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Development of glow discharge devices for steel and cast iron nitrification

***Abstract**. The modern and advanced technique for nitriding of steel is utility of glow discharge. Due to relatively long time required for the process, evolution of vacuum chamber furnaces and specialized DC and impulse power sources were major factors required for implementation and popularization of this technology. In the paper most popular and advanced types of glow discharge furnaces equipped with power electronic sources were presented. Special attention was put on the solutions characterized by high efficiency and protection against electric arc.*

***Streszczenie.** Jedną z nowszych technologii, a zarazem i dostosowywania urządzeń do jej realizacji, jest technika azotowania stali w warunkach wyładowania jarzeniowego. Ze względu na długie czasy realizacji tej technologii szczególnemu rozwojowi podlegały piece budowane w oparciu o komory próżnioszczelne oraz układy zasilające od stałoprądowych do impulsowych. W artykule przedstawiono kolejne próby zestawiania pieców jarzeniowych z zasilaczami energoelektronicznymi dającymi coraz efektywniejsze wykorzystanie energii elektrycznej i ochronę wsadu przed łukiem przy zachowaniu jakościowych zalet azotowania stali.. (**Rozwój urządzeń do azotowania stali w warunkach wyładowania jarzeniowego**).*

Keywords: glow discharge heating, devices, nitriding, vacuum chamber furnaces
Słowa kluczowe: in the case of foreign Authors in this line the Editor inserts Polish translation of keywords.

Introduction

The process of external layers of different materials modification by the chemical vapor deposition (CVD) with the utility of glow discharge (PACVD) wal applied since the middle of twentieth century. The most popular process realized by the utility of this technique is the nitrification in glow discharge conditions, called the ion nitrification or plasma nitrification. This process can be defined as thermo - chemical treatment and involves the saturation of external surfaces of steel or cast iron with the nitrogen. As the result, the surfaces are cured and their resistance for chemical corrosion increases. Basic disadvantage of the technique is relatively long time required for the process. Maximal values can reach 100 hours and more.

Despite the low temperature values (about 450 - 550°C), a very important factor that have a strong influence on design of glow discharge devices was a minimization of energy consumption, due to mentioned long process times. Only solutions characterized by abnormal discharge were acceptable according to possibility of ion bombing of whole workload surface. During the glow discharge process energy and ions (mass) are delivered together to the workload. Design of vacuum chambers is always connected with the type of used power supply. In the simplest solutions, DC power supplies are in use. But their characteristics are not optimal. Today, most important are advanced pulse power sources.

Glow discharge characteristics

Features and characteristics of discharges in sparse gases with pressure values from several to (about) fifteen hPa in industrial devices are completely different in comparison to the description obtained in laboratory devices. The observed variances result, mainly, from the fact that the workload (cathode) is characterized by different geometrical and material parameters for any process. Additionally, cathodes have a complicated shapes and anodes are relatively small in comparison to laboratory stands. Exemplary characteristics of the glow discharges for the hydrogen and nitrogen are shown in figure 1.

Major processes of carbon and nitrogen atoms exchange that are built-up in external surfaces of workload occur in vicinity of cathode.

In vicinity of cathode one can observe the strongest energy dissipation of whole space occupied by the discharge. This effect results from mutual collisions of electrons, positive ions and neutral particles and provides the heating effect. A large part of thermal energy flows to the cathode and increases its temperature value. Mentioned temperature increment in the vicinity of cathode causes to decrease the density of operating gas. Differences of gas density in the discharge is the basic reason of gas fluxes formation. Such fluxes reduce the discharge stability.

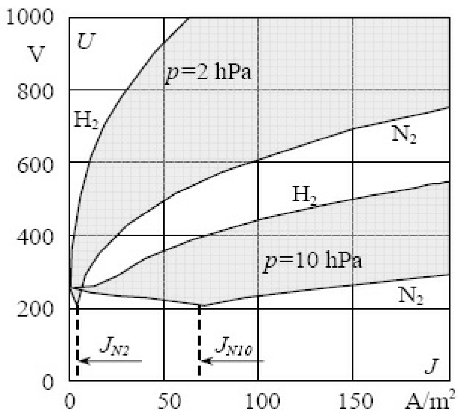

Fig.1. Electrical characteristics for DC glow discharge

Cathode voltage drop value is more than 80% of the supply voltage. Thickness of cathode drop area strongly depends on the pressure value. If the pressure increase, the thickness decrease. This feature is very important in all techniques, where concave surfaces and workloads with holes are treated.

Increment of operating atmosphere pressure provides that discharge (voltage vs. current) characteristics are more "flat". The discharge is not stable in such conditions and transition of glow discharge into electric arc that destroys treated surface, is relatively possible. To achieve a stable glow discharge in higher pressures, one have to use a larger power value that results a larger energy consumption of the process. In general, all processes of DC nitrification are not optimal. In such processes utilization of all advantages of glow discharge are not possible due to necessity to work in relatively low pressures in DC systems.

Design of glow discharge furnaces

Utilization of power electronic pulse supplies enable the significant modifications of glow discharge devices, especially vacuum discharge chambers. The most important feature of pulse discharge is the reduction of gas pressure influence on electrical characteristics. Another benefit of the utility of pulse glow discharge lays from another possibility of energy control. Except from voltage and current amplitudes adjustment, in pulse systems there is possibility to control the average power by changing the fill factor of pulses. Ions generated in similar environmental parameters are characterized by different energy values (for different pulse width).

As it was mentioned in previous section, in the volume characterized by the product of cathode surface F_k and width of cathode voltage drop δ_k, almost all energy is generated. Momentary value of volumetric power density of active area in vicinity of cathode can be described by equation (1).

(1) $$pv = E \cdot J \cdot w$$

where: *E* – electric field intensity; *J* – current density; *w* – fill factor.

The rapidity of forming and customization of glow discharge structure is instant, even for frequency of pulses repetitions of tens kilohertz. Pulsed stimulation of discharge area enable to enlargement of acceptable environmental parameters, especially pressure values, where stable abnormal discharge is possible.

In the figure 2, a four exemplary generations of vacuum discharge chambers were shown.

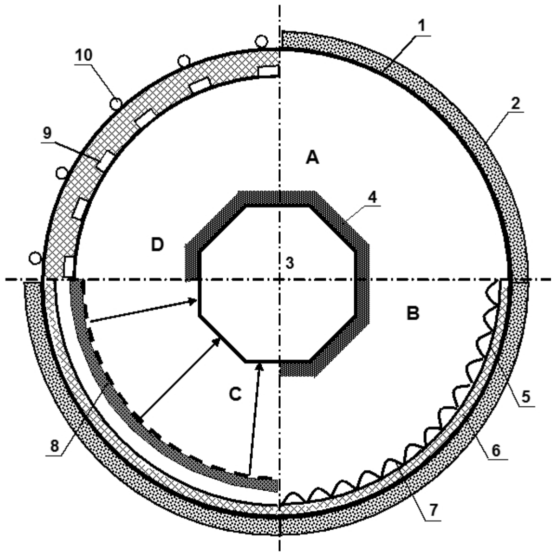

Fig. 2. Different generations of discharge vacuum chambers with power supplies: A - chamber without thermal insulation; B - insulated chamber with additional resistance heater; C - chamber with the shield used as the cathode; D - chamber with the direct discharge and series resistors. 1 - vacuum chamber; 2 - water cooled casing; 3 - workload (cathode); 4 - semi - cathode discharge; 5 - inner cathode; 6 - thermal insulation; 7 - resistance heating elements; 8 - shield used as the cathode; 9 - pockets for resistance heaters; 10 - tubular water cooling system

Chamber A:

At the beginning of glow discharge utility in nitrification process, the vacuum chambers of design shown in figure 2a were used. The direct glow discharge occurred between anode (conducting housing of the chamber) and workload (cathode) were maintained by DC power supplies. In such devices, delivered energy was consumed mainly for the compensation of thermal loses from the workload. Energy values were many times higher than energy required for activation of technological atmospheres. The participation of produced energy in relation to transferred mass was too large. According to this effect, exploitation costs of such devices were large. Basic advantages were related to relatively low costs of investments.

Chamber B:

Competitiveness of other nitrification methods caused the necessity for reduction of expensive energy consumed by glow discharge. In second generation of vacuum chambers, thermal insulation and additional resistance heaters were used. Such solutions enable for reduction of time required to heat up treated workloads. For this reason nominal power values of glow discharges power supplies were limited. The most important disadvantage of additional resistance heater was the utility of second power supply.

Reduction of thermal loses in thermally insulated vacuum chambers was determined by practical measurements performed in horizontal chamber without insulation (A), insulated with three radiation screens inside chamber (B) and insulated with chromite fibrous material (C). Received energy characteristics, referenced to current density on workload surface are shown in figure 3.

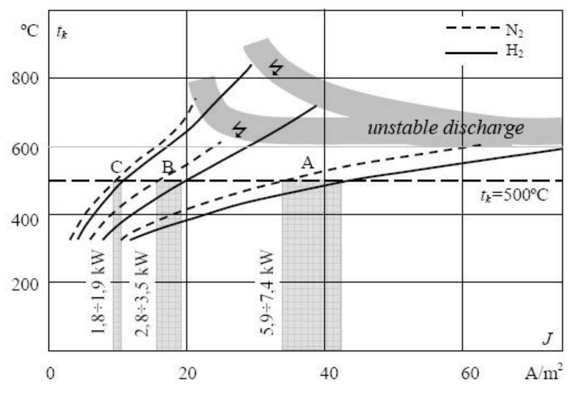

Fig. 3. Static characteristics of workload temperature in function of current density in insulated and non-insulated vacuum discharge chambers

Chamber C

Basic disadvantages of glow discharge nitrification process lays from the inhomogeneous temperature distribution in all vacuum chamber, especially fully filled with the workload and damages of workloads caused by electric arcs. These factors blocked development and implementation of this technique.

A new concept of discharge nitrification phenomena was developed. In spite of previous theoretical description, it was assumed that the neutral particles (not ions) contained in plasma are responsible for nitrification effects. According to this phenomena, it was assumed that it is not necessary to form plasma directly on surfaces of treated workloads. This discovery was used to develop new generation of glow discharge chambers, where plasma occurs between anode (cover of device) and active screen that surrounds the workload. The workload is free-from-plasma and only active gas can reach its surface [2]. In such solution, main aspects of generation of appropriate operating atmosphere for thermo-chemical processes was moved from electrical to gas-flow part. According to basic technical requirements, all treated details should be subjected to gas penetration. Final effects depend on homogeneity of temperature field and gas distribution. Maintain of such condition can be a very complicated task, especially when treated elements lay on worktable, they are densely stacked or characterized by complicated geometry.

Chamber D

The concept is based on design of glow discharge vacuum chamber, where energy for discharge is delivered from power supply by additional heating resistors connected in series to the discharge. This solution can reduce the hazard of electric arcs. Additionally, heating resistors can heat up the cover of heating chamber (anode). This concept was described in the next section.

Vacuum discharge chamber with series heating resistors

Power electronic pulse power sources are relatively cheap nowadays, due to progress in electronic components and control system design. It is profitable to use a single source to reinforce the series resistors and the discharge area simultaneously. This solution enables to elimination of expensive and complicated systems for protection from electric arcs. Simplified schematic diagram of the proposed idea is shown in figure 4.

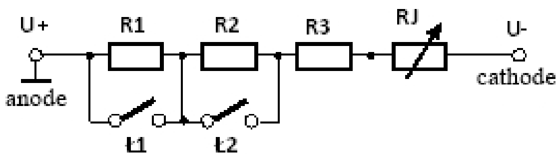

Fig. 4. Schematic diagram of D chamber power supply system. R1 - R3 - heating elements of the 4, 2, 1 resistance values; RJ - various resistance of the glow discharge; Ł1, Ł2 - transistor couplres

In the case of electric arc initiation, especially at the beginning of nitrification process, the value of RJ resistance decreases dramatically. For this reason, power supply voltage occurs mainly on resistors *R1* ÷ *R3*. Such resistances were selected to achieve requirement that when RJ equals to zero ($RJ \Rightarrow 0$) and chamber is powered by nominal voltage, they have to heat up anode to the temperature of 500°C. After initial phase of nitrification process (cleaning and conditioning workload by discharge in hydrogen) and reach required temperature value, resistances of heating elements can be reduced to control anodes temperature. If anode and cathode temperatures will be the same, the convection gas flow in operating area can be eliminated. This phenomena improves the stability of discharge and homogenizes temperature field in workloads surfaces, irrespective of its shape.

Vacuum chamber of described design is shown in figure 5. Heating elements were installed inside ceramic moulders, in atmospheric pressure. Such solution is very safe due to higher breakdown voltage value in atmospheric pressure than in vacuum. Only disadvantage of presented solution is increased energy consumption. Additional power from pulse power source have to be used for resistance heating of anode.

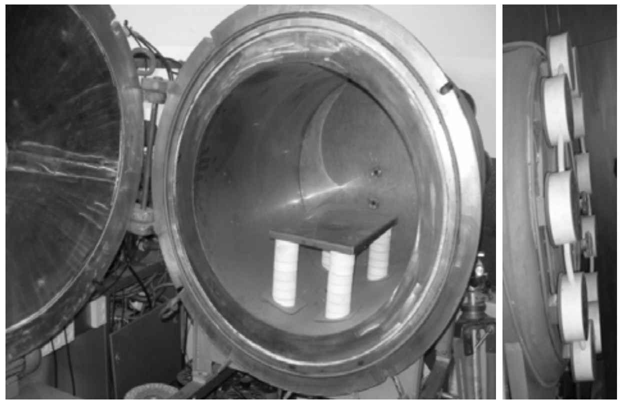

Fig. 5. Vacuum discharge chamber, where power supply is connected by series resistors

Conclusions

Progress and intensification of utility of CVD techniques are still current issues. In the article some possible mechanisms that provide a mass nitrogen transport were presented. However, today it is impossible to describe only one, universal theory for the process.

Proposed solution, where glow discharge electrodes are powered by series heating resistance elements (fig. 2c) is characterized by larger versatility in comparison to commonly used CVD devices. It has many advantages, like only one power source, reduction of overcurrents, self-extinction of electric arcs and additional heat source in a form of resistances.

Basing on presented description of gas activation, one can conclude that only slight amount of ionized and excited particles participates in nitrogen transport to the workload. This phenomena is used to excitation of operating atmosphere by pulses of different fill factors (Pulse Width Modulation).

Basing on general opinion, glow discharge nitrification is characterized by relatively large investment costs. However, calculations of operating costs in large period of time, show that this technique can be profitable. Additional benefits lays from the perfect quality of final products and environmental protection. Last advantage results from possibility of noise and pollutions reduction in comparison to other nitrification techniques (gas and salt bath). This technique is intensively introduced in the industry. More than 30% of nitrification devices use the glow discharge. This proportion will increase in the next years.

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