Comparison of ICP and DBD plasma process for the degreasing of metal reinforcements

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Abstract. This paper presents two different ways of degreasing metallic wires based on plasma technology. An ICP torch and a DBD with different electrodes shapes were compared using both conventional method and design of experiments. Results show that with both methods a good degreasing can be obtained but the process optimization is uneasy because of the large number of impacting parameters. For the ICP, significant temperature gradients also make it difficult to find a good repeatability while in the case of the DBD, the filamentary discharge does not affect the regularity of treatment.

1. Introduction
Metal reinforcements are used in many industries to confer rigidity to a soft structure. In that purpose, plasma technologies were tested, especially ICP and DBD technologies. Metal wires were treated using both technologies in wide variations of different parameters such as plasma power or wire displacement velocity in the active plasma. Degreasing efficiency was then evaluated using Scanning Electron Microscope and mechanical properties were tested. Designs of experiments were used instead of conventional ones. Relevant parameters of the process were deduced from the designs and optimization was achieved for a better degreasing.

2. Methodology
As each analysis requires a relatively long processing time, it is crucial to determine the right number of tests to carry out to study the effects of our different plasma reactors on the wire while maintaining quality analysis data. In order to obtain the best degreasing while keeping the initial mechanical properties of wire, a design of experiments was used. The principle of design of experiments is to link measurable physical quantities, called "response" $Y$, to varying experimental elements, the "factors" $x_i$, by a mathematical model, typically a polynomial equation. This type of packaging actually allows to achieve a minimum of experiments to determine all the model parameters. Indeed if there is $n$ unknowns in this model, $n$ equations thus $n$ measurements are required. For instance, a response $Y$ can be modelled using the first degree polynomial with interactions:
Based on this principle, the \( n \) factors requires \( 2n \) tests illustrated in a minimum space of \( n \) dimensions by points located at the apex of an \( n \)-dimensional hypercube to minimize errors. This type of model can be easily implemented in the screening phase. But once obtained ideas about the type of global influence of each factor it is necessary to pass into more faithful model called response surface. In these models we add the terms of the second degree:

\[
Y = a_0 + \sum_{i=1}^{n} a_i x_i + \sum_{j=1}^{n} \sum_{i,j \neq i} a_{ij} x_i x_j
\]

(1)

The optimization of the position of points in the measurement space allows different configurations among which we mention Doelhert plans where measurements points are uniformly distributed on a circle. For our measurements we use for targeting phase a composite plan. This type of plan has the advantage of being part of a plan consisting in first degree and change of a model to another is easier and it allows a gain in measure. To obtain model as accurate as possible, it is important to keep all other factors constant potentially influenced during all testing (hydrometric of the room, for example). In addition to this points, a measurement point with average values of all the factors is repeated at least three times. So, we obtained an information about the repeatability of the process.

Experimental design identify quickly the important experimental parameters on each study area defines but also to find local optimum if they exist. The results presented in this paper are the product of many experimental design and their successive optimizations.

3. Experimental setup and analytical devices

Here are presented the plasma technologies used as well as the characterization devices.

3.1. Plasma facilities

Two different plasma technologies were used:
- Inductive Coupled Plasma torch (ICP);
- Dielectric Barrier Discharges (DBD).

3.1.1. ICP torch. The inductively coupled plasma torch ICP-T64 can operate with different kinds of plasma gas (air, argon, CO2, N2 and gas mixtures). A seven-turn induction coil, made in inconel, cooled by an inner air flux is used to sustain the plasma. Figure 1b shows the experimental setup. The operating conditions of the experimental set-up are given in table 1.

The plasma is generated through the induction coil by a radio frequency (RF) of 64 MHz at an electrical applied power of up to 4 kW. The plasma is confined within a 28 mm wide cylindrical, vertically mounted quartz tube. The plasma gas, with a swirl injection, has a fixed total mass flow rate of 0.2 g/s.

| Applied voltage (kV) | 2.83 | 3.05 | 3.30 |
|----------------------|------|------|------|
| Anode current (mA)   | 537.5| 576.0| 620.5|
| Power supply (kW)    | 1.52 | 1.76 | 2.05 |
| Plasma gas flow rate (L/min) | 15 | 18 | 21 |
3.1.2. **DBD devices.** In this study, two different electrodes were used. One is called DBD strait figure 2 and the second DBD comb figure 3 in reference to their geometrical forms.

For both of them, planar dielectric is made of 1.6 mm thick polyepoxides and 35 µm thick copper electrodes. The power supply is done by a single phase angle controller, Celduc SG4, with Step-up transformer 230/10,000 V, allows to generate high voltage required for application. Power change is attained through an input setpoint 0-10 V on the phase angle controller. The experimental conditions presented in table 2 correspond at the optimal power value for each generator.

| Table 2. Operating conditions of the dielectric barrier discharge set-up. |
|--------------------------------------------------------------|
| Applied voltage (kV) | 10 |
| Frequency (Hz)       | 50 |
| Phase angle controller (°) | 98 |
| Operating gas        | network air |
| Operating pressure   | atmospheric pressure |

**Figure 2.** Geometric characteristics of DBD strait, length are expressed in cm.

**Figure 3.** Geometric characteristics of DBD comb, length are expressed in cm.

3.2. **Gas**

Gas used in experiments were argon and network air. The air composition of the laboratory network summarized in table 3 is supposed to be identical to that of dry air under standard conditions of temperature and pressure (molar proportion). The air moisture is neglected.
Table 3. Composition of network air.

|   |   |
|---|---|
| N₂ | 78.08 % |
| O₂ | 20.95 % |
| CO₂ | 0.03% |
| Ar | 0.93 % |

3.3. Analyses
Three methods of analysis are detailed below, one optical and two mechanical.

3.3.1. SEM. Wires visual studies were made with a scanning electron microscope (Phillips XL30), allowing a very low acceleration voltage, and therefore very surface sensitive. Treatment efficiency is evaluated with a mark between -10 and +10:

- 0 means that the process was useless for the wire degreasing (identical to the reference sample);
- +10 corresponds to a perfect degreasing;
- -10 to a complete damage of the wire surface.

Figure 4 shows for instance two different results with two different degreasing efficiency. Figure 4(a) is a typical view of untreated sample with the presence of grease at the surface identified by its dark tint and more random distribution. Figure 4 (b) shows the result in a particular treatment condition by ICP torch described in Part 4.1. The brighter areas at high and low ends of the pictures are caused by the fact that the sample is cylindrical.

3.3.2. Mechanical measurements. Plasma treatment should change anything in the intrinsic mechanical properties of the metal wire, which is why control tests are performed by measuring the resistance to mechanical forces that are applied by a standard method of pulling out. The comparison of the maximum permissible load (maximum load accepted before passing the deformation zone at break) with control wires can guarantee a certain quality of the finished product.

To study the impact of degreasing on adhesion properties of the wire, we have made wire eight test pieces (treated or untreated) embedded in a nylon base melted after heating in an incubator of beads of PA6 nylon. The study of these in traction specimens provides adhesion contact materials and also the support of our wire with this material. The multiplicity of wire into the sample provides information on the repeatability of the process.

![Figure 4](image_url)

**Figure 4.** Visual inspection of wire surface of 500µm by 90µm and marking. (a) Untreated sample (mark 0), (b) sample treated with the ICP torch with a mark of reference estimated at +10.

3.3.3. Contact angle. Such as tensile adhesion tests are lengthy process and requires a significant length of wire, we want to evaluate another parameter that could learn about the trends in this traction
grip. Measuring the contact angle can actually perform this function since it shares many concepts with common physical adhesion phenomena such as roughness and surface tension.

To perform this measurement, it is necessary to immerse the wire in a liquid and measure the angle between the meniscus and the wire at the triple point of contact \([7]\) (contact line between solid, liquid and gas phases). Usually done when the wire is upright and tense, inclining the wire (see figure 5) facilitates measures and makes it more accurate. Indeed it is sufficient to tilt the wire until a side of the wire meniscus disappears. In this condition the contact angle is precisely the angle formed between the wire and the free surface of the water.

![Contact angle measurement](image)

**Figure 5.** Contact angle measurement by the method of the surface level.

4. **Results**

4.1. **ICP**

Experiments were achieved using ICP torch whose parameters are described in table 4.

4.1.1. **SEM.** For this testing phase the distribution of scores obtained after SEM analysis is relatively diffuse. These results are exposed in figure 6. Eight studies have negative scores symbol of degradation upper layer of wire, two are semblable to the control and was therefore not affected by the plasma treatment. Finally eleven samples get a positive mark with perfectly treated sample, marked +10. For these tests a significant gain, for fives of them, is noted when the decrease of fat on the surface. With regard to the +10 test evaluated, the SEM image show an almost total disappearance of the latter figure 4.

From these results, it turned out to be very difficult to point out the most relevants parameters of the process. The configuration that allows this measure is tested when the perceived energy of the wire is the most intense that is to say when it is near the plasma, at maximum power and flow and a speed of scrolling weak. Repeatability is it more questionable indeed for all four grades obtained, based on an analysis of the same wire treated in the same way, the notes were +7, +2, +1 and 0.

| Table 4. Limits study of factors for ICP torch. |
|-----------------------------------------------|
| Factors            | Maximum value | Minimum value |
|---------------------|---------------|---------------|
| Distance plasma wire (cm) | 12            | 20            |
| Electrical power (kW)    | 1.5           | 3.5           |
| Argon flow (L/min)     | 10            | 15            |
| Displacement velocity (m/s) | 0.50         | 2.51          |
4.1.2. Stress tests. Behavioral studies after treatment of cables with respect to force traction do not show any major degeneration with an average maximum load and maximum displacement relatively close to the control (Table 5). For testing traction adhesion, the mechanism is more variable. Indeed, only three points allow us to gain adhesion, while all other trials are losing adhesion significantly, up to 14 % (Figure 7). So even if the generator provides a relatively good degreasing without damaging the mechanical properties it is not possible to maximize adherence with PA6 nylon.

Table 5. Stress tests ICP performed on 20 tests of the plan.

|                              | Reference | Metal wire after treatment |
|------------------------------|-----------|-----------------------------|
|                              | Average   | 99.73 % confidence interval (Student law) |
| Maximum load (N)             | 248.2     | 248.1 ±7.9                  |
| Maximum move of strength (mm)| 3         | 2.9 ±0.8                    |

4.1.3. Comparative study of the contact angle and adhesion. The comparative study of the contact angle and adhesion does not identify a real dependency between the two factors, one can only note that all samples submitted possess a contact angle greater than our samples control. It is possible to note that the maximum adhesion gain is observed for test 3 which is also the test number for which the angle of contact is the closest to that of the control.

4.1.4. Analyse by optical microscopy of the wire’s surface. The best score is obtained for higher thermal and chemical energies received by the wire, tests are carried out getting closer and closer over the plasma plume. In this way we can observe in figure 8 the evolution of the outer layer of the wire at the optical microscope according to this energy. Whereas the wire has a pale color and sometimes iridescent elements when it is not treated, it then goes through different stages. For medium energy, so it takes a relatively diffuse bright orange and pink.

Such measures tend to confirm a chemical oxidation at the surface of the elements forming the outer layer of the wire during the process. In addition, oxidation distribution shows the holistic character of the treatment. Finally when an energy threshold has been exceeded, the oxidation process is such that the surface of the wire disappear and reveals the wire core. Finally, these data allow us to think that the problem of repeatability of the phenomenon is mainly due to the system of movement of the wire and not to the plasma.
Figure 7. Comparison between maximum permissible load in tensile-adherence test and contact angle during a series of 17 tests with ICP devices. The red line represents the measured value for the same tests on a control untreated wires. Blue line with • markers is for the maximum load and green line with markers is associated with the contact angle.

Figure 8. Surface texture of the wire (90 µm-120 µm) for different energy (thermal and chemical) levels applied. Left picture shows the untreated wire, while right picture was taken after a treatment with low displacement velocity into the plasma plume.

4.2. DBD
Experiments were also achieved using DBD devices whose parameters are described table 6.

Table 6. Limits study of factors for DBD devices.

| Factors                              | Maximum value | Minimum value |
|--------------------------------------|---------------|---------------|
| Distance inter-electrode (mm)        | 3.2           | 4.8           |
| Electrical power (W)                 | 2             | 3.5           |
| Air flow (L/min)                     | 0             | 3             |
| Displacement velocity (m/s)          | 0.42          | 0.84          |

4.2.1. SEM. While distributions notes of torch ICP showed a lot of damage, the DBD system itself have only slightly damaged two trials, three are similar to untreated and eleven test with a degreasing efficiency of our wire. Results of degreasing efficiency is presented in figure 9. The maximum score in is only +6 which is lower than for the ICP torch but is still quite interesting especially that repeatability is greatly improved because its four test offers notes -2, -2, +1 and +2. This method of treatment is able to degrease and is repeatable. It has especially the advantage of not causing degradation of the wire if the conditions are respected. This conditions for the device are low power and low distance between electrodes without air gas flow. As regards the crolling system, must
privilege a fast speed of displacement to protect the wire. The application is therefore all the more interesting that she has the advantage of a possible industrial adjustment with higher speed. Disparate treatment due to filamentary DBD seems relatively well avoided by the movement of the wire.

Figure 9. Efficiency of degreasing obtained for several time exposition.

4.2.2. Stress tests. Similarly, the results of traction tests shown in table 7 are relatively close to the values of untreated cables. There can be a slight drop in quality though. A supplementary study of the rotating bending wire (test applies cyclically contractions and compressions efforts in the extreme surface of the wire) have been achieved to demonstrate that the mechanical characteristic of the wire are well respected even after treatment. Furthermore, the traction adhesion measurements are also consistent with those found for the ICP torch is no significant increase in membership with losses that may reach up to 20% in adhesion.

4.2.3. Comparative study of the contact angle and adhesion. With the DBD system, the behavior of the contact angle and adhesion seems more connected (See figure 10). We can find the same overall changes depending on test. However, and considering the test with the ICP torch it is difficult to clearly identify a correlation between the two variables. Thus the contact angle measurement cannot allow in any case, any deduction of the evolution of the adhesion of wire.

Table 7. Stress tests DBD performed on 16 tests of the plan.

|                     | Reference | Metal wire after treatment |
|---------------------|-----------|----------------------------|
|                     | Average   | 99.73 % confidence interval (Student law) |
| Maximum load (N)    | 248.9     | 246.8 ±9.2                  |
| Maximum move of strength (mm) | 3.6       | 3 ±0.4                     |

4.2.4. Analyse by optical microscopy of the wire’s surface. To compare the different geometry of the generator DBD, we first observed the optimal conditions previous planes. Unfortunately no significant difference appeared. In order to observed changes, some measurements were carried out under “extrem” conditions. To do this, we fix the wire speed at its minimum i.e. 0.25 m/s (corresponding to the passage of wire during one second in the plasma), some tests in static complemented these measures. Results are presented in figure 11. The static tests provide results of degreasing of 0 to 6 s for the DBD strait and comb DBD respectively: (0, 0, +2, +1 and +5) and (0, +1, +3, +7, and two negatives values). Logically the DBD comb focuses energy on narrower field having, in addition to tip effect, who thus encourages a more rapid degreasing of the wire for comb DBD. As regards the two dynamic tests (one second scroll processing), they are of +4 for DBD strait and of +3 for the DBD comb. We can clearly identify the fact that scrolling promotes degreasing without explanation at the
moment. Red elements appearing on the DBD comb pictures are actually oxide glasses, which relates the important local heating thus allowing the merger of oxide but also equally abrupt cooling to freeze the elements in this state.

**Figure 10.** Comparison between maximum permissible load in Tensil-adherence test and contact angle during a series of 16 test with DBD devices. The red line represents the measured value for the same tests on a control untreated wires. Blue line with point markers is for the maximum load and green line with square markers is associated with the contact angle.

**Figure 11.** Surface texture of the wire (90 µm - 120 µm) for different treatment times and geometrical DBD devices.
5. Conclusion
From this study, we show that wire degreasing was possible using plasma technologies like DBD and ICP torch. The use of design of experiments method was not so fruitful since we were not able to point out the most relevant parameters in each process. The possible reasons are many:

- some important parameters maybe were not taken in account like room temperature or moisture rate;
- some response measurements were only qualitative like degreasing efficiency.

Anyway, from all the results we can claim that:

- ICP process seems to be a workable process for degreasing, but degreasing efficiency is very sensible to parameters variations. Indeed near the plasma, temperature gradients are very important, leading to other side-effects like for instance turbulence. Therefore, it turned out to be very difficult to find the good parameters to put just energy enough for a good degreasing without oxidizing or deteriorating the wire. It also have an impact onto the measures repeatability;
- DBD results are very promising even if we did not get a +10 degreasing efficiency. Further studies will focus on the DBD improving, especially the electrodes shapes, the power supply and signal shape and frequency.

6. References

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