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Influence of applied plasma power on degradation of L-proline in an inductively coupled RF plasma reactor

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ABSTRACT

Surface treatments such as heat treatments, paints, plasma treatments and galvanizing are important in metal working industry. In those treatments, the required adhesion characteristics can be limited if contaminants are present, so there is a need to clean these surfaces. Conventional processes can be costly, some generated waste may be environmentally hazardous and, in some cases, due to part geometry, they are not effective. Alternatively, plasma treatments which are considered to be environmentally clean, more efficient and with lower operating costs can overcome those difficulties. Due to the reactional complexity of these treatments, there are many fields to be researched, such as which reactions are due to impacts of (neutral) chemical species and which are due to excited species and radiation. The present work aims to verify the interactions between Ar-10%O_2 plasma using amino acid L-proline in an inductively coupled radiofrequency plasma. This study showed that oxidative plasma promotes high degradation of the sample. A gas analyzer (quadrupole mass spectrometer) coupled to the gas outlet was used and many gaseous products are detected during treatment, such: H_2, H_2O, CO, NO (Nitric Oxide) and CO_2 while L-proline undergoes intense degradation. The conclusions allow to state that the interaction between the Ar/O_2 plasma and L-proline promotes intense degradation through the breakdown of the heterocyclic ring of the molecule.

Keywords: Plasma cleaning; RF plasma; mass spectrometry; L-proline; oxidative plasma.

1. INTRODUTION

Surface treatments such as nitriding, DLC (*Diamond Like Carbon*), carburizing, painting, galvanization, are important part in the metalworking industry. However, these treatments will not provide necessary characteristics if there are contaminants present on the surfaces, being necessary previous cleaning prior treatments. Conventional cleaning processes can become costly, generate environmentally hazardous waste and, in some cases, due to part geometry, may not be effective [1].

As an alternative technique, there is the plasma cleaning technology, which has been the object of study of several works [2–7] and shown to be an efficient technique in degradation of compounds with different organic functions. Plasma cleaning technologies are already being used in the cleaning of inputs in the semiconductor sectors [8], food industry [9], medical [10, 11], sputtering printed circuit boards [12], surface modification [13–16] and nitriding [17, 18]. However, due to the complexity of the plasma environment, it is necessary to obtain more information about the influence of the different species on the degradation of organic functions [19]. In addition, it is also important to study the structural changes of the treated material generated by the physical parameters of the discharge, both in organic [20–22] and in metallic materials [23].

Aiming for a better understanding on the degradation mechanisms of organic functions by plasma, different compounds were studied: Hexatriacontane ($C_{36}H_{74}$), which has only C-C and C-H bonds in its structure [6]; stearic acid ($C_{18}H_{36}O_2$) which has an acidic function (Carboxyl) [4] and bi-phenil ($C_{12}H_{10}$) which has an aromatic ring [24]. In these works, argon (Ar) and argon-oxygen (Ar-O_2) plasma were used to study the degradation, functionalization and branching.

From presented works above, the great majority shows the interaction of organic chains with the plasmas-generated species, however there are few studies that show the behavior of non-aromatic cyclic chains. Some studies show the degradation of amino acids, which have non-aromatic cyclic chains, in thermal media [25] and in nitrogen atmosphere [26, 27].

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ABDOUL-CARIME and SULZER [28, 29] analyzed the thermal degradation products of the L-proline using a furnace to vaporize it and later their vapors were bombarded by low energy electrons (less than 12 eV). The products of degradation were analyzed by mass spectrometry and the main product of the degradation of L-Proline was the anion Pro dehydrogenated (Pro-H)$^-$. In addition to other degradation products of the ring (glycil-il (HCO_2^-), O^-, CN^-). They concluded that the degradation of the proline ring occurred by the process of dissociation by electron incorporation or dissociative electron attachment (DEA).

Other amino acids have been degraded, such as valine [30, 31], adenine nucleotide, degradation of DNA [32], DNA strand breaks [33] and tryptophan [34]. They concluded that the most probable process by which the biomolecules are degraded occurs by the presence of free electrons with energies below the ionization threshold, which can generate the breakage of bonds by means of the formation and decay of temporary anionic states by means of the dissociation process with electron annexation (DEA).

In NOMINÉ'S work and co-workers [6], authors treated L-proline and glycine samples in an Ar/O_2 plasma (10% V), generated by microwave. The authors verified that the proline engraving process occurs in multiple steps, probably initiating the reaction with oxygen [O (^3P)] and subsequent disruption of the non-aromatic ring.

Despite the experimental evidence showing the efficiency of plasma in the degradation of L-proline, it is necessary to know more about the interaction mechanism of aromatic rings or cyclic chains with species produced in the plasmatic environment. In this work, investigations were carried out on the degradation products of L-proline by an inductively coupled plasma reactor, with Ar-10%O_2 gas mixture and using a Residual Gas Analyzer (RGA).

2. MATERIALS AND METHODS

Samples were prepared by compressing 120 mg of L-proline (Sigma-Aldrich ≥ 99%-HPLC standard) at a pressure of 14 kPa into a 16 mm diameter stainless steel matrix, using a mechanical press, obtaining a homogeneous surface and thus promoting a more uniform treatment. The treatments were performed with the samples conditioned in a PTFE sample holder (Figure 1) to be treated by plasma.

Figure 1 presents the plasma reactor, which has a RF source of the Tokyo Hi-Power RF-300 model, which uses a frequency of 13.56 MHz, and can provide up to 300 W of power. The coupling of the system was carried out by means of a coupling box (MB) of the same manufacturer, model MB-300, adapted with the use

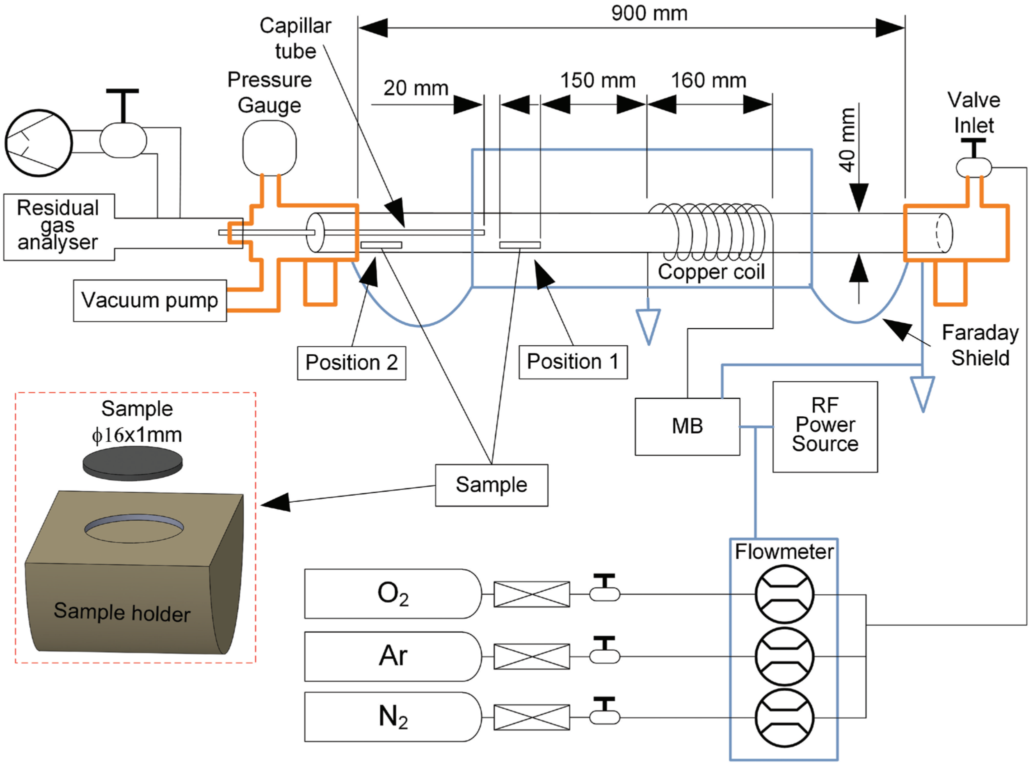

Figure 1: Experimental setup.

Table 1: Experimental conditions.

REACTOR PRESSURE (TORR)	RGA PRESSURE (TORR)	GAS	GAS FLOW (SCCM)	TIME (MIN)	APPLIED POWER (W)
10^{-1}	$8,5*10^{-4}$	Ar/(10%)O_2	300	90	100
				40	150
				20	200

of extra capacitors to provide a better inducible coupling. Gas mixture was controlled by means of an Edwards 825MFC flow meter for controlling the flow of argon (500 sccm model) and O_2 (100 sccm model).

A residual gas analyzer (Kurt J. Lesker – ACCUQUAD) was coupled to plasma reactor, as is visible in Figure 1. To collect the residual gas, a capillary tube glass connects the reactor to the gas analyzer, and is positioned 20 mm from the sample during the analysis. The gas is collected from plasma reactor due pressure difference between reactor (1 Torr) and RGA (~$8,4*10^{-4}$ Torr) interior.

Table 1 shows the experimental conditions. All treatments were initiated by introducing the sample into the quartz tube at position 2 (Figure 1) and vacuuming it to a 10^{-1} Torr pressure inside the plasma reactor. With the gas flow, the system was maintained operating at 1 Torr inside plasma reactor and at $8,5*10^{-4}$ Torr on the mass spectrometer. This condition was maintained for three hours to remove residual gases (Nitrogen (for the Air/O_2 mixture), water vapor, carbon monoxide and carbon dioxide) from within the reactor. Monitoring was done using the mass spectrometer, with the plasma switched off.

After stabilization period of residual gases, mass spectrometry was started and the background was obtained. While this condition was kept, sample was covered by a glass slide, to prevent reactive species that arrive in this position to promote surface reactivity prior to treatment. In this condition, RGA analyzes only shows residual gases not related to L-Proline treatment.

After background data collecting, the sample was moved to position 1 (Figure 1) and the glass slide was removed from the sample surface with aid of magnets and the analyzes started. All mass spectrometry measurements were obtained with electron energy at 70 eV, pressure of $8,4 \times 10^{-4}$ Torr, and scan rate of 20 points per a.m.u.. There were 7 scans for each experimental condition.

3. RESULTS AND DISCUSSION

The Figure 2 shows surface images of samples before (untreated) and after plasma treatment with different applied powers (AP). Using 100 W of AP, degradation of the sample is minimal in comparison with other conditions, darker regions indicate oxidation and degradation of L-proline. With 200 W of AP the entire sample is degraded, leaving only little residues of the degradation on sample holder at the end of the treatment. A similar behavior was observed in plasma treatment of hexatriacontane, where more etch-resistant compounds were created at higher temperatures [35]. BERNARDELLI *et al.* [36] also observed sample holder contamination when stearic acid was exposed to a plasma environment.

The higher degradation of the samples with the increase of the power is related to the greater density of the species chemically active in the plasma, ions and electrons. The temperature of the sample is another factor that should contribute significantly to a greater degradation with power increase [2, 5, 21, 22, 37]. Because of that, in the present work, a water circulation system was used to keep the temperature constant at about 0°C.

Figure 3 shows the mass spectra of residual gas formed during the treatment of plasma L-proline samples. The power increase from 100 to 150 W favored the increase of H_2, Ar^{2+}(20), O_2, Ar (36), Ar e CO_2, while partial pressure of the other compounds was minimally changed. With 200 W of AP, with the exception of O_2, there was an increase in the partial pressure of all the compounds. Formation of C_xH_x compounds was not observed at the powers of 100 W and 150 W. These results show that L-proline is being degraded in products of lower molecular mass.

Previous works that used Ar/O_2 mixture under different conditions (such as pressure, temperature and source power) [2, 5, 6, 35, 38] analyzed the residual products directly in the sample (after treatment) and evidenced the formation of products with lower molecular mass than that of L-proline [6]. This result corroborates with Figure 3, where the formation of volatile products of lower molar mass occurs from fragmentation of L-proline.

The presence of CO_2 and CO peaks (Figure 3) shows that under all conditions the reactive plasma species (O and O_2) are promoting the carbonylation of L-proline structure. The disruption of the L-proline ring can be evidenced by the presence of NO (30 a.m.u.) and C_2H_x/C_3H_x peaks since molecule configuration, with the

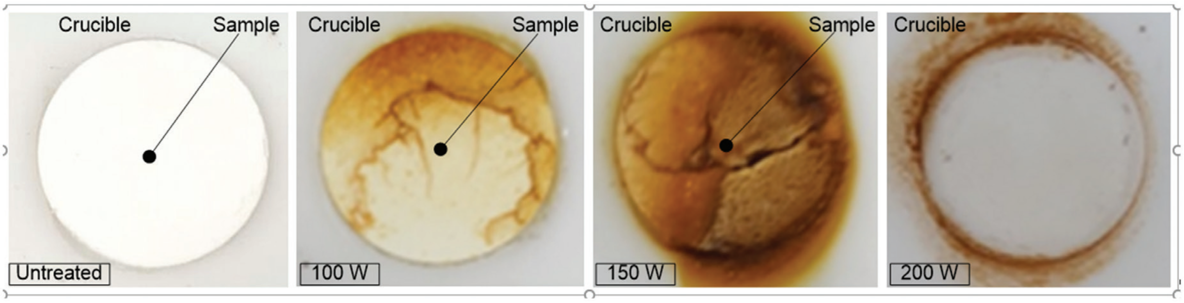

Figure 2: Samples untreated and after plasma treatment at different AP.

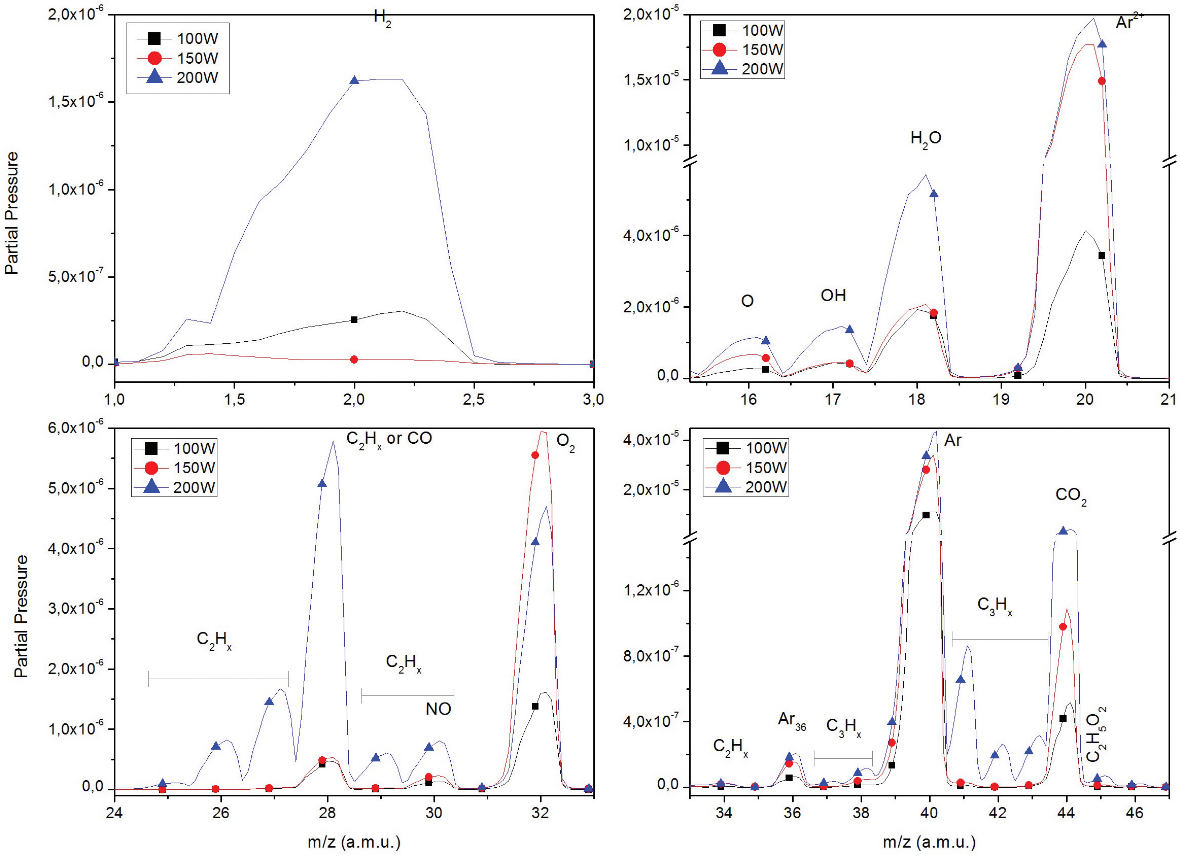

Figure 3: Mass spectrum of the volatile degradation products generated during the treatment of plasma samples as a function of the power used. Spectra obtained in the first 10 minutes of treatment.

intensity increasing as a function of the increase in applied potency. NOMINÉ [7] also showed the disruption of the non-aromatic L-proline ring, with no branching of the carbon chains after analyzing the residual products of degradation in a post-discharge microwave plasma.,

The peak at (30 a.m.u.) could also be related to formation of formaldehyde (H_2CO), however this possibility was excluded since there should be a peak at (29 a.m.u.) whose intensity would be close to twice the intensity of the peak at (30 a.m.u.) (based on RGA library). As can be seen from Figure 3, the peak that appears in this position (29 a.m.u), has approximately 3/4 of the peak intensity at (30 a.m.u.).

Another result in Figure 3, which shows the disruption of the non-aromatic ring of L-proline, is the peaks referring to the compounds C_nH_x, since these are present only in the non-aromatic ring. The presence of these compounds is more evident in the applied power of 200 W, since in this condition there is a higher rate of degradation. This result is corroborated by the shorter time required for degradation in the applied power of 200 W (Figure 2).

According to some works [4, 6, 33], degradation of organic molecules occurs through chemical reactions with species generated in the plasma like singlet oxygen, reactive oxygen atoms and even ozone molecules. Oxygen molecules are also responsible for the degradation of amino acid molecules in aqueous environment. Most reactive species are produced by several mechanisms [39, 40].

L-proline degradation products were monitored during treatment (Figure 4). It is observed that the increase of power correspondingly provided an increase in the intensity of the analyzed species. At 200 W of AP, once the plasma is started there is also has an intense process of degradation, which for the power of 150 W such process begins only at approximately 1100 seconds after the beginning of the plasma. With 100 W of AP, the production of residual species was lower and the variations that occur after 33 min (2000 s) are due to the correction of the radio frequency coupling, not evidencing modifications in the generation of compounds from the treatment.

At the power of 100 W (Figure 4) it is observed that there is a higher formation of carbon dioxide, carbon monoxide and nitrous oxide at the beginning of the treatment and after it decreases probably due to the formation of oxidative resistance compounds on sample surface. In this condition the partial pressure of ethane and hydrogen does not change throughout the experiment. There is a slight increase in the partial pressure of the Carbon, and as the time elapses the partial pressure of the water decreases until practically the same level of before the treatment.

For the power of 150 W (Figure 4), except for carbon, there is an increase in the partial pressures of all the compounds analyzed. Initially the partial pressure rises up to 4 min (240 s), reaches a plateau and remains in that plateau until 18 min (1100 s). After 18 minutes, the partial pressure increases rapidly and reaches a new level up to 28 min (1700 s), and then decreases until reaching the first landing condition. It is also observed that at the beginning of the second step an inversion of the partial pressures of CO and CO_2 occurs.

Correlating the results presented in Figure 4 with the results presented in Figure 3 both for the 150 W condition, it is observed that even reaching the third plateau, that is, a drop in the partial pressure of the compounds (1000 s), the sample has not been totally degraded as it happens at 200 W. This result indicates that on sample surface more oxidative resistant compounds were formed.

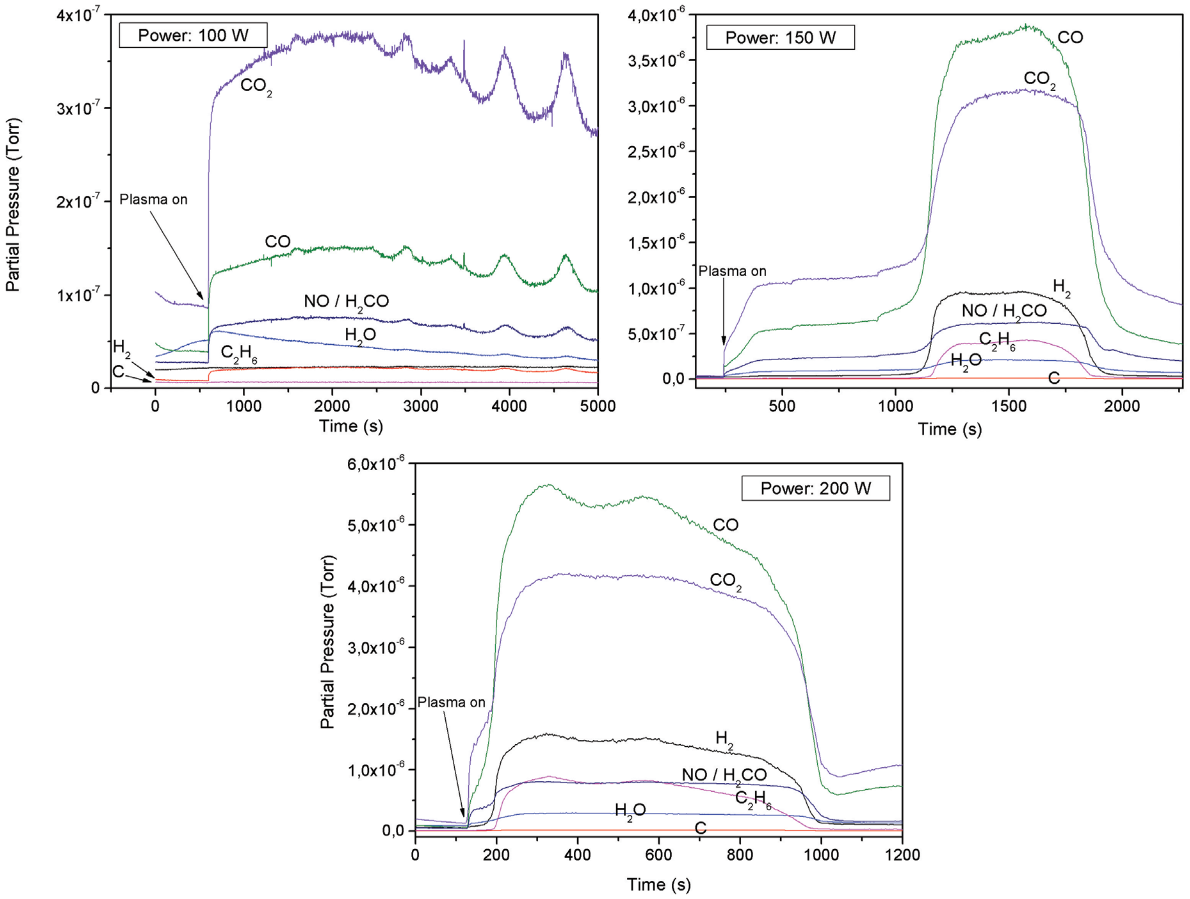

Figure 4: Time-related mass spectra for applied power.

For the power of 200 W the behavior is very similar to the one observed in the power of 150 W, with the difference that in this condition the first level is not evident. A slight level can be verified for CO_2, but it does not occur for other gases and the time elapsed between the beginning and the end of this level is lower (14 min). There is also a higher partial pressure of the same molecules studied.

In a highly oxidizing environment such as the Ar/O_2 plasma the CO/CO_2 partial pressure should be lower than that observed in Figure 4, since the appearance of CO is characteristic of a low oxidative environment. It is hypothesized that part of the CO_2 produced can be degraded in CO by the plasma, obtaining a greater partial pressure of CO.

4. CONCLUSIONS

As the objective of this work is to evaluate the effect of applied power on the degradation of L-proline, we can conclude: The mixture of Ar-O_2 (90–10%) is very reactive, producing the degradation of L-proline and the higher the applied power is, the greater is the degradation; The degradation of L-proline was initiated by the disruption of the non-aromatic ring by means of oxidative processes, forming H_2, C, NO, CO, H_2O, CO_2 and gaseous compounds of lower molecular weight such as C_nH_x and probably H_2CO (formaldehyde); Applied powers of 100 and 150 W formed products more resistant to degradation by plasma; The higher partial pressure of CO to CO_2 should be better studied, since in extremely oxidizing environment the partial pressure of CO_2 should be higher than the partial pressure of CO.

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6. BIBLIOGRAPHY

[1] AMES, D.P., CHELLI, S.J., "Surface contamination effects on film adhesion on metals and organic polymers", *Surface and Coatings Technology*, v. 187, n. 2–3, pp. 199–207, 2004. doi: http://dx.doi.org/10.1016/j.surfcoat.2004.03.027.

[2] BERNARDELLI, E.A., SOUZA, T., MALISKA, A.M., *et al.*, "Plasma etching of stearic acid in Ar and Ar-O_2 DC discharges", *Materials Science Forum*, v. 660–661, pp. 599–604, 2010. doi: http://dx.doi.org/10.4028/www.scientific.net/MSF.660-661.599.

[3] BELMONTE, T., BERNARDELLI, E.A., MAFRA, M., *et al.*, "Comparison between hexatriacontane and stearic acid behaviours under late Ar-O_2 post-discharge", *Surface and Coatings Technology*, v. 205, pp. S443–S446, 2011. doi: http://dx.doi.org/10.1016/j.surfcoat.2011.03.041.

[4] BERNARDELLI, E., BELMONTE, T., DUDAY, D., *et al.*, "Interaction mechanisms between Ar–O_2 post-discharge and stearic acid I: behaviour of thin films", *Plasma Chemistry and Plasma Processing*, v. 31, n. 1, pp. 205–215, 2011. doi: http://dx.doi.org/10.1007/s11090-010-9264-1.

[5] FARIAS, C.E., BIANCHI, J.C., OLIVEIRA, P.R., *et al.*, "Evaluation of sample temperature and applied power on degradation of stearic acid in inductively coupled radio frequency plasma", *Materials Research*, v. 17, n. 5, pp. 1251–1259, 2014. doi: http://dx.doi.org/10.1590/1516-1439.270714.

[6] NOMINÉ, A.V., MAFRA, M., FRACHE, G., *et al.*, "Treatment of glycine and proline in late Ar-O_2 afterglow", *Plasma Processes and Polymers*, v. 12, n. 12, pp. 1459–1469, 2015. doi: http://dx.doi.org/10.1002/ppap.201500126.

[7] REIS, R.R.F., NEIDERT, R., "Influência da limpeza prévia por sputtering na nitretação por plasma de aços inoxidáveis", *Matéria*, v. 16, n. 2, pp. 683–689, 2011. doi: http://dx.doi.org/10.1590/S1517-70762011000200004.

[8] TABUCHI, T., TAKASHIRI, M., MIZUKAMI, H., "Hollow electrode enhanced RF glow plasma for the fast deposition of microcrystalline silicon", *Surface and Coatings Technology*, v. 173, n. 2–3, pp. 243–248, 2003. doi: http://dx.doi.org/10.1016/S0257-8972(03)00664-9.

[9] ALVES JUNIOR, C., COSTA, I.K.F., VITORIANO, J.O., *et al.*, "Effect of atmospheric cold plasma on carnauba wax coating on inactivation of colletotrichum brevisporum", *Matéria*, v. 26, n. 2, e12975, 2021. doi: http://dx.doi.org/10.1590/s1517-707620210002.1275.

[10] CVELBAR, U., JUNKAR, I., MODIC, M., "Hemocompatible poly(ethylene terephthalate) polymer modified via reactive plasma treatment", *Japanese Journal of Applied Physics*, v. 50, n. 8S1, pp. 08JF02, 2011. doi: http://dx.doi.org/10.7567/JJAP.50.08JF02.

[11] GUERRA, T.D.B., "*Estudo da adesão de pinos endodônticos modificados superficialmente por plasma de oxigênio Estudo da adesão de pinos endodônticos modificados superficialmente por plasma de oxigênio*", Tese de M.Sc., Universidade Federal do Rio Grande do Norte, Natal, 2007.

[12] GOGOLIDES, E., BOUKOURAS, C., KOKKORIS, G., *et al*., "Si etching in high-density SF6 plasmas for microfabrication: surface roughness formation", *Microelectronic Engineering*, v. 73–74, pp. 312–318, 2004. doi: http://dx.doi.org/10.1016/S0167-9317(04)00117-0.

[13] KNIZIKEVIČIUS, R., KOPUSTINSKAS, V., "Anisotropic etching of silicon in SF6 plasmaz", *Vacuum*, v. 77, n. 1, pp. 1–4, 2004. doi: http://dx.doi.org/10.1016/j.vacuum.2004.07.063.

[14] ROCHA, R.C.S., BRAZ, D.C., BARBOSA, J.C.P., "Modificação da superfície e das propriedades tribológicas do titânio por carbonitretação a plasma", *Matéria*, v. 16, n. 3, pp. 768–774, 2011. doi: http://dx.doi.org/10.1590/S1517-70762011000300004.

[15] GOBBI, S.J., GOBBI, V.J.G., REINKE, G., "Reinke, "Improvement of mechanical properties and corrosion resistance of 316L and 304 stainless steel by low temperature plasma cementation", *Matéria*, v. 25, n. 2, e12636, 2020. doi: http://dx.doi.org/10.1590/s1517-707620200002.1036.

[16] REIS, R.F., TONELLA JUNIOR, J.L., CARDOSO, R.P., *et al*., "Obtaining S-phase layer: Glow-discharge nitriding at low temperature x SHTPN – part 3", *Matéria*, v. 24, n. 1, e12326, 2019. doi: https://doi.org/10.1590/S1517-707620190001.0608.

[17] REIS, R.F., DURANTE, G.C., "Obtenção de austenita expandida (fase S): nitretação por plasma em baixa temperatura x SHTPN – parte 2", *Matéria*, v. 20, n. 2, pp. 316–321, 2015. doi: http://dx.doi.org/10.1590/S1517-707620150002.0032.

[18] COSTA, E.S., SOUSA, R.R.M., MONÇÃO, R.M., *et al*., "Plasma nitriding and deposition in AISI M2 and D2 steel tools used in nail forming and stamping: a viability study", *Matéria*, v. 26, n. 1, e12922, 2021.

[19] MAFRA, M., BELMONTE, T., PONCIN-EPAILLARD, F., *et al*., "Treatment of hexatriacontane by Ar-O_2 remote plasma: Formation of the active species", *Plasma Processes and Polymers*, v. 6, n. S1, pp. S198–S203, Jun. 2009. doi: http://dx.doi.org/10.1002/ppap.200932406.

[20] BERNARDELLI, E.A., MAFRA, M., MALISKA, A.M., *et al*., "Influence of neutral and charged species on the plasma degradation of the stearic acid", *Materials Research*, v. 16, n. 2, pp. 385–391, 2013. doi: http://dx.doi.org/10.1590/S1516-14392013005000008.

[21] FARIAS, C.E., BERNARDELLI, E.A., BORGES, P.C., *et al*., "Determination of surface temperature in ICP RF plasma treatments of organic materials", *Materials Research*, v. 20, n. 5, pp. 1432–1443, 2017. doi: http://dx.doi.org/10.1590/1980-5373-mr-2017-0238.

[22] FARIAS, C.E., BERNARDELLI, E.A., BORGES, P.C., *et al*., "Dependence of E-H transition in argon ICP discharges for treatment of organic molecules", *Matéria*, v. 22, e11920, 2017. doi: https://doi.org/10.1590/S1517-707620170005.0256.

[23] DISCONZI, O.H.A., SANTOS, D.M.C., BORDIGNON, B.C., *et al*., "Evaluation of heat transfer in steel samples immersed in plasma", *Matéria*, v. 26, n. 3, e13028, 2021. doi: http://dx.doi.org/10.1590/s1517-707620210003.13028.

[24] Dal'Maz SILVA, W., BELMONTE, T., DUDAY, D., *et al*., "Interaction mechanisms between Ar-O_2 post-discharge and biphenyl", *Plasma Processes and Polymers*, v. 9, n. 2, pp. 207–216, 2012. doi: http://dx.doi.org/10.1002/ppap.201100119.

[25] YABLOKOV, V.Y., Smel'tsova, I.L., ZELYAEV, I., *et al*., "Studies of the rates of thermal decomposition of glycine, alanine, and serine", *Russian Journal of General Chemistry*, v. 79, n. 8, pp. 1704–1706, 2009. doi: http://dx.doi.org/10.1134/S1070363209080209.

[26] HUANG, M., LV, S., ZHOU, C., "Thermal decomposition kinetics of glycine in nitrogen atmosphere", *Thermochimica Acta*, v. 552, pp. 60–64, 2013. doi: http://dx.doi.org/10.1016/j.tca.2012.11.006.

[27] LI, Y.G., ZHOU, W.H., HUANG, L.F., *et al*., "Theoretical simulation of thermal behavior in transient heat loads testing of plasma-facing materials", *Fusion Engineering and Design*, v. 86, n. 12, pp. 2812–2820, 2011. doi: http://dx.doi.org/10.1016/j.fusengdes.2011.04.011.

[28] SULZER, P., ALIZADEH, E., MAURACHER, A., *et al*., "Detailed dissociative electron attachment studies on the amino acid proline", *International Journal of Mass Spectrometry*, v. 277, n. 1–3, pp. 274–278, Nov. 2008. doi: http://dx.doi.org/10.1016/j.ijms.2008.06.001.

[29] ABDOUL-CARIME, H., ILLENBERGER, E., "Fragmentation of proline induced by slow electrons", *Chemical Physics Letters*, v. 397, n. 4–6, pp. 309–313, 2004. doi: http://dx.doi.org/10.1016/j.cplett.2004.08.119.

[30] PAPP, P., URBAN, J., MATEJCÍK, S., *et al*., "Dissociative electron attachment to gas phase valine: a combined experimental and theoretical study", *The Journal of Chemical Physics*, v. 125, n. 20, pp. 204301, 2006. doi: http://dx.doi.org/10.1063/1.2400236. PubMed PMID: 17144694.

[31] DENIFL, S., FLOSADÓTTIR, H., EDTBAUER, A., *et al.*, "A detailed study on the decomposition pathways of the amino acid valine upon dissociative electron attachment", *The European Physical Journal D*, v. 60, n. 1, pp. 37–44, 2010. doi: http://dx.doi.org/10.1140/epjd/e2010-00060-5.

[32] HUBER, D., BEIKIRCHER, M., DENIFL, S., *et al*., "High resolution dissociative electron attachment to gas phase adenine", *The Journal of Chemical Physics,* v. 125, n. 8, pp. 084304, 2006. doi: http://dx.doi.org/10.1063/1.2336775. PubMed PMID: 16965009.

[33] BOUDAÏFFA, B., CLOUTIER, P., HUNTING, D., *et al*., "Resonant formation of DNA strand breaks by low-energy (3 to 20 eV) electrons", *Science*, v. 287, n. 5458, pp. 1658–1660, 2000. doi: http://dx.doi.org/10.1126/science.287.5458.1658. PubMed PMID: 10698742.

[34] ABDOUL-CARIME, H., GOHLKE, S., ILLENBERGER, E., "Fragmentation of tryptophan by low-energy electrons", *Chemical Physics Letters*, v. 402, n. 4–6, pp. 497–502, 2005. doi: http://dx.doi.org/10.1016/j.cplett.2004.12.073.

[35] MAFRA, M., BELMONTE, T., MALISKA, M., *et al*., "Argon-oxygen post-discharge treatment of hexatriacontane: heat transfer between gas phase and sample", *Key Engineering Materials*, v. 373–374, pp. 421–425, 2008. doi: http://dx.doi.org/10.4028/www.scientific.net/KEM.373-374.421.

[36] BERNARDELLI, E.A., BELMONTE, T., FRACHE, G., *et al*., "Interaction mechanisms between Ar–O_2 post-discharge and stearic acid II: behaviour of thick films", *Plasma Chemistry and Plasma Processing*, v. 31, n. 1, pp. 205–215, 2011. doi: http://dx.doi.org/10.1007/s11090-010-9264-1.

[37] MAFRA, M., BELMONTE, T., PONCIN-EPAILLARD, F., *et al*., "Role of the temperature on the interaction mechanisms between Argon–oxygen post-discharge and hexatriacontane", *Plasma Chemistry and Plasma Processing*, v. 28, n. 4, pp. 495–509, 2008. doi: http://dx.doi.org/10.1007/s11090-008-9140-4.

[38] BERNARDELLI, E.A., SOUZA, T., MAFRA, M., *et al*., "Modification of stearic acid in Ar and Ar-O2 pulsed DC discharge", *Materials Research*, v. 14, n. 4, pp. 519–523, 2011. doi: http://dx.doi.org/10.1590/S1516-14392011005000068.

[39] MARTINEZ, G.R., "*Geração química de oxigênio molecular no estado singleto*". Tese de D.Sc., Universidade de São Paulo, São Paulo, 2004.

[40] RONSEIN, G.E., MIYAMOTO, S., BECHARA, E., *et al*., "Oxidação de proteínas por oxigênio singlete: Mecanismos de dano, estratégias para detecção e implicações biológicas", *Química Nova*, v. 29, n. 3, pp. 563–568, 2006. doi: http://dx.doi.org/10.1590/S0100-40422006000300027.