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CORROSION BEHAVIOR IN ARTIFICIAL SALIVA OF MEDICAL GRADE SS316L SPUTTER-COATED WITH DLC FILMS: THE EFFECT OF ADHESION LAYERS

A. Fróis [1,2,3]; P. M. Faia [4]; L. F. Santos [5]; A. C. Santos [1,2,3]; C. S. Louro [1*]

[1] CEMMPRE, Department of Mechanical Engineering, Faculty of Sciences and Technology, University of Coimbra, Rua Luis Reis Santos, 3030-177 Coimbra, Portugal, cristina.louro@dem.uc.pt

[2] Faculty of Medicine, Biophysics Institute, University of Coimbra, Coimbra Institute for Clinical and Biomedical Research/Centre for Innovative Biomedicine and Biotechnology (iCBR/CIBB), 3000-548 Coimbra, Portugal

[3] Area of Environment Genetics and Oncobiology (CIMAGO), 3000-548 Coimbra, Portugal

[4] University of Coimbra, CEMMPRE – Electrical and Computer Engineering Department, FCTUC, Polo 2, Pinhal de Marrocos, Coimbra 3030-290, Portugal

[5] Centro de Química Estrutural, Institute of Molecular Sciences and Dept. de Engenharia Química; IST, University of Lisbon, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

* Corresponding author

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ABSTRACT

Hydrogenated amorphous carbon (a-C:H) top layer was deposited onto 316L medical grade stainless steel by reactive magnetron sputtering with two types of interlayers, based on Cr and Ti. The goal was to evaluate the effect of the adhesion-promoting layers on the overall coating/substrate system. After the immersion test in acidic artificial saliva, no surface signs of corrosion were detected. However, the Cr-based interlayer enhanced the metallic ions release, whereas the Ti-based one seems to improve the corrosion resistance. Electrochemical Impedance Spectroscopy was also used to evaluate galvanic corrosion evolution at the adhesion interfaces.

Keywords: DLC coatings, Metal release, Impedance spectroscopy, Orthodontics

1. INTRODUCTION

Biometallic alloys thrive in fixed orthodontics for their unmatched balance of mechanical properties, corrosion resistance and biocompatibility. Ti-based alloys, and several stainless steel (SS) grades are widely used for manufacturing brackets, archwires, tubes and bands that will remain inside the oral cavity for approximately 2 years. However, oral cavity is an ultimate corrosion-promoting environment bioalloys: oscillations on pH, temperature and chemical composition are enhanced by multiple factors, including diet and hygiene, oral biofilm activity and even the time of the day. The *in vivo* degradation of metals and alloys is therefore inevitable, disrupting any oxide passive layer and releasing metallic ions into the oral cavity [1]. Among those ions, some are toxic and can elicit hypersensitive reactions (allergies). Ni stands out as the International Agency for Research on Cancer (IARC) classifies Ni (II) and all Ni compounds as carcinogenic or potentially carcinogenic to humans [2].

Looking for a safe solution to improve human health, a surface engineering approach was chosen for this study: the outstanding diamond-like carbon (DLC). A promising group of materials is the hydrogenated amorphous carbon (a-C:H) coatings, with suitable mechanical and tribological properties, and other desirable characteristics for orthodontic applications, including bioinertness and electrical insulating character by hydrogen presence. The coatings quality and durability are governed by both H content and sp^2/sp^3 C–C bond ratio, which are further tunable by doping, in addition to their known strong adhesion to substrates. However, adhesion to metallic substrates is the DLC's "*Achilles Heel*". While such issue has been overcome by using metallic-based adhesion layers [3], previous works suggested that such interlayers may influence the overall oral corrosion resistance of the coated orthodontic alloys [4, 5].

Thus, the present study aims to evaluate the *in vitro* corrosion resistance of the DLC/M/ SS316L system by tailoring two different adhesion layers: M = Cr- and Ti-based materials.

2. DESCRIPTION

Following author's previous research work [4, 5], a-C:H coatings were deposited on polished SS 316L (AISI) substrates by reactive magnetron sputtering in CH_4 atmosphere. Preceding the external a-C:H layer, the substrates were sputter-etched by Ar^+ bombardment for 30 minutes, followed by the deposition of an adhesion-promoting layer. Two systems were prepared: DLC/CrC-Cr/SS and DLC/TiC-Ti/SS, termed DLC1 and DLC2, respectively (Table 1).

Table 1 – Main characteristics of the as-deposited DLC-based coatings.

System	Thickness		Contact angle	Roughness (S_a)	Hardness
	Interlayer [nm]	a-C:H [nm]	[º]	[nm]	[GPa]
DLC1	342	743	75±1	~4	19±2
DLC2	357	764	70±1	~6	23±2

Corrosion tests were conducted using a Fusayama-Meyer artificial saliva with pH=2.3 for 30 days (according to ISO 10271). The released metallic ions (Fe, Cr, Ni, Ti) were quantified by Inductively-Coupled Plasma – Optical Emission Spectroscopy (ICP-OES). Different metal release behaviors were observed, as seen in Fig. 1 for iron. Cr-based interlayers (DLC1) seem to decrease the overall corrosion resistance of the DLC/SS system in comparison to Ti-based adhesion layers (DLC2). The SEM/EDS analysis contradicts the ICP results and evidences a clear stability of the top a-C:H layer (Fig. 1), similar to that observed for DLC2.

Both systems were further characterized by Atomic Force Microscopy, Static Contact Angle, Raman and FTIR Spectroscopy, and Scratch Testing. Furthermore, Electrochemical Impedance Spectroscopy was performed to evaluate galvanic corrosion evolution at the adhesion interfaces along the time: results in the form of Nyquist and Bode plots will be used to analyze the evolution and to conclude of the existence or not of corrosion phenomena in the interfaces.

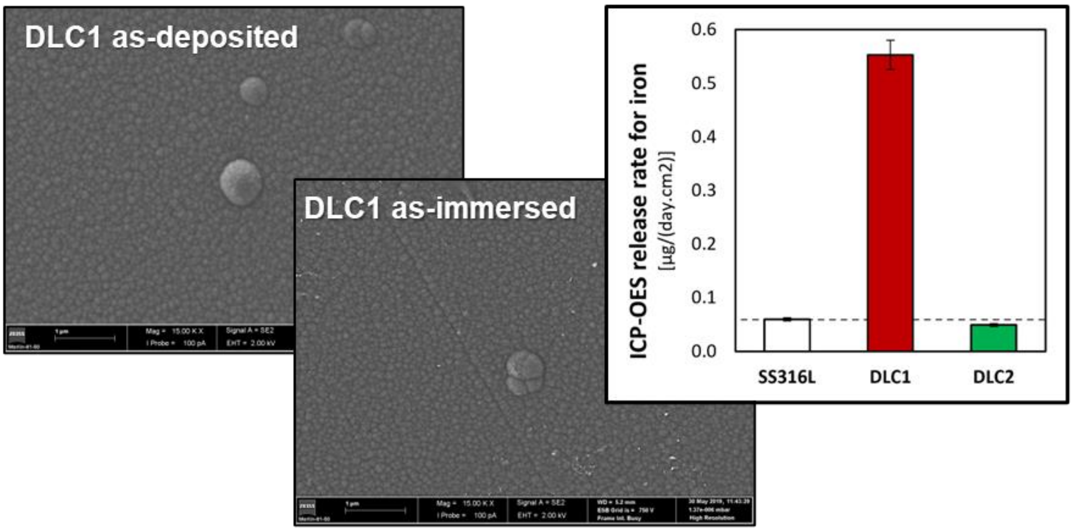

Fig. 1 – SEM micrograph of DLC1 surface before and after immersion, coupled with the iron release rates from SS316L, DLC1 and DLC2.

3. CONCLUSIONS

Hydrogenated amorphous carbon-based coatings were successfully deposited onto SS316L samples by reactive magnetron sputtering. Two adhesion interlayers were selected: Cr- and Ti-based (DLC1 and DLC2 system, respectively). After a 30-day immersion in acidic artificial saliva, no segregation, metallic inclusion, delamination, or detachments were detected on the a-C:H top film, regardless their interlayer configuration. However, metallic ions release rates from both systems showed significant differences, depending on the interlayer chemical composition, when compared with the uncoated SS316L samples. While the Cr-based interlayer enhances metal release, the Ti-based seems to improve the overall corrosion resistance. Such findings illustrate the crucial importance of coating/substrate systems when DLC-based coatings are to be considered for Orthodontics.

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