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Tribological study of lubricious DLC biocompatible coatings

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DLC (diamond-like carbon) coatings have remarkable tribological properties due mainly to their good frictional behavior. These coatings can be applied in many industrial and biomedical applications, where sliding can generate wear and frictional forces on the components, such as orthopaedic metal implants.

This work reports on the development and tribological characterization of functionally gradient titanium alloyed DLC coatings. A PVD-magnetron sputtering technique has been used as the deposition method.

The aim of this work was to study the tribological performance of the DLC coating when metal to metal contact (cobalt chromium or titanium alloys) takes place under dry and lubricated test conditions.

Prior work by the authors demonstrates that the DLC coating reduced considerably the wear of the ultra-high-molecular-weight polyethylene (UHMWPE).

The DLC coating during mechanical testing exhibited a high elastic recovery (65%) compared to the values obtained from Co–Cr–Mo (15%) and Ti–6Al–4V (23%). The coating exhibited an excellent tribo-performance against the Ti–6Al–4V and Co–Cr–Mo alloys, especially under dry conditions presenting a friction value of 0.12 and almost negligible wear.

This coating has passed biocompatibility tests for implant devices on tissue/bone contact according to international standards (ISO 10993).

1. Introduction

Titanium and cobalt–chromium alloys are of great interest in the biomedical field because of their excellent combination of properties, such us high strength and corrosion resistance. This is one of the reasons why these materials are so widely used in total joint replacements against ultra-high molecular weight polyethylene (UHMWPE) components. However, titanium alloys under medium to high contact stresses show a poor tribological performance often leading to severe seizure by adhesive wear or to scratching when a three body abrasive wear is operative. The authors have previously reported [1, 2] that diamond-like-carbon (DLC) coatings deposited on Ti–6Al–4V or Co–Cr–Mo alloys induce a change in the operative wear mechanism when rubbing against ultra-high-molecular-weight polyethylene (UHMWPE) and, as a result, there is a reduction in friction in the tribo-system and a significant wear reduction of the mating UHMWPE material. The UHMWPE wear rate is one of the most important factors affecting life and performance of hip joints and knee implants, since the generated UHMWPE debris has been linked to complications such as tissue inflammation, bone loss (osteolysis) and implant loosening [3] and has been the subject of extensive research in the field of orthopaedics [4, 5].

A new functionally gradient and bio-compatible DLC coating for orthopaedic metal implants has been developed by a physical vapor deposition (PVD) – magnetron sputtering technique [6]. This coating has passed all bio-compatibility tests for long term implantable devices on tissue/bone contact in accordance with FDA regulations and ISO 10993 international standard (e.g. cytotoxicity tests – biocolonization, mutagenicity assays, irritation and sensitization tests, hemo-compatibility, biodegradation tests, and implantation in animals) [7].

This DLC coating has demonstrated a remarkable performance up to 5 million wear cycles in a knee wear simulation machine against UHMWPE plates, reducing considerably the wear of the counteracting UHMWPE without any sign of damage on the coating [2].

The objective of the present work is to evaluate the behavior of the DLC coating in a tribo-system in which metal against metal (such as cobalt chromium o titanium alloys) takes place, without the presence of UHMWPE in the wearing contact to avoid the generation of polymeric debris associated to the clinical complications aforementioned. Additionally, DLC coatings can be applied in other biomedical products or components owing to the excellent combination of bi-inertness and low friction, therefore the metal against metal tribocontact should be

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also evaluated. Micro-mechanical together with dry and lubricated ball-on-disk wear tests have been performed on DLC coated materials.

2. Experimental work

Titanium alloyed DLC coatings with a thickness of 3.4 μm were deposited for tribo-mechanical tests only on Co–Cr–Mo discs of 40 mm diameter × 5 mm thick with a surface finish of 0.01 μm Ra. A CemeCon CC800/8 magnetron sputtering PVD unit was used for the deposition work. The Ti doped DLC film was produced by dc magnetron sputtering from four Ti targets (cathode power from 500 to 100 W) in a mixture of Ar and acetylene discharge at a pressure of 0.4–0.9 Pa at a variable Ar flow of 100–150 sccm and a variable acetylene flow from 0 to 50 sccm.

The biological evaluation of the DLC coating was carried out complying with ISO 10993 standard and following the FDA guidelines for implantable materials. The tests performed on the DLC coated Co–Cr–Mo samples were:

- *In vitro* cytotoxicity (according to UNE-EN 30993-5:1995 standard).
- Bacterial mutagenicity (UNE-EN 30993-3:1994 and the guideline 472 from OCDE).
- Haemolysis (UNE-EN ISO 10993-4:1993 and ASTM F756-93 standards).
- Cutaneous reaction (based on the standard UNE-EN ISO 10993-10:1996 and USP 23 ⟨88⟩).
- Sensitization (based on the standard UNE-EN ISO 10993-10:1996 and the ASTM F720-92).
- Systemic toxicity (based on UNE-EN ISO 10993-11:1996 and UPS 23 ⟨88⟩ standards).
- Subchronic toxicity (based on the standard UNE-EN ISO 10993-11:1996 and guideline 408 from OCDE).
- Bone implantation (based on the standard UNE-EN 10993-6:1995).

Hardness under load, elastic recovery, and modified Young modulus of DLC thin film and the two substrate alloys were measured with a Fischerscope H100 dynamic microprobe apparatus using a conventional Vickers indenter under maximum load of 10 mN and following a procedure reported previously [8].

Wear and friction tests were performed with a pin-on-disc Falex ISC 320 tribometer both under dry conditions (with a controlled humidity of 50% RH) and lubricated with bovine serum. The load applied on the tests was of 0.981 N by means of a Co–Cr–Mo or Ti–6Al–4V pin with a spherical tip of 10 mm diameter. The tests were conducted at a constant sliding speed of 0.1 m/s for 60 min. The material combinations tested were Co–Cr–Mo with and without DLC coating against uncoated Co–Cr–Mo or Ti–6Al–4V and Ti–6Al–4V against itself, the latter taken also as a reference material combination. Wear volume and surface morphology were evaluated on worn areas of discs and balls after testing by using noncontact laser surface profilometry and scanning electron microscopy (SEM). The volume of the material removed in both counteracting samples was used to determine the wear rate. The wear rate is defined as $V/(L \times D)$, where V is the volume of material removed in mm^3, L is the load applied in Newtons, and D is the sliding distance in metres.

3. Results and discussion

3.1. Bio-compatibility tests

The DLC coated Co–Cr–Mo did not present any evidence of adverse reactions in all biocompatibility tests [7]. In the *in vitro* cytotoxicity test the growth of the monolayer cell was not affected by the DLC coating neither the cell colonization. According to UNE-EN 30993-5:1995 the DLC coating was not cytotoxic and fulfilled all standard requirements.

In addition, the DLC coated Co–Cr–Mo did not show mutagenic character according to the standard UNE-EN 30993-3:1994. The haemolytic index measured on the DLC coating was less than 0.16% (direct measurement) and less than 0.04% (in extract) which also proved that this DLC coating was not haemolytic according to ASTM F 756-93 standard.

The index of primary irritation was also measured with a value less than 0.022, fulfilling the UNE-EN ISO 10993-10:1996 and USP 23⟨88⟩ standards. Moreover, the DLC coated Co–Cr–Mo did not present any risk in sensitization when contacting the body in the tests performed under UNE-EN ISO 10993-10:1996 and ASTM F 720-92 standards.

The coated material did not produce systemic toxicity and also fulfilled the requirements of UNE-EN ISO 10993-11:1996 and USP 23 ⟨88⟩ standard.

The subchronic toxicity tests carried out on the DLC coated Co–Cr–Mo presented negative results and no evidence of adverse reactions.

Finally, the bone implantation test showed the good biocompatible character of the DLC coating. Table I shows the results and clearly demonstrates the excellent osseointegration achieved by the coating.

3.2. Mechanical and tribological tests

Table II presents a summary of the mechanical properties of the biocompatible Ti alloyed DLC coating and Co–Cr–Mo and Ti–6Al–4V alloys, obtained from the dynamic microprobe apparatus.

The results show the high elastic recovery of the DLC coating (65%) compared to the values obtained for the Ti–6Al–4V alloy (23%) and the Co–Cr–Mo alloy (15%). This is typical of DLC coatings, indicating that the coating recovers mostly after the indentation load has been released, producing a load versus indentation depth graph such as the displayed in Fig. 1 in which loading and unloading curves are almost coinciding. The

TABLE I Results from the bone implantation tests

	Co–Cr–Mo uncoated	Co–Cr–Mo coated with DLC
High power field elements	0.5	0
Necrosis ratio	0	0
Toxicity ratio	0	0
Osseointegration (%)	42.5	97.5

TABLE II Mechanical properties of DLC coating and alloys

	Material		
	Ti-DLC coating	Ti–6Al–4V	Co–Cr–Mo
Hardness at 10 mN (N/mm^2)	6109 ± 457	6096 ± 231	8395 ± 347
Elastic recovery (%)	65.33 ± 0.81	22.98 ± 0.80	15.44 ± 0.68
Modified Young modulus (GPa)[1]	66 ± 2	224 ± 9	222 ± 6

[1] $(E/(1-v^2)$.

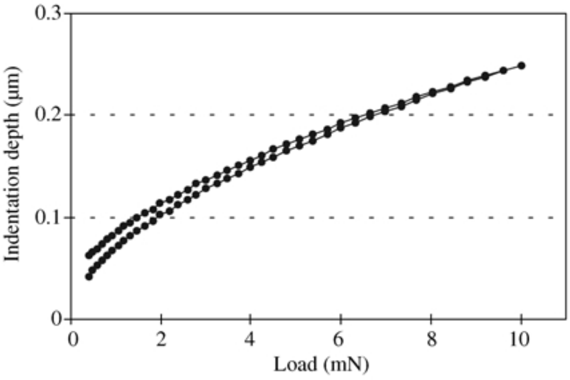

Figure 1 Load-indentation depth curve for DLC coating.

hardness obtained for this Ti alloyed DLC coating, under the maximum indentation load of 10 mN, was 6.1 GPa and similar to the value obtained from the Ti–6Al–4V alloy (6.1 GPa), but lower than the hardness of the Co–Cr–Mo alloy (8.4 GPa).

Table III and Fig. 2 summarize friction and wear results from the tribology tests. Table II presents the wear rate of discs and balls for the different material combinations tested and also the friction coefficient at the end of the test. Fig. 2 depicts graphically the friction coefficient values achieved at the end of the test as a function of material combinations and type of test, either dry or lubricated.

The highest friction coefficient (0.97) were obtained for the uncoated materials in dry, unlubricated testing, especially in the case of Co–Cr–Mo alloy disc vs. Co–Cr–Mo pin and the Ti–6Al–4V disk vs. Co–Cr–Mo pin. SEM analysis of the wear tracks on both pin and disc showed that these high friction values were due to a combined abrasive and adhesive wear mechanism promoted in the contact during the test (see Figs. 3 and 4 for the unlubricated test of Co–Cr–Mo disk vs Co–Cr–Mo pin), where some ploughing, material deformation, and transfer are evident.

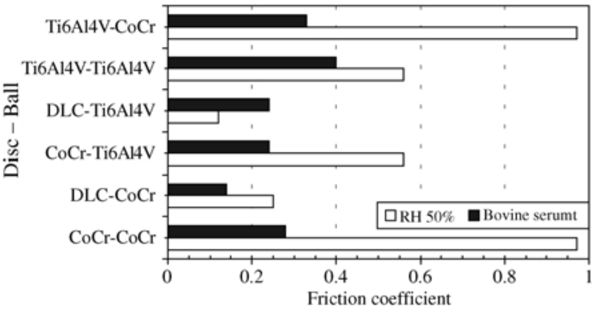

Figure 2 Friction coefficient at the end of the test as a function of contact materials and lubricating condition.

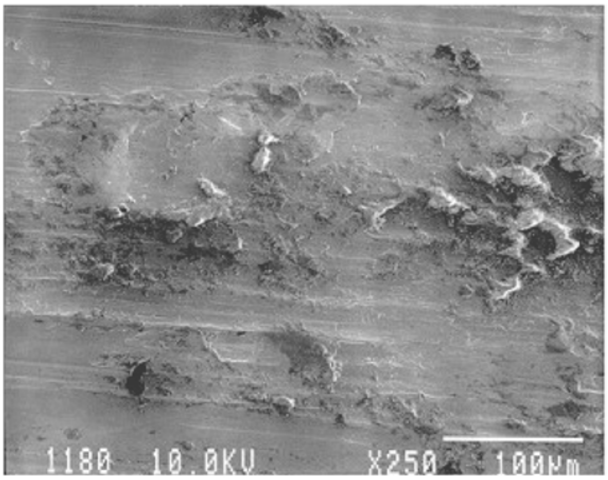

Figure 3 SEM micrograph from worn track of Co–Cr–Mo disk after dry testing (RH = 50%). Co–Cr–Mo disk vs. Co–Cr–Mo pin.

When testing was carried out between uncoated Ti–6Al–4V and Co–Cr–Mo alloys, the higher hardness of the Co–Cr–Mo caused a more severe abrasive ploughing on the Ti–6Al–4V with entrapped oxide debris and; therefore, producing higher wear rates on the latter material, both on ball and disk.

When these tests were performed under bovine serum a significant reduction in friction was observed. SEM analysis of worn surfaces showed less abrasion wear with fewer embedded particles or adhesion of counterface material. Fig. 5 presents an example of this wear mechanism.

TABLE III Friction and wear rate values for pin and disc counterfaces

Material		Dry wear test: under air (RH 50%)			Lubricated wear test: under Bovine serum		
Disc	Ball	μ	Disc wear rate (mm^3/Nm)	Ball wear rate (mm^3/Nm)	μ	Disc wear rate (mm^3/Nm)	Ball wear rate (mm^3/Nm)
Co–Cr	Co–Cr	0.97	3.9×10^{-5}	1.3×10^{-5}	0.28	3.7×10^{-5}	1.3×10^{-7}
Co–Cr + DLC	Co–Cr	0.25	0	6.1×10^{-7}	0.14	0	2.5×10^{-6}
Co–Cr	Ti–6Al–4V	0.56	1.3×10^{-4}	6.5×10^{-4}	0.24	6.9×10^{-5}	3.4×10^{-6}
Co–Cr + DLC	Ti–6Al–4V	0.12	0	5.7×10^{-7}	0.24	0	1.5×10^{-5}
Ti–6Al–4V	Ti–6Al–4V	0.56	6.0×10^{-4}	2.3×10^{-4}	0.4	6.1×10^{-4}	2.0×10^{-5}
Ti–6Al–4V	Co Cr	0.97	2.3×10^{-4}	1.7×10^{-5}	0.33	6.5×10^{-4}	5×10^{-6}

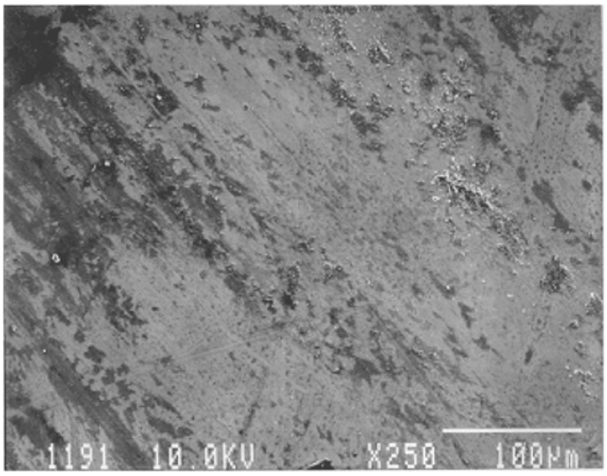

Figure 4 SEM micrograph from the worn Co–Cr–Mo pin after dry testing (RH = 50%). Co–Cr–Mo disk vs. Co–Cr–Mo.

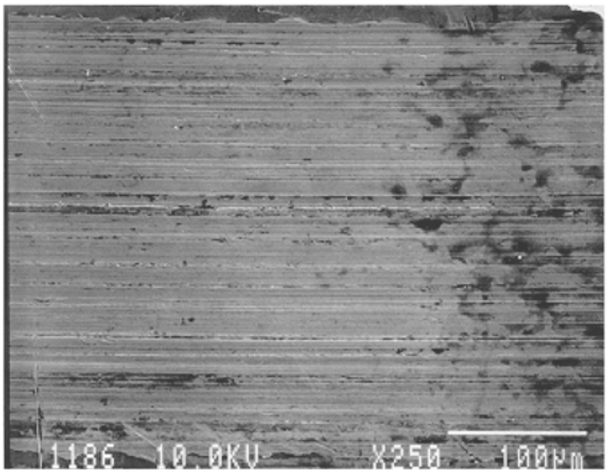

Figure 5 SEM micrograph from worn track of Co–Cr–Mo disk after bovine serum lubricated testing. Co–Cr–Mo disk vs. Co–Cr–Mo pin.

The bovine serum performs as a lubricant, allowing the removal of the debris from the wear track and hence reducing the ploughing effect of third body particles and also avoiding adhesive wear. Wear rates, mainly in pins and Co–Cr–Mo discs, were lower than in the case of tests carried out under dry conditions.

When testing the DLC coating against Ti–6Al–4V and Co–Cr–Mo a remarkable reduction in the friction is clearly observed. In tests with Co–Cr–Mo as the pin material against DLC coated discs under dry conditions the friction coefficient at the end of the test was 0.25 compared to 0.97 when the disc material is either Co–Cr–Mo or Ti–6Al–4V alloy. In the same way when Ti–6Al–4V is the pin counter material against the DLC coated disk, the friction also experimented a reduction to a value of 0.12, as opposed to the measured value of 0.56 against uncoated Ti–6Al–4V and Co–Cr–Mo discs. Furthermore, the wear was negligible on the DLC coated disc surfaces and could not be measured by laser profilometry, and wear rates of the pins were reduced by two or three orders of magnitude. The morphology of the worn tracks on the discs, as observed by SEM, was very smooth without any sign of abrasive or adhesive wear (see for example Fig. 6).

The worn surface of the Ti–6Al–4V alloy pin when tested against the DLC coated disk revealed under the SEM a smooth plastically deformed surface with little abrasive wear (see Fig. 7).

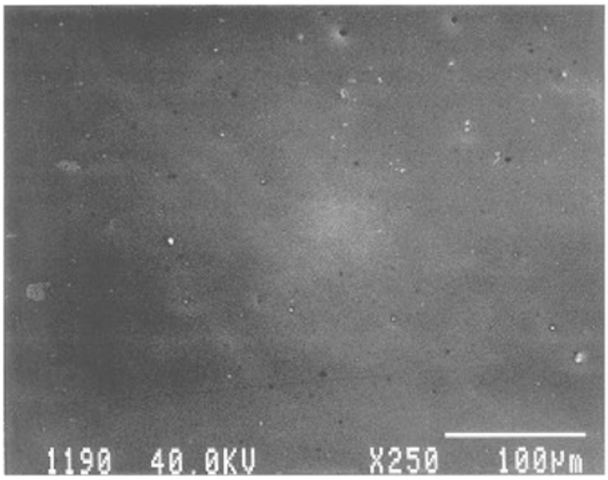

Figure 6 SEM micrograph from worn track of DLC coated Co–Cr–Mo disc after dry testing (RH 50%). DLC coated Co–Cr–Mo disc vs. Co–Cr–Mo pin.

Figure 7 SEM micrograph from worn area of Ti–6Al–4V pin after testing under dry conditions (RH 50%) against a DLC coated Co–Cr–Mo disc.

Only on the Co–Cr–Mo alloy pin some scratches could be observed (see Fig. 8), but both pin materials showed analogous low wear rates when run against the DLC coating. The reduction in friction coefficient is not surprising, owing to the good solid lubricating behavior of the DLC coating.

Similar low friction values and decrease in wear have been observed by other authors [9–11] when amorphous hydrogenated metal doped carbon films were tested against different materials.

In addition, when the same tests were carried out under bovine serum lubricant, two different behaviors were observed. If the Co–Cr–Mo alloy is the counterface material, then there is a decrease in friction from 0.25 (dry test) to 0.14 and a reduction in wear rate of two orders of magnitude. On the other hand, if the Ti–6Al–4V is the counterface material the friction coefficient increases from 0.12 (dry test) to 0.24 and also the pin wear rate increases by two orders of magnitude. This tribological phenomenon cannot be fully explained with

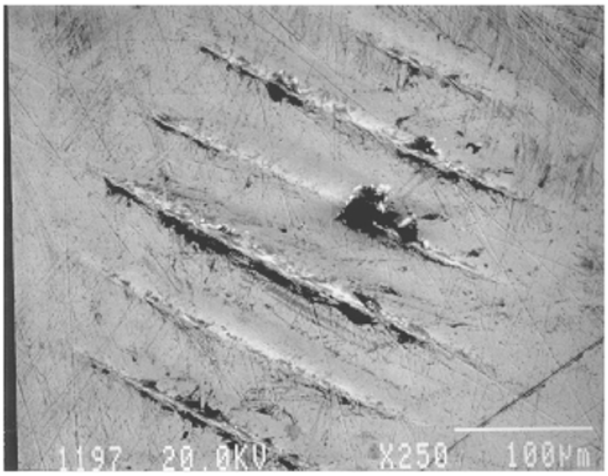

Figure 8 SEM micrograph from worn area of Co–Cr–Mo pin after testing under dry conditions (RH 50%) against a DLC coated Co–Cr–Mo disc.

the present data and further work should be carried out. It seems that the bovine serum inhibits the lubricating behavior of the DLC when tested against Ti-6Al4-V and the tribochemistry at the surface should be investigated. Besides that, no traces of wear could be measured on the DLC coated disk surfaces in any of the test performed under bovine serum.

When Oñate *et al*. [2] carried out long range wear performance of a DLC coated Co–Cr–Mo against UHMWPE in a knee wear simulation apparatus, the wear produced on the DLC coated surface was also negligible.

4. Conclusions

The following conclusions can be drawn from this study:

1. New functionally gradient DLC biocompatible coating previously developed for orthopaedic metal implants greatly improves the tribological properties when metal to metal contact occurs (e.g. cobalt chromium or titanium alloys) under dry conditions.
2. Wear and friction on both, coated disc and uncoated counterface material, were significantly improved by eliminating severe abrasive and adhesive wear.
3. The friction coefficient was markedly reduced by the DLC coating to a value of 0.12 (for the DLC coated Co–Cr–Mo disk worn under dry conditions against the Ti–6Al–4V pin).
4. Tribological properties under bovine serum were also improved by the DLC coating, although to a lesser extent.
5. The DLC coating during mechanical testing exhibited a high elastic recovery (65%) compared to the values obtained from Co–Cr–Mo (15%) and Ti–6Al–4V (23%).
6. The lubricious and biocompatible properties of the titanium alloyed DLC coating make it highly suitable for improving the performance of devices and microdevices for mechanical or biomedical applications. For the latter application, this DLC coating has passed all standard biocompatible tests for implant devices on tissue/bone contact.

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