

**RESEARCH**

# Automotive Plasma Painting Process

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## ABSTRACT

This study investigates the deposition of hydrogenated diamond-like carbon (DLC) films on SAE 1045 alloy samples using a plasma-enhanced chemical vapor deposition (PECVD) system and evaluates their potential as automotive coatings. Copper doping was performed via a hollow copper cathode to examine its effects on the DLC films. The primary focus was to determine the structural properties, color variations, and friction resistance of the coated samples, with the goal of establishing their applicability in the automotive industry. Raman spectroscopy confirmed the successful deposition of DLC films, while energy dispersive X-ray spectroscopy (EDS) analysis demonstrated the variation in copper atom concentrations in the samples based on the sputtering duration during the doping process. The observed color changes in the DLC films correlated with the copper atom concentrations, with the interference phenomenon and refractive index differences between DLC films and copper proposed as the primary factors influencing color variations. Scratch tests were conducted to evaluate the resistance to friction and delamination of the coated materials compared to conventionally painted steel samples. The results indicated that the DLC-coated materials exhibited higher resistance, with an estimated 15% increase in delamination resistance. The enhanced resistance was hypothesized to result from the high hardness of DLC films and the potential accumulation of nanoparticles in the valleys of the sample surface, reducing irregularities.

## KEYWORDS

DLC, PECVD, painting, automotive

## INTRODUCTION

Although there have been significant advancements in automotive coatings driven by innovative technologies and performance improvements over the past century, it is essential to acknowledge that these coating processes contribute significantly to the environmental burden compared to other aspects of vehicle manufacturing.

The present-day automotive coating process encompasses four to five stages, adaptable to accommodate specific manufacturing requirements [1]. Initially, a pre-treatment is conducted using a blend of acidic, alkaline, and rust-converting agents such as sodium hydroxide (caustic soda), trisodium phosphate, and sodium carbonate. This stage eradicates contaminants and primes the surface for optimal adhesion. Pre-treatment comprises three further

procedures: degreasing, which utilizes surfactants as detergents to dissolve oils and lubricants on the body-in-white (BIW); surface conditioning, which employs a titanium orthophosphate aqueous dispersion with a pH between 8 and 10 to initiate nucleation sites for phosphate crystal development; and phosphating, where a solution of phosphoric acid, phosphate ions, nitrate ions, zinc ions, and other divalent metal ions is applied to form a compact, uniform conversion layer on the cleaned and prepared metal surface.

Subsequently, an anti-corrosion layer is electrodeposited via an electrolytic bath containing a 90% Zn-10% Fe SCGA electrodeposition solution, utilizing the cathodic E-coat process, which exhibits exceptional performance and remarkable corrosion resistance [1,2]. The pH of the solvent in the electrodeposition tank reflects the

equilibrium of acidic and caustic constituents, primarily influenced by the resin's functional groups and neutralizing agents.

Following this, a corrosion-resistant sealant such as Polyvinyl Chloride (PVC) is administered to impede water leakage and mitigate cracking and vibrational noise. A primer is then applied to enhance adhesion and generate a more even surface. Lastly, top coatings, comprising base and clear layers, are applied to establish the desired surface characteristics, including color, appearance, gloss, texture, and weather resistance.

To attain these properties, automotive basecoats utilize three varieties: solvent-borne medium solids (MS), solvent-borne high solids (HS), and water-borne. These basecoats employ pigments and effect materials to produce a vast array of automotive finishes with distinctive color values, shades, and saturations<sup>1</sup>. Pigment effects are achieved using aluminum flakes, micas, and other light interference agents.

A clearcoat layer is added for enhanced durability, environmental resistance, and scratch resistance, which relies on the crosslink density and elasticity of the polymer network. Two primary categories of clearcoats exist: 1K and 2K. The most prevalent type of paint is 1K acrylic melamine due to its favorable cost-performance balance[1, 3]. Hindered amine light stabilizers (HALS) and UV light absorbers (UVA) are incorporated into automotive clearcoats during production to ensure UV durability.

The complex multilayered structures that determine the final coating's appearance and performance are the result of the intricate interdependence between coating compositions and application processes. Surface characteristics, such as color, gloss, and texture, play a crucial role in shaping consumer perceptions of product quality<sup>1</sup>. Consequently, the need for high-quality, aesthetically pleasing surfaces has to be balanced with the growing impetus to reduce the environmental impact of coating processes [4]. This has led to legislative efforts, prompting the development and implementation of novel coating formulations and application technologies.

Water-borne, powder, and UV-cured coatings have been developed as substitutes for solvent-borne coatings [5], but this paper introduces a superior alternative: Diamond-like Carbon (DLC) coatings doped with copper atoms, which are applied via plasma deposition. These coatings exhibit exceptional hardness, low friction, and superior wear resistance, while the addition of copper atoms enhances their corrosion resistance and self-lubricating properties [6]. Moreover, plasma deposition, a precise, efficient, and environmentally friendly technique, enables the uniform application of the doped DLC coatings to the automotive chassis, thereby improving the coating's performance attributes.

Diamond-like carbon (DLC) coatings possess exceptional mechanical properties, such as high hardness ranging from 70 to 90 GPa, stiffness comparable to diamond and other superhard materials, and superior

environmental resilience against corrosive, chemical, and biological agents [6]. The origin of these remarkable mechanical properties probably reside in the coatings' extreme atomic density and short interatomic bond lengths, facilitating strong covalent bonding between carbon atoms. DLC coatings have great potential for withstanding harsh tribological conditions, including exposure to open air, hydrogen, liquid lubricants, moderate temperatures, and sliding velocities. The unparalleled combination of hardness, stiffness, and environmental durability in DLC coatings is attributed to their disordered amorphous structure and tetrahedrally-coordinated hybridization of carbon atoms.

The proposed methodology integrates advanced materials and cutting-edge processes to optimize automotive coatings' overall performance, addressing both durability and corrosion resistance challenges while minimizing the environmental footprint of the painting process. By offering DLC coatings as an alternative, this eco-friendly and efficient approach to automotive painting enables manufacturers to balance product aesthetics, durability, and ecological sustainability. This innovative strategy not only contributes to a cleaner and more sustainable automotive industry but also addresses contemporary legislative, ecological, and social concerns.

## METHODS

Six 2 cm<sup>2</sup> x 1 mm thick samples of SAE 1045 alloy were prepared for this study. The root mean square (RMS) roughness of the samples was leveled at 15 nm. Three sample groups were produced in duplicate. The polishing process was performed using abrasives with increasing particle size, from 400 to 2000, and finished with a 2-micron diamond paste.

The plasma painting process consisted of growing a DLC layer doped with copper using a PECVD (plasma-enhanced chemical vapor deposition) system. The deposition occurred in three stages: (I) substrate cleaning by argon plasma, (II) deposition of an intermediate silicon layer using the hexa-methyl-disiloxane (HMDSO<sub>4</sub>) precursor, and (III) deposition of the DLC coating by methane plasma. The experimental parameters maintained during each deposition stage are the same as described by Santos *et al.* (2016) [7].

Copper atom doping was performed using a hollow copper cathode. Depositions were carried out at 100 W for varying durations of 1 min, 5 min, and 10 min.

The scratch test was performed using a CSM Instruments Revetest model, a instrument widely employed to assess the adhesion, wear resistance, and mechanical properties of thin films and coatings. This machine features a moving indenter head, typically equipped with a Rockwell or Vickers diamond tip, designed to apply a precisely controlled progressive normal load to the material's surface as it traverses a pre-defined distance at a

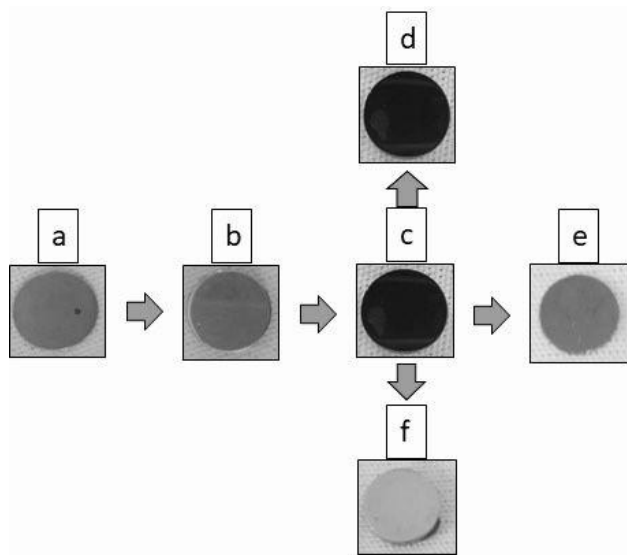
constant rate. The apparatus is capable of continuously and accurately measuring various parameters, such as scratch depth, frictional force, and acoustic emissions, by employing high-resolution sensors, including a depth-sensing LVDT (Linear Variable Differential Transformer) and an acoustic emission sensor. These measurements provide valuable insights into the behavior of the coating under different stress conditions, allowing for in-depth analysis of critical load points corresponding to film cracking, delamination, and substrate exposure.

The analysis of the structure and degree of disorder of the DLC films was performed by Raman spectroscopy, using an Ar ion laser ( $\lambda = 514 \text{ nm}$ ), operated with a backscattering geometry and ambient temperature of  $22^\circ\text{C}$ . The laser incidence point diameter was maintained at  $2.5 \mu\text{m}$ , and the power was set to  $0.6 \text{ mW}$ .

The determination of the concentration of copper atoms in the sample was carried out by energy dispersive X-ray spectroscopy (EDS).

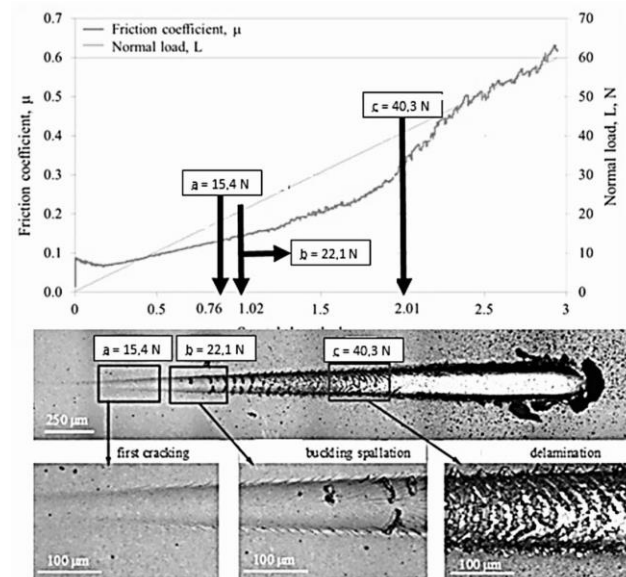
## RESULTS

**Fig. 1** shows images captured at 100x objective on a bright field inverted optical microscope (**Fig. 1a, b, c**). These images illustrate a significant reduction in average roughness for the samples (**Fig. 1a**) after the polishing process (**Fig. 1b**). The polished samples, with an RMS value of  $15 \text{ nm}$ , underwent DLC deposition using a PECVD system (**Fig. 1c**). Following this, the DLC coated alloys were doped with copper using the hollow cathode, resulting in samples exhibiting distinct colorations based on their exposure time to copper sputtering (**Fig. 1d, e, f**).



**Fig. 1.** Sample improvement process by deposition of copper-doped DLC film. The figure shows: (a) sample in original condition ; (b) polished sample; (c) DLC-coated sample; (d) DLC-Cu sample produced for 1 min; (e) DLC-Cu sample produced for 5 min; (f) DLC-Cu sample produced for 10 min.

The scratch test (**Fig. 2**) was meticulously conducted on the material coated with diamond-like carbon (DLC) to quantitatively and qualitatively evaluate the adhesive and cohesive strength of the DLC film layer on the substrate.



**Fig. 2.** Scratching test. All groups showed the same behavior regardless of copper concentration in the sample: (a) Critical load 1; (b) critical load 2; (c) critical load 3.

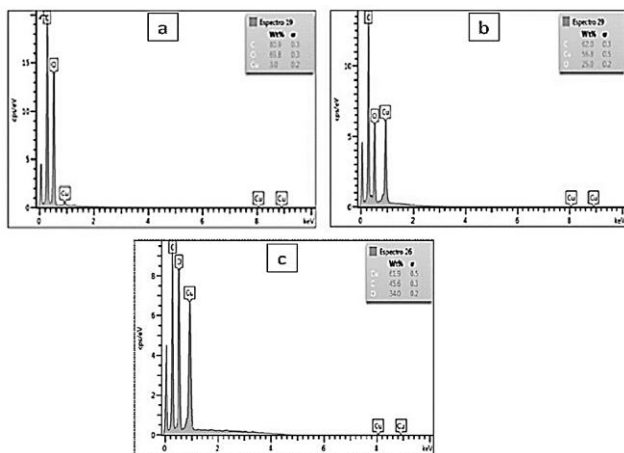
The tested samples exhibited similar characteristics in terms of the adhesive and cohesive strength of the DLC film on the substrate, indicating consistent and uniform deposition of the DLC coating across all samples. This homogeneity can be attributed to the careful optimization and control of deposition parameters, such as the temperature, pressure, and precursor gas composition. During the testing procedure, the machine applied a normal load that ranged from 0 to 60 N, incrementing in stages. This load range was strategically chosen to investigate the material's response to different stress levels and to thoroughly understand the interfacial and bulk properties of the coating. The incremental increase in load allowed for a detailed analysis of the coating's behavior under various stress conditions, highlighting critical load points that correspond to different failure mechanisms.

Upon reaching an applied normal load of approximately 15 N, the DLC film began to display brittleness, indicating that the film's tensile strength limit was reached at this point. As the normal load increased to 22.1 N, the sample began to demonstrate film fragmentation. This observation suggests that the escalated stress caused the cohesive bonds within the coating to break, leading to further deterioration of the film's structure.

When the normal load reached 40.3 N, the DLC film began detaching from the substrate, leading to delamination. Delamination is indicative of adhesion failure between the film and the substrate, leading to the partial or complete removal of the coating. The applied

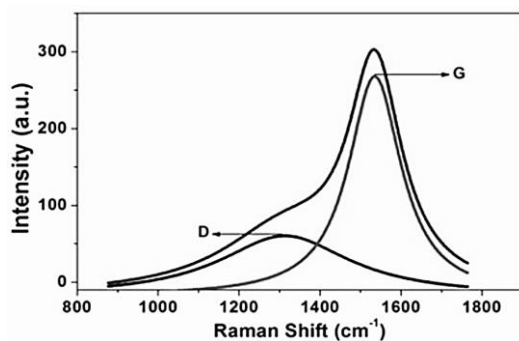
normal load varied from 0 to 60 N, and the results provided a comprehensive understanding of the mechanical and adhesion properties of the DLC coating. The DLC film began to display brittleness at 15 N, fragmentation at 22.1 N, and delamination at 40.3 N.

The analysis of the samples with EDS revealed the presence of copper in varying proportions. Among the sample groups, those subjected to sputtering treatment for 1 minute showed the lowest concentration of copper. Samples produced with the 5-minute process showed intermediate concentration, while samples produced with the 10-minute treatment showed the highest concentration of copper.



**Fig. 3.** EDS spectrum of samples: (a) 1 min deposition; (b) 5 min deposition; (c) 10 min deposition.

**Fig. 4** displays the Raman spectrum of the DLC films, represented by the superior line. The deconvolution of the original spectrum is represented by the red and black lines. It is observed that the D band and the G band are centered at approximately  $1350\text{ cm}^{-1}$  and  $1580\text{ cm}^{-1}$ , respectively, which is typical of DLC films. The ratio of the intensities of the D and G bands (ID/IG) was calculated as 0.2, indicating that the film is a hydrogenated DLC. All the coated groups displayed the same Raman spectrum typical of DLC films.



**Fig. 4.** Raman spectrum of DLC films (Blue line) of PA-DLC and RA-DLC coated groups. The black and red lines respectively show the spectrum of the deconvoluted DLC or which reveals the D( $1350\text{ cm}^{-1}$ ) and G ( $1580\text{ cm}^{-1}$ ) bands.

## DISCUSSION

The system proved to be effective in depositing DLC films as the peaks of the deconvoluted RAMAN spectra of the samples were centered at  $1350\text{ cm}^{-1}$  and  $1580\text{ cm}^{-1}$ , typical positions of the D and G bands found in diamond-like carbons. The ratio between the band intensities (ID/IG) was estimated to be approximately 0.2, which, based on equation 6.1 proposed by C. Casiraghi *et. al.* (2005) [8], indicates a hydrogenation of around 35%.

The two peaks observed at  $1380\text{ cm}^{-1}$  and  $1560\text{ cm}^{-1}$  correspond to the centers of the D and G bands, respectively. The presence of these bands confirms the nature of the hydrogenated amorphous carbon (a-C: HDLC) deposited film. According to A. C. Ferrari and J. Robertson (2004) [9], the D and G peaks are sensitive to the content of  $\text{sp}^3$  and  $\text{sp}^2$  bonds present in the films. The ID / IG ratio presented in these films corresponds to a content of  $\text{sp}^3$  bonds of approximately 20%.

According to the theory of ionic bonding, the application of metallic sputtering to hydrogenated carbon films results in the substitution of hydrogen atoms by the metal. In this case, the metal used was copper, which forms an ionic bond that is stronger than the covalent bond between carbon and hydrogen. The newly formed ionic bond is stronger than the covalent bond between carbon and hydrogen. This observation was confirmed by previous studies, such as Santos, Ramu, and Esposito (2020) [10], who found the same phenomenon in another substrate (cotton). However, further research is needed to gain a deeper understanding of this phenomenon.

The deposited samples showed 3 distinct colors: black, green, and pink. The thickness of the films remained constant, ruling out this variable as the cause of the varied colors. However, the semiquantitative determination of copper atoms in the film varied greatly depending on the deposition time, which seems to affect the way light is reflected on the samples. A positive correlation was observed between the semiquantitative determination of copper atoms and the color of the films, as represented by the equation  $Y = -0.952 + 1.571X$ , with a correlation coefficient of 0.7.

It is hypothesized that the DLC color comes from interstitial ions, also called color centers, which can trap electrons or electron holes and create transparent crystals to display various colors.

In contrast, a study by QiongYu, FuMing, and Ling (2013) [11] found that color centers are not the determining factor in the color of DLC films. Rather, the phenomenon of interference is responsible. In our daily lives, we commonly observe certain colors due to the diffraction and refraction of white light (e.g., through prisms and glass reflections). Specifically, in the case of soap bubbles and oil puddles, what we observe is the interference between two surfaces of the same very thin film, that is, the interaction of multiple beams of light.

Furthermore, the colors resulting from transmissive interference are subject to periodic oscillations that can be observed, and these interference colors are darker the thicker they are. Proportionally, the films appear clearer (up to transparency) when they are thinner and have a greater optical gap.

The study by Qiong Yu, Fu Ming, and Ling (2013) [11] also suggests that the similarity between the refractive indices of DLC films and SiO<sub>2</sub> leads to a decrease in the amplitude of the reflected light wave, resulting in a clearer color. On the other hand, the use of Si as a dopant results in a darker color due to a greater difference between the refractive index of DLC films and Si. In both cases, the color of the films is related to the phenomenon of interference, but with different intensities depending on the dopant used.

As the refractive index of copper is different from the refractive index of DLC films, this can lead to an amplification of the reflected light wave, resulting in a darker color. Therefore, the darker coloration of films produced with copper as a dopant can be explained by the difference in refractive index between DLC and copper.

The result analysis by EDS suggests that the change in color of the films is due to increased exposure to copper deposition during the sputtering process. Samples subjected to the process for 1 min did not show a difference compared to the initial sample (with DLC, without dopants), but those subjected to 5 min and 10 min showed a notable change in color. The comparison between these sample groups revealed a noticeable difference in the percentage of copper atoms found in the sample in the EDS spectra, and confirmed the hypothesis that the change in coloration was due to an increase in the concentration of the dopant in the film. As the concentration of copper atoms increased, the resulting film changed from a predominantly black color to a predominantly red color.

The scratch test conducted on SAE 1045 steel coated with diamond-like carbon (DLC) using a Micro-Scratch Tester demonstrated mechanical and adhesion properties that outperformed conventional multi-layered automotive chassis coating systems. With normal loads ranging from 0 to 60 N, the DLC coating exhibited brittleness at 15 N, fragmentation at 22.1 N, and delamination at 40.3 N. This performance is notably superior when compared to the scratch resistance of the individual layers typically used in automotive chassis painting systems, which include epoxy-based primers, acrylic or polyurethane basecoats, and polyurethane or acrylic clearcoats.

For primers, epoxy-based primers that are commonly used in automotive coatings had adhesion strengths between 1000 to 2000 psi, much lower than the 40.3 N (roughly 9000 psi) required to delaminate the DLC coating [12]. The failure modes of epoxy primers were also due to their low cohesive or adhesive strength [13].

For basecoats, acrylic and polyurethane basecoats had critical loads for visible scratches between 4 to 8 N, much

lower than the 15 N required to cause brittleness in the DLC coating (Shao et al., 2016). Although acrylic basecoats had better scratch recovery, their scratch resistance was still inferior to that of the DLC coating [14].

For clearcoats, polyurethane and acrylic clearcoats had critical loads for visible scratches between 10 to 18 N, again much lower than that of the DLC coating. Polyurethane clearcoats provided slightly better scratch resistance than acrylic clearcoats but were still outperformed by the DLC coating [15].

One hypothesis to explain this phenomenon is that, during the deposition of the film, the nanoparticles accumulated in the valleys more than in the peaks, reducing the sample irregularities. In addition, DLC films are known for their high hardness, so it is possible that they are able to protect the underlying surface from mechanical damage, increasing its resistance to friction and the risk of delamination. Further studies are still needed to confirm the relationship between nanoparticles and the reduction of sample irregularities.

## CONCLUSION

This study successfully demonstrated the deposition of DLC films on SAE 1045 alloy samples using a PECVD system and copper doping through a hollow copper cathode. The Raman spectroscopy analysis confirmed the presence of hydrogenated DLC films, with peaks centered at 1350 cm<sup>-1</sup> and 1580 cm<sup>-1</sup>, corresponding to the D and G bands. The ID/IG ratio of 0.2 indicated a hydrogenation level of approximately 35%. Furthermore, the EDS analysis revealed a varying concentration of copper atoms in the samples, depending on the sputtering duration.

The observed color change in the samples, ranging from black to green and pink, was found to be positively correlated with the concentration of copper atoms. While the exact mechanism responsible for the color change remains to be fully understood, interference phenomena and differences in the refractive indices between DLC films and copper are suggested as potential factors. The study supports the theory that increased exposure to copper sputtering alters the film's coloration due to the dopant concentration.

In addition to the color change, the coated materials demonstrated a higher resistance to friction and delamination compared to conventionally painted steel samples. The results suggest that these coated materials are at least 15% more resistant to delamination. It is hypothesized that the high hardness of DLC films, as well as the possible accumulation of nanoparticles in the valleys of the samples, contribute to the increased resistance to friction and mechanical damage.

This research contributes to the understanding of DLC film deposition and the effects of copper doping on the film's properties, such as color change and resistance to friction. The improved resistance to delamination offers potential applications in industries where surface wear and

tear are critical factors, such as automotive painting. However, further studies are needed to confirm the relationship between nanoparticles and the reduction of sample irregularities and to investigate the underlying mechanisms responsible for the observed color change in the DLC films.

Overall, the findings of this study provide a solid foundation for future research in the field of DLC coatings and their potential applications. By understanding and optimizing the deposition process and exploring the effects of various dopants, researchers can develop innovative solutions to enhance the performance and durability of materials in various industries.

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