Application of Electrolytic Plasma Process in Surface Improvement of Metals: A Review

Vitthal R. Jumbad 1, Arvind Chel 2, Updesh Verma 3, Geetanjali Kaushik 4,*

1 Research Scholar, MGM’s JNEC Research Center, Aurangabad-431003, Maharashtra, India
2 Dept. of Mechanical Engineering, MGM’s Jawaharl Nehru Engineering College, Aurangabad-431003, Maharashtra, India
3 Raman Postdoc Fellow at Princeton Plasma Physics laboratory (PPPL) Princeton University, Princeton, New Jersey-08544. MKR Government Degree College, Ghaziabad-201003, Uttar Pradesh, India
4 Dept. of Civil Engineering, Hi-Tech Institute of Technology, Waluj- 431136, Maharashtra, India
* Correspondence: geetanjaliac@gmail.com; Scopus Author ID 24335102900

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Abstract: Electrolytic plasma heat treatment is becoming a popular heat treatment process in the field of surface engineering. In this paper, research data from different research works have been analyzed. The basic mechanism of the electrolytic plasma heat treatment process is discussed along with its scope in the industry. The review is done to extend the research work of this novel process and its scope from the industrial point of view. The study will explore the electrolytic plasma process to target industrial benefits and to attract the researchers for improving the various aspects of the process. Different types of electrolytic plasma treatment have been discussed to show the capabilities of the process for improving surface properties of different metals. It is found that the treatment is less time consuming, economical, eco-friendly, and dynamic as compared to the existing heat treatment processes. Its dynamic ability makes it possible to perform carburizing, nitriding, coating, cleaning, polishing, and hardening operations in the same experimental setup with little modification.

Keywords: Plasma Electrolytic Treatment (PET); Electrolytic Plasma Heat Treatment (EPHT).

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1. Introduction

Surface improvement of metals is made to increase working life, improve the performance, and giving an aesthetic look to the metallic components. Surface properties of steel, such as wear resistance, hardness, and corrosion resistance, can be improved by surface modification processes that involved hardening, nitriding, carburizing, and nitrocarburizing. Similarly, a protective layer of a particular material can also be introducing on the surface of metals.

In the industry where steel is used in the manufacturing of every component, surface improvement plays a vital role in introducing desired mechanical properties in the steel. Press tool shops, automobile companies, press part manufacturers, aerospace industry, shipbuilding industry, Biomedical equipment manufacturer, weapon manufacturing industry are some of the areas where steel is a common metal, and hence improving the properties of steel by different techniques becomes important. Traditionally only heating and cooling of steel was the most common method of surface treatment that exist as time passed, different surface treatments evolved. Conventional heat treatment consists of heating metal in the furnace and cooling in
air, water, or oil. There are also other heat treatment processes used to improve surface properties of steel such as nitriding, carburizing, vacuum heat treatment, cryogenic heat treatment, laser heat treatment, ion beam heat treatment, etc. All these processes require high-cost setup, time of treatment is more, some processes are not eco-friendly and some are having bulky apparatus. The electrolytic plasma treatment is a novel method to encounter all these disadvantages. It is proving that it can successfully improve desired mechanical properties with much less time about few minutes as compared to traditional heat treatment processes, which require hrs and days. Also, very low-cost equipment is required, and the process is eco-friendly.

The purpose of this review is to study and focus on the various aspects of a novel method of heat treatment known as Plasma Electrolytic treatment for identifying its scope and exploring areas of challenges in it.

It is proved that electrolytic plasma treatment can successfully improve wear resistance and corrosion resistance of steel. Also, a considerable depth of hardness can be achieved in the case of tool steel to increase tool life. Single setup of an experiment can perform a different type of surface treatment such as hardening, nitriding, carbonitriding, plating, polishing, and cleaning. However, though the process is carried out for the different type of steel as well as aluminum, there is no standardized material-wise heat treatment cycle have been established till the date. Also, as the plasma formation is an instantaneous process and occurs within a fraction of seconds, it becomes difficult to stabilize the input process parameters to gain the output parameters as per our need. Due to its present technical challenges, the process is still in the development phase and not commercialized worldwide, like other processes such as cryogenics and vacuum heat treatment. Cathodic electrolytic plasma hardening of cast iron based camshaft has been carried out, and it was observed that the hardness of cast iron based automotive camshaft increased to 60HRC with 5mm depth of hardness [20]. A 20µm thick layer of hardness around 460HV has achieved by plasma electrolytic nitriding at 850°C only for 5min in the case of Titanium alloy [23]. The highest microhardness of 950HV is achieved by Plasma Electrolytic Nitriding, and also surface roughness was reduced from 4.5 to 1.9 µm [40].

Anode plasma electrolytic nitro hardening in 15 wt.% NH4Cl as an electrolyte has been successfully carried out, and microhardness of about 1060HV was obtained within 5min at a temperature of 750°C [49]. Low carbon steel, when treated with plasma electrolytic nitrocarburizing at 850°C, shown an increase in hardness up to 750HV with 0.2mm depth of hardness. It was proposed that anode plasma electrolytic nitrocarburizing increases wear resistance and decrease surface roughness of low carbon steel [50]. Plasma electrolytic nitriding carried out with plasma electrolytic hardening has achieved a combination of high hardness and wear resistance. The hardness of 56-62 HRC was obtained by plasma electrolytic hardening, and after that, the corrosion resistance was improved by nitriding. Both processes were carried out in the same electrolyte and same setup [51]. Cathodic electrolytic plasma hardening has also been carried out, and it was found that the hardness of cast iron based automotive camshaft increased to 60HRC with 5mm depth of hardness [20]. High surface finishing of a 38KH2N2MA Structural alloy steel was achieved by using a combination of Electrolytic Discharge Machining and Plasma Electrolytic Polishing. It was concluded that the surface roughness reduced by a factor of 5 within a 5min anodic plasma electrolytic process [52]. A coating thickness of 80µm was successfully achieved by electrolytic plasma oxidation. The specimen used was VT6 titanium alloy and coating formed was of Titanium oxide [53]. Electrolytic plasma hardening of Banding steel has increases microhardness by 2.4 times of
substrate within 4s of heating [55]. The phase composition of electrolytic plasma carbonitrided steel specimen has been studied by Transmission Electron Microscopy, and it was observed that martensite, cementite, and carbonitrides lamellas were successfully formed on the steel surface [56].

The electrolytic plasma process has been studied by the direct current method and pulse current method. It was proved that for surface hardening of AISI 1050 steel, the pulse current method requires less voltage and time as compared to the direct current method [41]. The corrosion resistance of carbonyl iron powder was increased by depositing the SiO\textsubscript{2} layer on the carbonyl surface with the help of plasma electrolytic deposition [54]. Corrosion behavior of SS304 also been studied in which ball-milled specimens were first annealed and then treated with Electrolytic Plasma Process. It was found that the corrosion resistance improved significantly [101]. The deposition rate of oxide coating on Magnesium alloy increases when the Electrolytic Plasma Process was used in pulse polarization mode [70]. Sequential coating and polishing are also possible by using the electrolytic plasma process, which makes this process dynamic and multifunctional [84]. Boriding of structural steel and Titanium alloys was done by using the electrolytic plasma process. It was observed that both wear resistance and corrosion resistance improved significantly in the case of structural steel as well as Titanium alloy [87].

The plasma electrolytic Oxidation process has been used for the coating of aluminum alloy, nickel alloy, titanium alloy, carbon fiber, and many more metals. Machining of aluminum alloy coated with ceramic oxide by electrolytic plasma oxidation process also studied, and it is shown that wear resistance property of aluminum alloy increases and abrasive polishing suggested for final machining of such component [94]. Ti alloy used for bio-implant application shows an increase in wear resistance and corrosion resistance after treated with plasma electrolytic oxidation, and also weldability in terms of contact angle also improved [104].

This electrolytic plasma process is an electrolysis process that is carried out at high voltage to create plasma for heating the metal at high temperatures. A combination of plasma and electrolysis has achieved a novel contribution in the field of surface heat treatment technologies, as shown in figure 1.

The process aspects of the technology have been explained as follows:

1.1. Plasma.

There are three states of matter solid, liquid, and gases. Nevertheless, there exists a fourth state also, which is beyond the gaseous state, and it is called plasma. If heat is applied to a liquid, it gets vaporized at high temperatures, and liquid state changes to a gaseous state. When this gaseous is further heated, the free electrons separate from particles, and positive ions with free electrons are formed. These free electrons conduct electricity. The plasma formation phase is indicated by a glow discharge for a very short duration of time, and this glow can heat the metal up to 2000°C [1]. This heat is utilized for the surface modification of metals.

1.2. Electrolysis.

For the surface modification of steel, it may require to deposit carbon or nitrogen particles on the surface of steel with the help of an external agent. This can be done by electrolysis in which electrode is deposited with carbon or nitrogen atoms by supplying high
voltage across the electrode dipped in a particular electrolyte. This electrolyte plays an important role in conducting electricity. The combination of plasma and electrolysis can be used to carry out a novel method of surface treatment, which is called as Electrolytic Plasma Surface Treatment.

![Figure 1. The combination of electrolysis and plasma improves surface properties.](https://nanobioletters.com/)

### 1.3. Electrolytic Plasma Process.

In the conventional electrolysis process, the voltage applied across the electrodes is very less as compared to the electrolytic plasma technique in which the voltage is around 200V to 400V. A DC power supply is used to apply a high voltage across the cathode and anode. The workpiece may be a cathode or may be an anode. If cathode works as a work piece, then it is cathodic plasma electrolytic heat treatment, and if anode works as a specimen, then that will be an anodic plasma electrolytic heat-treatment process. As the application of electric potential is very large as compared to conventional electrolysis, the gas liberation density at the surface of the electrode is very much and which leads to continuous gas envelope around the electrode along with an electric discharge. This electric discharge is responsible for extensive heating of the specimen above its recrystallization temperature within a fraction of seconds. The specimen can then be quenched in the same electrolyte by disconnecting the power supply. Various research works show that after the plasma electrolytic heat treatment, the surface properties of steel improved considerably.

The process can be categorized into four main phases, which begins with the formation of vapor around the electrode being treated. Figure 2 shows stages of the electrolytic plasma process in which, after supplying power, the temperature goes on increasing and reaches the highest point when plasma formation occurs. After plasma glows, the power supply is disconnected and electrode quenched in the same electrolyte.

The author studied the relation between current and voltage for AISI 1080 high carbon steel to demonstrate plasma formation in the EPHT process. The spark ignition phase is followed by the continuous plasma envelope which is supposed to be a treatment phase for the metals. Gas liberation phase involves the highest peak of current, and after that increase in voltage, causes an increase in accumulation of charges, and spark ignition occurs. Spark ignition results in heating of electrolyte around the cathode and continuous vapor envelop formed, which results in resistance to the current flow [1].

The cathode can be cooled in the same electrolyte after disconnecting the voltage supply for quenching purposes, which is the requirement of the hardening process. Carbon and nitrogen atoms can be imparted on the surface of electrolytes in the continuous plasma envelope phase.
Figure 2. Stages in Electrolytic plasma heat treatment: I) Power on II) Vapour formation III) Plasma formation IV) Quenching

2. Surface morphology

2.1. Alternate heating and cooling method.

When AISI 4140 was treated with electrolytic plasma thermo cyclic treatment, the stereo microscopic view of the material cross-section clearly indicated the hardened zone and unaffected zone [2]. In this technique, a higher of 300-320 V is applied for a few seconds, and then a lower voltage of 230-250 V applied. Alternate high and low voltage application results in heating and cooling, which results in the development of the high thickened hardened layer within just 42s. In this way, in a very shorter time, the higher thickness can be obtained by optimizing the process parameters.

The microstructure of the treated specimen depends on heating and cooling cycles in electrolytic plasma hardening. The lower number of cycles results in two layers, namely the hardened zone and transition zone on base material [33]. Higher number of cycle results in three zones namely remelted zone, hardened zone and transition zone on base material. The depth of the hardness increases with the number of cycles. However, there is a requirement of an optimum condition.

2.2. Deposition methods.

The deposition of carbon, nitrogen, boron on the surface of steel has been successfully carried out with electrolytic plasma heat treatment [34, 35]. After treating Q235 steel with electrolytic plasma carbonitriding, it was found that the highest thickness of 75 microns was obtained within just 75s with hardness value up to the 750HV. When the relation between time and hardness was studied, it was observed that for a higher time, the depth of hardness is higher hardness profile was wider than lower treatment time profile. At higher treatment time, which was more than 75s, the quality of the layer was deteriorated due to the reticular pattern of the carbide layer [34].

Boronizing of different steel grades steel was carried out by electrolytic plasma process, and it was observed that steel containing more percentage Cr can exhibit more boron diffusion
and highe thickness of the boride layer was developed [35]. The maximum hardness for medium carbon steel was obtained up to 1200HV, which was less as compared to the traditional boronizing process, but the thickness of the boride layer was higher and fabricated in a short duration. Tool steel is the backbone material of advanced manufacturing industries, and different technologies have been developing to increase the surface properties of tool steel. Plasma electrolytic nitriding of tool steel has been carried out by using ammonium nitrate and ammonium chloride solution [36]. When tool steel treated with Plasma Electrolytic Nitriding (PEN) it was found that maximum microhardness was obtained 1280HV with improvement in corrosion resistance.

Commercial grade austenitic stainless steel developed 20-60 micron nitride layer when treated by plasma electrolytic nitriding during 20-60 min in the temperature range of 375 to 480 °C with manual control of temperature. It was proposed that the process will be more efficient after more accurate process control parameters like the temperature of the sample and composition of electrolyte [37].

2.3. Surface coating and polishing.

Plasma electrolytic oxidation was used to fabricate oxide film on the surface of a Titanium alloy by using Ac power source. In this work, PEO film was produced by using a silicate electrolyte. The film produced is having a good combination of thickness, hardness, wear-resistance, and adhesion. The type of electrolyte determines the corrosion resistance property and friction coefficient based on the process of chemical reaction stability of the coating [38]. Alumina coating technique is very effective for improving hardness, wear resistance, and corrosion resistance of steel and aluminum alloys. Plasma electrolysis has been successfully implemented on BS Al 6082 for Al₂O₃ coating. XRD and TEM analyses were conducted to analyze the microstructure of the coated layer. Results have shown that PEO technique successfully improves wear and corrosion resistance of Al alloy and even better than stainless steel [39].

The polishing process can be integrated with the nitriding process in the same experimental setup by changing the electrolyte and voltage range. The nitriding process and polishing process is the best possible combination of surface improvement technique and successfully achieved by plasma electrolysis technology. Polishing of specimen was carried out after plasma electrolytic nitriding for a very short period of time, such as 2min. The surface roughness of the PEN treated sample was found to be increased, which was compensated by the polishing process by removing loose parts of oxide layers formation takes place on the surface of the specimen [40]. The polishing process can also be studied for plasma electrolytic carbonizing, electrolytic plasma thermo cyclic treatment, and other plasma electrolysis process.

3. Ranges of metals being treated

Ferrous, as well as non-ferrous metals, have been treated by using electrolytic plasma surface treatment. The major focus is given on steel, as it is the backbone material of the manufacturing industry. Different grades of steel have shown positive results for different kinds of surface treatments such as carburizing, nitriding, boronizing, hardening, coating, cleaning, and polishing. Aluminum alloys have also been treated for coating protective surface layers with different materials.
Table 1 shows the ranges of metals being treated with electrolytic plasma processes, and all metals shown significant results after the treatment. Aluminum and titanium alloy are generally treated by plasma electrolytic oxidation for coating purposes, and steel was treated by plasma electrolytic hardening. Different types of steel, such as low carbon steel to high-speed tool steel, have developed high wear resistance and corrosion resistance. For corrosion resistance, plasma electrolytic nitriding was used. Both anodic and cathodic processes were conducted, and both processes are shown positive results. In future Chemical Vapour Deposition, can be replaced with Electrolytic Plasma Oxidation due to its fast response and low equipment cost. The coating and polishing industry should focus on the development of the electrolytic plasma process as significant results have been achieved by Electrolytic Plasma Process in this field. Pulse current electrolytic plasma process, and electrolytic plasma hardening processes are mainly used for hardness and wear resistance without the deposition process. In this case, martensite is formed at the surface of the substrate, which causes an increase in hardness and wears resistance. Nickel-based alloy and ductile iron also shown improvement in wear resistance property. In the case of a tool, the steel electrolytic plasma process has proven a novel process for increasing wear resistance and decreasing surface roughness. The friction coefficient has also been studied by using the plasma electrolytic carburizing process. In all types of metals that are treated by the electrolytic plasma process have shown drastically increment for wear resistance, and it is the best-suited process to increase the wear resistance of components. Thus by using the electrolytic plasma process, we can treat types of steel, aluminum alloys, Nickel alloys, Titanium alloys, and ductile iron effectively.

Table data clearly shows that generally, alloy elements were treated by deposition methods such as nitriding, carbonitriding, boriding, and carburizing. The process is suitable for increasing hardness without modification of the chemical composition as well as by changing the chemical structure of the surface of the specimen. Electrolytic plasma hardening introduces martensite and cementite at the surface of the heat treatment, and electrolytic plasma nitriding introduces nitrides at the surface of the specimen.

### Table 1. Ranges of metals being treated by PET and industrial scope.

| Year | Metal                        | Type of treatment               | Results                                                                 | Industrial Scope                                      |
|------|------------------------------|--------------------------------|------------------------------------------------------------------------|-------------------------------------------------------|
| 1997 | Medium carbon steel          | Pulse current electrolytic plasma heat treatment | Martensite found in hardened steel and the highest heating rate can be achieved by pulse current as compared to D.C. voltage [41] | Toolroom and press tool die                           |
| 1998 | High-speed steel (circular saw) | Electrolytic plasma pulse heating | Service life increases from 1000 to 3000 cuts. Martensite obtained with hardness increased to 62 HRC [42] | Hex saw and cutter                                    |
| 2002 | BS A16082 Aluminium alloy    | Plasma electrolytic oxidation   | Alumina coating was successfully deposited [39]                        | Aerospace, automobile and aluminum parts industry     |
| 2007 | Q235 steel                   | Plasma electrolysis carbonitriding | When steel treated with 150V for 75s carbonitriding layer of 70-micron forms with hardness 750HV[34] | Machine parts                                         |
| 2008 | 4340, 4140, 1045, 3215 and 1020 steel | Plasma-electrolysis boronizing | Greater value of hardness and boron layer thickness obtained for 1020 steel[35] | Tool steel                                             |
| 2009 | Medium carbon steel (AISI 1040) | Electrolytic plasma thermocyclic treatment | Reliable microstructure and surface hardness were obtained on medium carbon steel [43] | Machine parts                                         |
| Year | Metal | Type of treatment | Results | Industrial Scope |
|------|-------|-------------------|---------|------------------|
| 2010 | AISI 4140 steel | Electrolytic plasma thermocyclic treatment | Thickness of hardness layer obtained for different thermo cycles and highest thickness obtained for 300-320V in 42s | Machine parts |
| 2011 | AISI 1045 (CK45) carbon steel | Plasma electrolytic nitrocarburizing | Within 8 to 9 min at 200V nitrocarburized layer formed | Tool steel and dies |
| 2012 | 12Cr18Ni10Ti steel | Electrolytic-plasma cementation (EPC) | Within 7 min carbide layer was formed of thickness 45-65 micron | Punch and die of press tool steel |
| 2014 | Q235 low carbon steel | Anodic plasma electrolytic carburizing | Carbon diffused into compound layer successfully, and surface roughness also reduced | Machine parts |
| 2015 | St 14 steel | Plasma electrolysis boronizing | Only above 20% borax in electrolyte shows the development of the boride layer on component | Automotive components |
| 2016 | T8 carbon steel | Plasma electrolytic carburizing | Steel friction coefficient is reduced from 0.4 to 0.1, and the wear rate also reduced to ¼ | Special purpose tools |
| 2017 | 0.34C-1Cr-1Ni-1Mo-Fe steel | Electrolyte plasma nitriding | Chromium and nitrides increase hardness as well as wear resistance | Tool steel industry |
| 2018 | T8 carbon steel | Cathodic plasma electrolysis | Significantly improved the wear resistance of carbon steel | Machine parts |
| 2019 | Ductile Iron | Electrolytic Plasma Hardening | 1050HV hardness achieved with a decrease in wear rate from $4.74 \times 10^{-4}$ to $0.968 \times 10^{-7}$ mm$^3$/m | Piping, the Pump housing industry |
| 2019 | Nickel-based K418 superalloy | Cathodic plasma electrolytic deposition | Successfully deposited Si into the surface of the sample for improving layer mechanical properties at high temperature | Coating industry |
| 2019 | VT6 Titanium alloy | Plasma Electrolytic Oxidation | After treatment, 80µm thick titanium oxide layer was formed with an increase in wear resistance. | Aerospace Industry and Biomedical industry |

4. Future scope in the industry

4.1. Press tool industry.

Electrolytic plasma treatment has shown significant positive results on various types of tool steels. In the press tool industry wear resistance and corrosion resistance, both are necessary, and these properties can be achieved by the electrolytic plasma process. Carbon was successfully transferred on low carbon steel surface by electrolytic plasma carburizing, which results in an increase in hardness up to 700HV, and also anodic process results in reducing surface roughness [45]. The process can be modified for complicated components in which carburizing is needed only on a small portion of the component.

4.2. Biomedical implants.

Titanium alloy is mostly used in biomedical implants, and many researchers have successfully carried out the surface modification of Ti by plasma electrolytic coating and polishing. Surface properties of V22 Titanium alloy have been improved significantly by plasma electrolytic nitriding with 460HV hardness and 20µm hardened layer [23].

4.3. Automobile industry.

Cast iron-based camshaft shown 50-60 HRC after treating with electrolytic plasma hardening [20]. Automotive components like camshafts can be treated with electrolytic plasma processes to induce necessary hardness and wear resistance. Also, performance study may be
carried out for conventionally treated components, and PEP treated components. AISI 4140 is the largest and most common material used in tool holders, dies, jigs, and fixtures. Overall mechanical prosperities of this steel have been successfully improved by the electrolytic plasma process [3,43].

4.4. Aerospace industry.

Aluminum, such as BS Al 6082, has also been treated with plasma electrolytic oxidation in which a protective layer of Al2O3 was successfully deposited on the aluminum surface. The wear and corrosion resistance were improved significantly [39]. Aluminum and its alloy are used in large quantities in the aerospace manufacturing industry. The electrolytic plasma process can be considered for the growth of the aerospace industry in terms of quality and production.

5. Summary

Electrolytic Plasma Technology is a novel method for improving surface properties of the low, medium, and high carbon steels. For aluminum alloy also EPT shows positive results for the fabrication coating layer of different materials such as alumina and silicon. Nickel-based Superalloys have also been treated and show improvement in surface properties. The setup required for the process is economical, and no environmental hazardous occurs. The time required to introduce desire properties is in the range of 60s to 5min, which very less as compared to current surface treatments. EPT is a dynamic process, which means hardening, deposition, coating, cleaning, polishing can be done in the same setup with little modification. The coating process can be explored for EPT for different materials where surface properties play an important role. Process parameter optimization, advanced sensors, and data logger system can control the process in a more accurate sense, and better results can be obtained by EPT.

Following conclusions may be drawn from this study:

Electrolytic Plasma hardening and nitriding can be done in the same apparatus within a short time in which hardening is done for hardness improvement, and nitriding is done for corrosion resistance. Electrolytic plasma nitriding and polishing can be done one after another in the same setup.

Surface roughness is affected by the type of electrolytic plasma process. In the cathodic electrolytic plasma process, the surface roughness increases, and in anodic electrolytic plasma process, the surface roughness decreases.

For corrosion resistance, we can increase the corrosion resistance of the metal even greater than stainless steel.

A coating layer of very small thickness, which is in the range of nanometres, can also be deposited successfully on the surface of metals by the electrolytic plasma process.

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Conflicts of Interest

The authors declare no conflict of interest.

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