P9

Functionalization of CoCr surfaces with graphene oxide

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Synopsis

Improvements regarding durable lubrication together with minimized wear are mandatory for obtaining long-term, functioning metallic joint prostheses. For this goal, CoCr surface was functionalized with Graphene Oxide (GO), characterized by FTIR and XPS, and tested at tribocorrosion. Deposition of GO was carried out by consecutive steps: alkalinization of CoCr; intermediate coupling via 3-aminopropyltriethoxysilane (APTES) which was cured at 45 °C for 24 h; and final assemble of GO layers at 60 °C for 24 h upon exposure with silane-coated CoCr. Tribocorrosion test was performed by using a pin-on-disk tribometer with an integrated cell that contains the hyaluronic acid (HA) solution 3 g/l. GO incubated on silane-coated CoCr (CoCr-OH-Si-GO) and CoCr disks were submitted to tribocorrosion against alumina balls, applying a normal load of 5 N and a rotation rate of 120 rpm for 500 m.

Introduction

CoCr alloy for total hip and knee arthroplasties is widely extended due to, among others, the excellent tribocorrosion behavior. Nevertheless, it is unavoidable that the continuous sliding between the contact areas shorten prosthesis durability. In fact, the released degradation products as wear particles and metal ions cause inflammatory and immune reactions, as well as systemic toxicity and genotoxicity.

All the efforts addressed to decrease wear-corrosion on contacting areas are welcomed. In particular, the aim of this study is to simulate the carbon-enriched chemical composition found on the surface of the retrieval prosthesis associated with the lowest wear rate [1]. The strategy described in this work tries to take advantage of the mechanical properties of graphene to generate biocompatible carbon-enriched layers on CoCr surfaces.

Experimental

Biomedical grade CoCr alloy supplied by International Edge was immersed in 5 M NaOH for 2 h for surface hydroxylation. After that, activated surfaces were soaking in hydrolyzed APTES (2 vol % in isopropanol-water (200: 1 v/v) and stirred for 1 h at room temperature for 1 min. Then, silane-coated samples were curated at 45 ºC for 24 h. Final step was the incubation of silane-coated samples in 4 g/l graphene oxide aqueous suspension at 60 ºC for 24 h [2]. Tribocorrosion response was studied by using a pin-on-disk tribometer with an integrated cell that contains the hyaluronic acid (HA) solution 3 g/l. The wear-corrosion tests were performed on GO incubated on silane-coated CoCr (CoCr-OH-Si-GO) and CoCr disks against alumina balls. A normal load of 5 N was applied at a rotation rate of 120 rpm for 500 m.

Results and Discussion

Table 1 shows the % peak area from high-resolution XPS spectra. After incubation of GO on silane-CoCr, a reduction of the primary amine peak areas together with an increase in the secondary amine is observed. C-O-C peak area decreased in GO incubated silane-surfaces compared to epoxy contribution in Reference GO. Finally, C=O peak area is significantly increased and COOH slightly diminishes in comparison with Reference GO [2].

Table 1. % peak area from high-resolution XPS spectra for multilayer system on CoCr.

Spectrum	O 1s	N 1s		C 1s						
peak	OH^-	NH_2	NH	C sp^2	C sp^3	C-N	C-O	C-O-C	C=O	COOH
BE (eV)	(532.1)	(399.61)	(401.34)	(284.5)	(285.4)	(285.9)	(286.19)	(286.83)	(288)	(289.01)
% peak area										
CoCr	56,76									
CoCr-OH	94,21									
CoCr-OH-Si	90,20	85,78	14,22							
CoCr-OH-Si-GO		40,43	59,57	55,58	2,01	2,79	16,77	11,35	6,84	4,66
Reference GO				53,2	0,5		2,0	34,42	2,61	7,27

Figure 2 shows the coefficient of friction (COF) versus distance for CoCr and CoCr-OH-Si-GO surfaces in HA solution. The presence of GO modifies the surface performance decreasing the coefficient of friction (lower than 0.20) from the beginning to the end of the test with respect to CoCr disks.

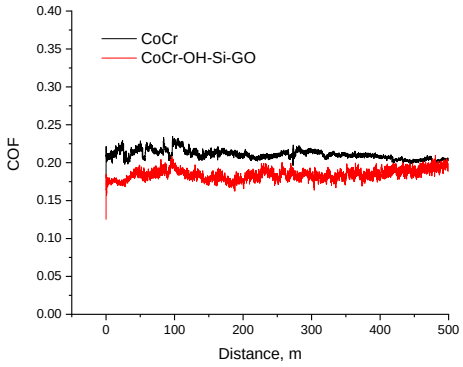

Figure 1. COF versus distance for CoCr and CoCr-OH-Si-GO in HA.

Conclusions

- Covalent silane/GO reactions occurred mainly between primary amines of APTES silane and epoxy groups of GO.

- Graphene oxide on silane-CoCr decreases COF values.

References

[1] A. García-Argumánez, et al. Electrochemical Reduction of Graphene Oxide on Biomedical Grade CoCr Alloy. Appl. Surf. Sci. 465 (2019) 1028.

[2] L. Sánchez-López, et al. Covalent immobilization of Graphene Oxide on biomedical grade CoCr alloy by an improved multilayer system assembly via Silane/GO bonding. Materials Chemistry and Physics. (2022) Under revision.