



POWDERS AND PLASMA TECHNOLOGY LABORATORY (LTPP) AT UFPR: TWENTY YEARS WORKING WITH 'GREEN' PULSED DC PLASMA

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INTRODUCTION

In the last 20 years, since the foundation of LTPP (Powders and Plasma Technology Laboratory) at UFPR, DC Plasma obtained from Glow Discharge Processes has been increasingly used for Heat Treatment and Thermochemical Surface Treatment applications. Such practices agree very well with the provisions of Target 4 of Goal 12 ("Ensure sustainable consumption and production patterns") of the United Nations 2030 Agenda for Sustainable Development. That indicated to achieve by 2020 an environmentally sound management of chemicals and all waste throughout their life cycle, and to significantly reduce their release into air (and also into water and soil), in order to minimize their adverse impacts on human health and the environment (United Nations, 2021). In this context, significant attention has been paid mainly for the R&D of Plasma Carburizing (Carburization) applied to different classes of Stainless Steel, and to metals such as Niobium in LTPP. It should be remembered that some carburizing industrial processes widely used in the last century and even today in some places, such as liquid carburizing, are characteristically non-green technologies, since they can release vapors or liquid residues of cyanide- and carbonate-based salt baths into the air and river systems. Thus, the present work aims to emphasize the good practice of using DC Plasma for Carburizing Thermochemical Treatment purposes, which is widely used for different applications in the field of Mechanical and Metallurgical Engineering, as a significant manufacturing technology to obtain parts with wear-corrosion-fatigue resistant surfaces.

Direct current (DC) plasma for carburizing purposes can be easily obtained from a glow discharge process by applying a potential difference between two electrodes (cathode and anode) in a gaseous environment at low pressure, which leads to a convenient gaseous mixture, usually composed of $\text{Ar} + \text{H}_2 + \text{CH}_4$ to be partially ionized and excited, to ionization degree levels ranging in the order of 10^{-4} to 10^{-5} , originating a glow discharge that characterizes the formation of a typical cold plasma (Brunatto et al., 2016; Chapman, 1980). In the plasma carburizing process, the methane molecule is destabilized by dissociative collisions (Scheuer, 2021), which lead to carbon atoms being produced in profusion in the glow discharge (the plasma phase). Thus, a large source of atomic carbon is provided, and such atoms (which could include ionized, excited, or neutral states) tend to be easily condensed on the treated metallic surface.

In this case, the highly reactive physicochemical interaction at the plasma-surface interface successfully carburizes the plasma-exposed metallic layer. In addition, both hydrogen and carbon atoms produced from dissociative collisions also act as oxide-reducing species. On the other hand, high-energy plasma species bombarded by argon ions or even fast neutrals can also activate surface diffusion mechanisms as well as heat the material, thus aiding the removal of the passive oxide layer, usually present on the metal surface, facilitating the carbon diffusion into the substrate bulk. The power of using cold plasma as a

green technology for metal carburizing purposes basically remains in the fact that it has low environmental impact, since the process occurs in vacuum, under relatively low oxygen partial pressures, with negligible CO₂ formation. Thus, it can be stated that in the DC plasma carburizing process, the fractions of CO₂ released into the air tend to be minimal or even null. This characteristic agrees well with the Kyoto protocol for the reduction of greenhouse gas emissions (mainly CO₂) and global warming, which was cited by Broniszewski & Werle (2020). Advantages such as good microbial decontamination efficiency, low cost, and simple operation also explain the increasing and widespread use of plasma for many different applications in the food (Chakka et al., 2021), biomedical (Yuvaraj et al., 2021) and biomaterial (Liu et al., 2021) industry.

The aim of this work is to show how the use of 'green' DC plasma technology has made it possible for researchers from the Powders and Plasma Technology Laboratory (LTPP) at UFPR to obtain significant results in the carburizing of different metallic materials. This was done respecting the main bases of the Target 4 of the Goal 12 ("Ensure sustainable consumption and production patterns"), determined on the United Nations 2030 Agenda for the Sustainable Development for all these years, since its foundation about 20 years ago.

MATERIALS AND METHODS

Typical DC plasma carburizing apparatus and the linear glow discharge (LGD) aspect employed by LTPP (UFPR) researchers for carburizing purposes (Scheuer et al., 2021), for different metals and alloys, are shown in FIGURE 1.



FIGURE 1. Typical DC plasma carburizing apparatus and the appearance of a linear glow discharge (LGD). (LGD – Courtesy: Dr. Cristiano José Scheuer)



Low temperature DC plasma carburizing and simultaneous tempering of as-hardened martensitic stainless steel alloys are generally performed at a pressure of 400 Pa (vacuum), for gas mixtures containing 0.25, 0.5, 0.75, and 1.00 vol.% CH₄ (on a basis of 80 vol.% H₂ + 20 vol.% Ar), for treatment times ranging from 4-48 hours, and treatment temperatures in the range of 200-450 °C. For niobium plasma carburizing (Brunatto & Veles, 2015), temperatures as high as 1250 °C can be specified using similar gas mixtures as mentioned above, but for increased Ar contents, as observed for sintering purpose in hollow cathode discharge (Brunatto, 2022), or additionally by increasing the pressure when working with LGD, as observed in niobium plasma nitriding (Borcz et al., 2013; Kertscher & Brunatto, 2020). Finally, regarding the electrical parameters, the samples acting as cathode, and thus being negatively biased, are subjected to pulse voltages ranging in the order of 500-750 V.

RESULTS AND DISCUSSION

Figure 2 shows the microstructure and typical Vickers indentation marks along the diffusion layer obtained from a low-temperature DC plasma carburized AISI 420 martensitic stainless steel sample. The results clearly show smaller indentation marks on the outermost layer (indicating higher hardness values), which increase in size towards the interior of the bulk substrate (indicating lower hardness values). In this case, microhardness profiles of the treated samples showed diffusion layers up to $\approx 150 \mu\text{m}$ in depth, and the surface hardness increased up to $\approx 1050 \text{ HV}$ at $2.5 \mu\text{m}$ in depth, for substrate bulks presenting hardness of $\approx 350 \text{ HV}$. In addition, the large increase in surface hardness that leads to enhanced wear resistance is due to the formation of an outer layer composed of cementite (Fe₃C, iron-carbide) and carbon-expanded martensite ($\alpha'_c\text{-Fe}$) phases.

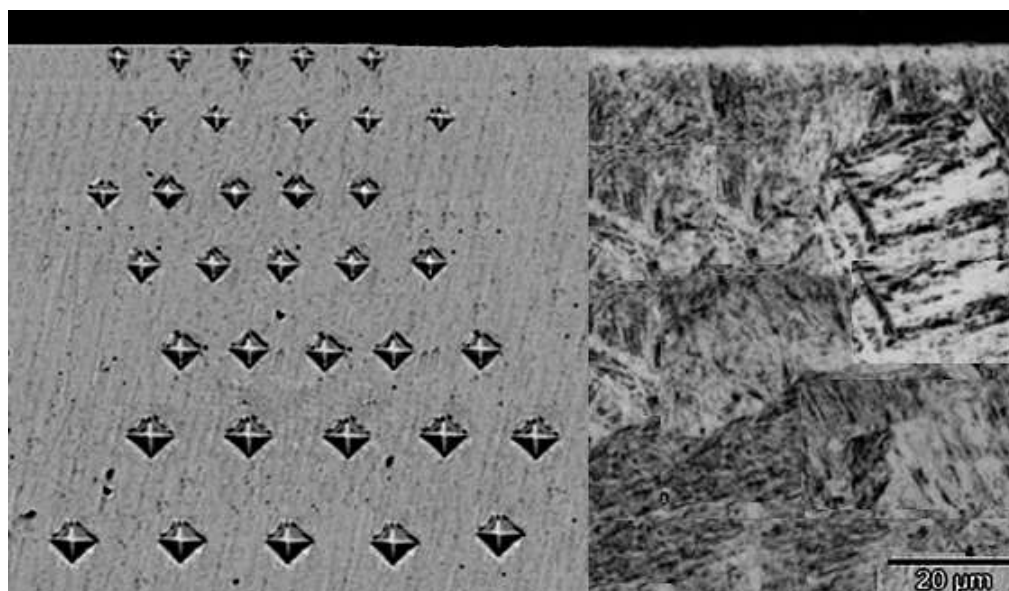


FIGURE 2. Microstructure and some typical Vickers indentation marks along the diffusion layer obtained from a low-temperature DC plasma carburized AISI 420 martensitic stainless steel sample. (Courtesy: Dr. Cristiano José Scheuer)

CONCLUSION

This work emphasized the use of 'green' DC plasma technology for carburizing purposes, from the Powders and Plasma Technology Laboratory (LTPP) at UFPR, respecting the main bases of the Target 4 of Goal 12 ("Ensure sustainable consumption and production patterns") of the United Nations.



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