up. *J Bone Joint Surg Am* 2006;88(6):1183–91.
- [14] Savarino L, Granchi D, Ciapetti G, Cenni E, Nardi Pantoli A, Rotini R, et al. Ion release in patients with metal-on-metal hip bearings in total joint replacement: a comparison with metal-on-polyethylene bearings. *J Biomed Mater Res* 2002;63(5):467–74.
- [15] Dowson D, Hardaker C, Flett M, Isaac GH. A hip joint simulator study of the performance of metal-on-metal joints: Part I: the role of materials. *J Arthroplasty* 2004;19(8):118–23.
- [16] Bowsher JG, Nevelos J, Williams PA, Shelton JC. ‘Severe’ wear challenge to ‘as-cast’ and

- 'double heat-treated' large-diameter metal-on-metal hip bearings. Proc Inst Mech Eng [H] 2006;220(2):135–43.
- [17] Brizuela M, Garcia-Luis A, Viviente JL, Braceras I, Onate JJ. Tribological study of lubricious DLC biocompatible coatings. J Mater Sci Mater Med 2002;13(12):1129–33.
- [18] Gutmanas EY, Gotman I. PIRAC Ti nitride coated Ti-6Al-4V head against UHMWPE acetabular cup-hip wear simulator study. J Mater Sci Mater Med 2004;15(4):327–30.
- [19] Bowsher JG, Hussain A, Williams P, Nevelos J, Shelton JC. Effect of ion implantation on the tribology of metal-on-metal hip prostheses. J Arthroplasty 2004;19(8):107–11.
- [20] Oka M, Ushio K, Kumar P, Ikeuchi K, Hyon SH, Nakamura T, et al. Development of artificial articular cartilage. Proc Inst Mech Eng [H] 2000;214(1):59–68.
- [21] Ushio K, Oka M, Hyon SH, Yura S, Toguchida J, Nakamura T. Partial hemiarthroplasty for the treatment of osteonecrosis of the femoral head. An experimental study in the dog. J Bone Joint Surg Br 2003;85(6):922–30.
- [22] Moro T, Takatori Y, Ishihara K, Konno T, Takigawa Y, Matsushita T, Chung UI, Nakamura K, Kawaguchi H. Surface grafting of artificial joints with a biocompatible polymer for preventing periprosthetic osteolysis. Nature Mater 2004;3:829–37.
- [23] Kyomoto M, Moro T, Konno T, Takadama H, Yamawaki N, Kawaguchi H, et al. Enhanced wear resistance of modified cross-linked polyethylene by grafting with poly(2-methacryloyloxyethyl phosphorylcholine). J Biomed Mater Res A, in press.
- [24] Kyomoto M, Moro T, Konno T, Takadama H, Kawaguchi H, Takatori Y, et al. Effects of

- photo-induced graft polymerization of 2-methacryloyloxyethyl phosphorylcholine on physical properties of cross-linked polyethylene in artificial hip joints. *J Mater Sci Mater Med*, in press.
- [25] Ishihara K, Ueda T, Nakabayashi N. Preparation of phospholipid polymers and their properties as polymer hydrogel membranes. *Polym J* 1990;22(5):355–60.
- [26] Ishihara K, Aragaki R, Ueda T, Watanabe A, Nakabayashi N. Reduced thrombogenicity of polymers having phospholipid polar groups. *J Biomed Mater Res* 1990;24:1069–77.
- [27] Ishihara K, Ziats NP, Tierney BP, Nakabayashi N, Anderson JM. Protein adsorption from human plasma is reduced on phospholipids polymers. *J Biomed Mater Res* 1991;25(11):1397–407.
- [28] Goda T, Konno T, Takai M, Moro T, Ishihara K. Biomimetic phosphorylcholine polymer grafting from polydimethylsiloxane surface using photo-induced polymerization. *Biomaterials* 2006;27(30):5151–60.
- [29] Sibarani J, Takai M, Ishihara K. Surface modification on microfluidic devices with 2-methacryloyloxyethyl phosphorylcholine polymers for reducing unfavorable protein adsorption. *Colloids Surf B Biointerfaces* 2007;54(1):88–93.
- [30] Ueda H, Watanabe J, Konno T, Takai M, Saito A, Ishihara K. Asymmetrically functional surface properties on biocompatible phospholipid polymer membrane for bioartificial kidney. *J Biomed Mater Res A*. 2006;77(1):19–27.
- [31] Abraham S, Brahim S, Ishihara K, Guiseppi-Elie A. Molecularly engineered p(HEMA)-based hydrogels for implant biochip biocompatibility. *Biomaterials* 2005;26(23):4767–78.

- [32] Konno T, Hasuda H, Ishihara K, Ito Y. Photo-immobilization of a phospholipid polymer for surface modification. *Biomaterials* 2005;26(12):1381–8.
- [33] Palmer RR, Lewis AL, Kirkwood LC, Rose SF, Lloyd AW, Vick TA, Stratford PW. Biological evaluation and drug delivery application of cationically modified phospholipid polymers. *Biomaterials* 2004;25(19):4785–96.
- [34] Snyder TA, Tsukui H, Kihara S, Akimoto T, Litwak KN, Kameneva MV, Yamazaki K, Wagner WR. Preclinical biocompatibility assessment of the EVAHEART ventricular assist device: Coating comparison and platelet activation. *J Biomed Mater Res A*. 2007;81(1):85–92.
- [35] Kuiper KJ, Nordrehaug JE. Early mobilization after protamine reversal of heparin following implantation of phosphorylcholine-coated stents in totally occluded coronary arteries. *Am J Cardiol* 2000;85:698–702.
- [36] Galli M, Sommariva L, Prati F, Zerboni S, Politi A, Bonatti R, et al. Acute and mid-term results of phosphorylcholine-coated stents in primary coronary stenting for acute myocardial infarction. *Cathet Cardiovasc Intervent* 2001;53:182–7.
- [37] ASTM F75-01: Standard specification for cobalt-28 chromium-6 molybdenum alloy casting and casting alloy for surgical implants (UNS R30075). In: *Annual Book of ASTM Standards* 13 (2004).
- [38] ASTM F86-04: Standard practice for surface preparation and marking of metallic surgical implants. In: *Annual Book of ASTM Standards* 13 (2004).
- [39] Seo M, Sato N. Differential composition profiles in depth of thin anodic oxide films on

- iron-chromium alloy. *Surface Science* 1979;86:601–9.
- [40] Ishihara K, Nakabayashi N. Adhesive bone cement both to bone and metals: 4-META in MMA initiated with tri-n-butyl borane. *J Biomed Mater Res* 1989;23(12):1475–82.
- [41] Yoshida K, Greener EH. Effects of coupling agents on mechanical properties of metal oxide-polymethacrylate composites. *J Dent* 1994;22(1):57–62.
- [42] Givan DA, Fitchie JG, Anderson L, Zardiackas LD. Tensile fatigue of 4-META cement bonding three base metal alloys to enamel and comparison to other resin cements. *J Prosthet Dent* 1995;73(4):377–85.
- [43] Bryant SJ, Nuttelman CR, Anseth KS. Cytocompatibility of UV and visible light photoinitiating systems on cultured NIH/3T3 fibroblasts in vitro. *J Biomater Sci Polym Ed.* 2000;11(5):439–57.
- [44] International Organization for Standardization 15989: *Plastics - Film and sheeting - Measurement of water-contact angle of corona-treated films*, 2004.
- [45] Wang JH, Bartlett JD, Dunn AC, Small S, Willis SL, Driver MJ, et al. The use of rhodamine 6G and fluorescence microscopy in the evaluation of phospholipid-based polymeric biomaterials. *J Microsc.* 2005;217(Pt 3):216–24.
- [46] Kumar P, Oka M, Ikeuchi K, Shimizu K, Yamamuro T, Okumura H, et al. Low wear rate of UHMWPE against zirconia ceramic (Y-PSZ) in comparison to alumina ceramic and SUS 316L alloy. *J Biomed Mater Res.* 1991;25(7):813–28.
- [47] ASTM F732-00: Standard test method for wear testing of polymeric materials used in total joint

- prostheses. In: Annual Book of ASTM Standards 13 (2004).
- [48] International Organization for Standardization 14242-1: Implants for surgery: Wear of total hip-joint prostheses Part 1: Loading and displacement parameters for wear-testing machines and corresponding environmental conditions for test, 2002.
- [49] Suzuki T, Yuasa M, Sekine I, Yamabe H, Fujiwara T, Amano S. Investigation of the improvement of the adhesion durability of stainless steels in wet environment by surface treatment with polymer containing carboxyl groups. *Shikizai* 1998;71(12):746–54.
- [50] Yamabe H. Stabilization of the polymer-metal interface. *Progr Org Coating* 1996;28:9–15.
- [51] Saldívar-García AJ, Lopez HF. Microstructural effects on the wear resistance of wrought and as-cast Co-Cr-Mo-C implant alloys. *J Biomed Mater Res A*. 2005;74(2):269–74.
- [52] Sheeja D, Tay BK, Nung LN. Tribological characterization of surface modified UHMWPE against DLC-coated Co–Cr–Mo. *Surf Coat Technol* 2005;190(2-3):231–7.
- [53] Saikko V. Wear and friction properties of prosthetic joint materials evaluated on a reciprocating pin-on-flat apparatus. *Wear* 1993;166(2):169–78.
- [54] Ho SP, Nakabayashi N, Iwasaki Y, Boland T, LaBerge M. Frictional properties of poly(MPC-co-BMA) phospholipid polymer for catheter applications. *Biomaterials* 2003;24(28):5121–9.
- [55] Naka MH, Morita Y, Ikeuchi K. Influence of proteoglycan contents and of tissue hydration on the frictional characteristics of articular cartilage. *Proc Inst Mech Eng [H]*. 2005;219(3):175–82.