Effect of nitrogen doping of DLC film on application as biomaterial

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Abstract: In this work, we studied the effect of nitrogen addition on the properties of the DLC film deposited by PECVD on F138 stainless steel used as a bioimplant. The medium %N₂ added to the treatment enhanced the wear behavior, the low %N₂ added to the treatment improved the L929 cell adhesion, while the organosilicon impaired these properties, showing that DLC(N) films can improve the tribological and biological properties of the metal.

1. Introduction

Surface treatments of metals used in biomedical applications have been applied as an alternative method to control the significant cytotoxicity associated with bioimplants [1]. DLC has excellent properties that can be improved by doping the film with elements such as N, F, and B [2]. Specifically, DLC films doped with nitrogen (DLC(N)) improve adhesion of the film to the metal substrate [3], significantly affect bacterial adhesion on the studied material, enhance compatibility compared to untreated substrate, and demonstrate superior performance compared to the DLC film [4].

Therefore, a comprehensive study needs to be carried out to determine the effectiveness of adding nitrogen to DLC films for application as a biomaterial.

2. Methods

The films were deposited on a F138 stainless steel substrate by PECVD using a pulsed DC-power supply in three steps, starting with an ablation process using 80% Ar and 20% H₂ for 1 h, followed by the deposition of the organosilicon interlayer using 70% HMDSO and 30% Ar for 15 min, and ending with the films deposition using a total gas flow of 40 sccm (0,3 torr) for 2 h. The DLC film was deposited using 90% CH₄ and 10% Ar, and the DLC(N) films were deposited using a gas composition ranging from 90-40% CH₄ and 10-60% N₂. A multilayer film was performed by depositing the organosilicon interlayer below and above the DLC and DLC(N) films.

3. Results and Discussion

The DLC film showed an I(D)/I(G) of 0,53 and 38% de H, characterized as a hard film. The increase in the N_2 added to the treatment increased the I(D)/I(G) ratio of the films due to the transformation of the sp^3 bond into the sp^2 bond, turning the film with more graphitic characteristics, explained by the increase in the nitrogen incorporated into the film [3]. The nitrogen incorporation into the film decreased the contact angle when using the RMOI 1649 cell culture medium of the DLC(N) compared to DLC film, and a higher ${}^6\!N_2$ added to the treatment produced thinner films with lower hardness and roughness. The DLC(N) films with $30{}^6\!N_2$ added to the treatment showed

intermediate hardness and thickness, less delamination, and greater wear resistance among the studied films.

Both the substrate and all the studied films, except for the multilayer films, did not cause changes in cell morphology, showing adhesion and viability of the L929 cell, with an increase in cell proliferation, survival and viability after 48 h of cell culture for films with 10 and 20% of N₂ added to the treatment. Films with a higher percentage of N₂ added to the treatment (40, 50, and 60%) showed greater cell adhesion. However, the culture medium caused the film delamination, decreasing cell viability. The film defects, observed in greater numbers for films with higher %N₂ added to the treatments, allow the penetration of the culture medium, formed by the fetal bovine serum, antibiotic, and essential amino acids, between the film and the substrate, generating stress and instability in the films deposited on the metal substrate.

Although multilayer films showed better results than the substrate, they showed a higher contact angle and lower wear resistance than the DLC and DLC(N) films. The organosilicon films deposited on the DLC and DLC(N) films decreased cell adhesion, survival and viability, impairing the biocompatibility of the studied metal.

4. Conclusion

The DLC(N) films with 10 and 20% N₂ added to the treatment, despite not having the best physical and tribological properties than the DLC and DLC(N) with 30% added to the treatment, showed better characteristics in relation to the substrate and allowed an increase in number of cells present on the metal surface, indicating greater viability for application in bioimplants.

Acknowledgement

We would like to thanks FAPESP (2021/06386-4).

References

- [1] K. K. A. Mosas et al., Gels, **8(5)**, 323, 1-35 (2022).
- [2] D. F. Franceschini, Braz. J. Phys., **30**, 3, 517-526 (2000).
- [3] L. S. Almeida et al., Mater. Res. Exp., 7, 6, 1-18 (2020).
- [4] N. Sunthornpan, Adv. Mater. Sci. Eng., **2019**, 1–11 (2019).