Chapter 4

Application of Direct Current Plasma Sintering Process in Powder Metallurgy

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Additional information is available at the end of the chapter

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Abstract

Direct current (dc) plasma-assisted sintering of metal parts is a promising and relatively new research and development field in powder metallurgy (PM). In the present entry, it is intended to introduce the reader to the main applications of the dc plasma sintering process in PM. To achieve this goal, the present entry is divided in a brief introduction and sections in which the bases of the dc plasma abnormal glow discharge regime and its influence in the sintering process are carefully treated. In this case, a clear language is purposely used to didactically introduce the reader to this "fascinating glow world", the dc plasma-assisted sintering of metal parts, aiming to put in evidence the main points on physicochemical aspects of the plasma environment, basic knowledge of the plasma heating, and surface-related phenomena during dc plasma sintering of parts. All these aspects are treated considering the main techniques of the dc plasma-assisted sintering process applied to PM. Finally, some results on DC plasma heating, sintering and surface modification are presented.

Keywords: DC plasma-assisted sintering, DC glow discharge sintering, DC hollow cathode discharge sintering, floating potential sintering

1. Introduction

New technologies tend to require more and more advanced materials and manufacturing processes. Additionally, due to environmental problems that the world is facing, especially in developed countries, the regulation concerning the environmental impact of these materials and processes are becoming increasingly restrictive. In this context, plasma-assisted processes are very competitive since they usually are low-environmental-impact processes and they can produce high-performance materials in a very efficient way. Such aspects, allied to the possibility of producing very reductive atmospheres, motivated the development of the plasma-assisted sintering process, being that in most of research carried out in this domain, plasma is generated using direct current (dc) power supply.

In the dc plasma-assisted sintering process performed in an abnormal regime glow discharge, pressed metal parts to be sintered are subjected to a highly reactive plasma environment [1–4]. It is due to the presence of a great number of ionized and excited gas species, created by collision processes, that leads the species present in a gas mixture, usually constituted of reductive (like H_2) and neutral (like Ar) gases, to be ionized, excited, and/or dissociated. Due to the interaction of plasma and the pressed part, temperatures sufficiently high to sinter metals can be reached by the energy transfer from the plasma species to the part surface by collisions of accelerated species (this heating mode is termed "cathode heating mode"). It is also possible to heat pressed parts by an indirect way, in which the plasma energy is transferred to heating components, acting as cathode of the discharge, that heat the parts to be sintered mainly by radiation (here termed "anode and/or floating potential heating mode"). Depending on the design of the electrical discharge (electrode arrangement), different electrical configurations and heating modes are possible. In each case different potentialities of the plasma-assisted process can be explored, giving rise to different dc plasma sintering techniques [5, 6]. In addition, the very active physicochemical plasma environment, besides heating, can lead the metallic parts to present surface characteristics that are directly related to the plasma species bombardment and, so, exclusive for the plasma sintering process. The plasma environment can promote oxide-reduction reaction, cleaning, sputtering, deposition, and redeposition phenomena, all of them can be conveniently explored to tailor the sintered part surface. The abovementioned aspects suggest that during sintering, several phenomena related to the plasma will have influence in the part sintering processes, so to understand the dc plasma-assisted sintering process as a whole it is necessary to introduce some basis of plasma. In the next sections bases of dc plasma physics for the sintering purpose are presented, considering the different dc plasma sintering techniques, followed by the presentation of some results on plasma heating and surface modification. So the chapter ends by a discussion on the advantages of the plasma-assisted over the conventional sintering process and the final remarks.

2. Bases of dc plasma for sintering: the abnormal regime glow discharge

Plasmas commonly used in dc plasma sintering process characteristically present a degree of ionization of about 10^{-5} [1]. For the sintering purpose, an abnormal glow discharge can be easily obtained by applying a potential difference between two electrodes (cathode and anode) placed inside a chamber at low pressure, containing the gas mixture, which is usually constituted of 80 vol.% Ar + 20 vol.% H_2 for sintering. In the initial state, electrons are accelerated by the electric field and collide with neutral species (atoms/molecules), in much higher number density, resulting in partial ionization/excitation of the gas. When the number density of the produced ionized and excited species is great enough, a self-sustained bright-aspect glow electrical discharge is attained; thus, the plasma is formed [1–4].

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Among the different discharge regimes which can be established from the current-voltage characteristic of a dc plasma system, namely Corona, Townsend, Subnormal, Normal, Abnormal, Transition to arc, and Arc [1, 4, 7], the abnormal regime is of special interest for dc plasma sintering process. This is mainly due to the following aspects:

- It is the discharge regime in which the cathode can be totally covered by the glow, condition necessary to perform homogeneous heating; and
- It presents the basic feature for which the electrical current monotonically increases with the applied voltage. This allows the application of high voltages resulting in increased ionization/excitation of the gas and makes possible to control the plasma reactivity and the cathode (or sintering) temperature.

The abnormal regime is sustained for current densities typically higher than 2 mA/cm^2 [1] and for pressures generally in the range of 10^{-2} to 10^2 Torr [8–10].

Figure 1 schematically presents the normal, abnormal, transition to arc, and arc regime regions in a hypothetical current-voltage characteristic of a dc discharge [1, 4, 7], being the abnormal and arc regimes typically applied for materials processing [1, 4]. It is worth to be mentioned that for certain operation conditions a specific critical voltage (V_c) for the considered dc plasma system can be attained, at least locally. In this case, the working abnormal regime discharge can abruptly change to arc (passing through the transition from abnormal regime to the arc regime), and the sintering process is interrupted by the power supply security system (arc management system). There are two main aspects that can contribute to the critical voltage of a dc plasma system to be achieved. The first one is the presence of organic constituent in the electrode surface, directly related to the dc plasma device cleanness, which is detrimental for dc plasma processes and also increases the risk of arc formation. The second one is the geometrical

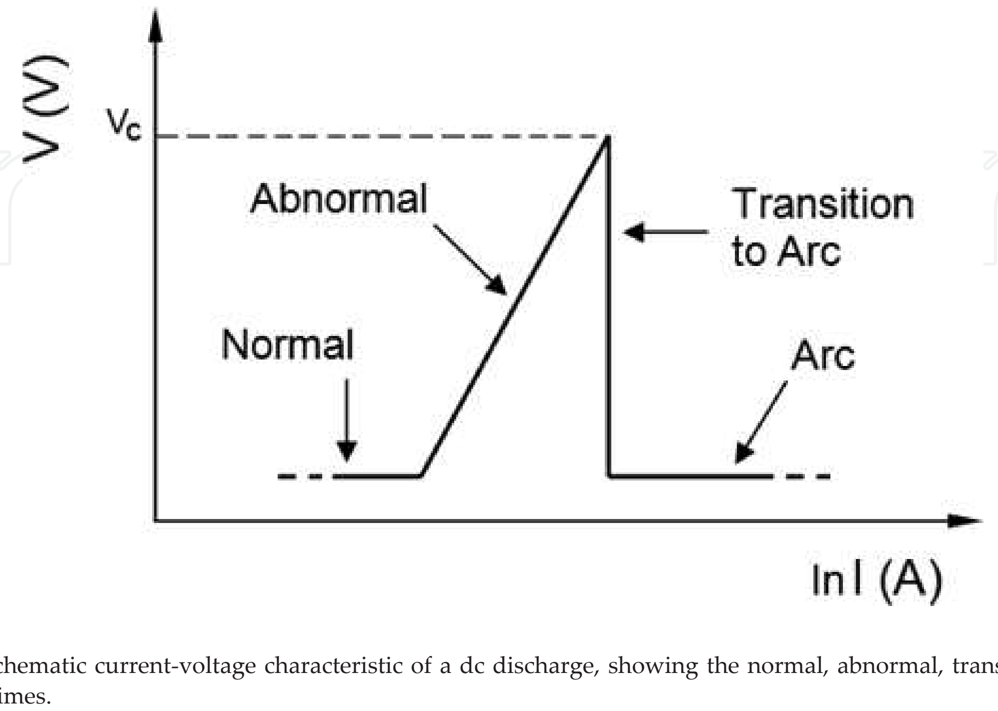

Figure 1. Schematic current-voltage characteristic of a dc discharge, showing the normal, abnormal, transition to arc, and arc regimes.

and dimensional arrangement related to the design of the electrodes and their respective insulating components.

Arc formation represents the main limitation for the use of dc plasmas in industrial applications. If the arc regime is established, high current density and high temperature (usually over 3000°C) are observed, and it can lead to surface damages in the sintering part or in the power supply system. It is to be noted that the arc formation risk in plasma processing was partially overcome in the half of the last century with the introduction of the pulsed dc plasma power supplies, and nowadays industrial plasma power supplies are additionally equipped with advanced arc managing systems to minimize such problem. In this case, for each switched-off time of the pulse (see **Figure 2a**, **b**), the system current is decreased, tending to zero, so the risk for arc formation is reduced. Despite these advances, it remains an important challenge regarding the know-how and R&D of dc plasma sintering devices.

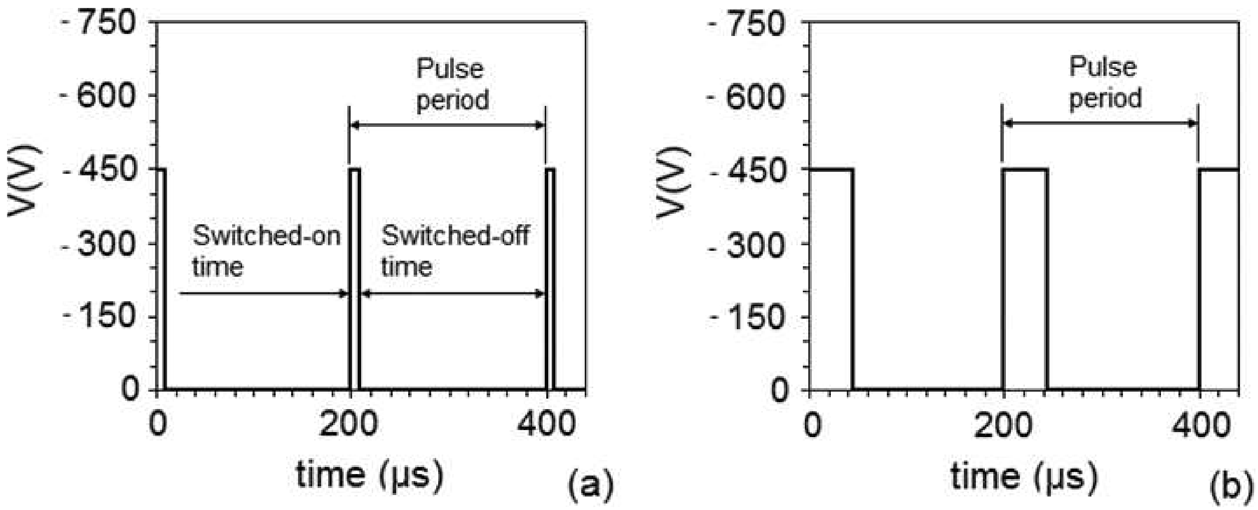

Figure 2. Scheme of square wave pulses (case of pulse voltage of −450 V and period of 200 μs) for two different switched-on times (for values of random choice): (a) 10 μs and (b) 40 μs.

By considering that the arc formation risk increases as the plasma power is increased, another strategy used in the industry to overcome this important problem is the use of hot-wall plasma chamber. In this case the power needed to reach the processing temperature is mainly provided by an auxiliary heating system, reducing the necessary plasma power to achieve the desired sintering temperature, decreasing the risk of arc formation.

To go further on the understanding of the plasma-assisted sintering, it is necessary to stress in more details how the potential distribution along the discharge is changed after breakdown (when the glow discharge or the plasma itself is obtained).

2.1. Potential distribution in the discharge

As the plasma is obtained by the gas ionization, mainly due to the collisions between high-energy electrons and neutral gas species, the potential distribution (indicated by red lines in **Figure 3a**, **b**) between the two electrodes is changed from that represented in **Figure 3(a)** to

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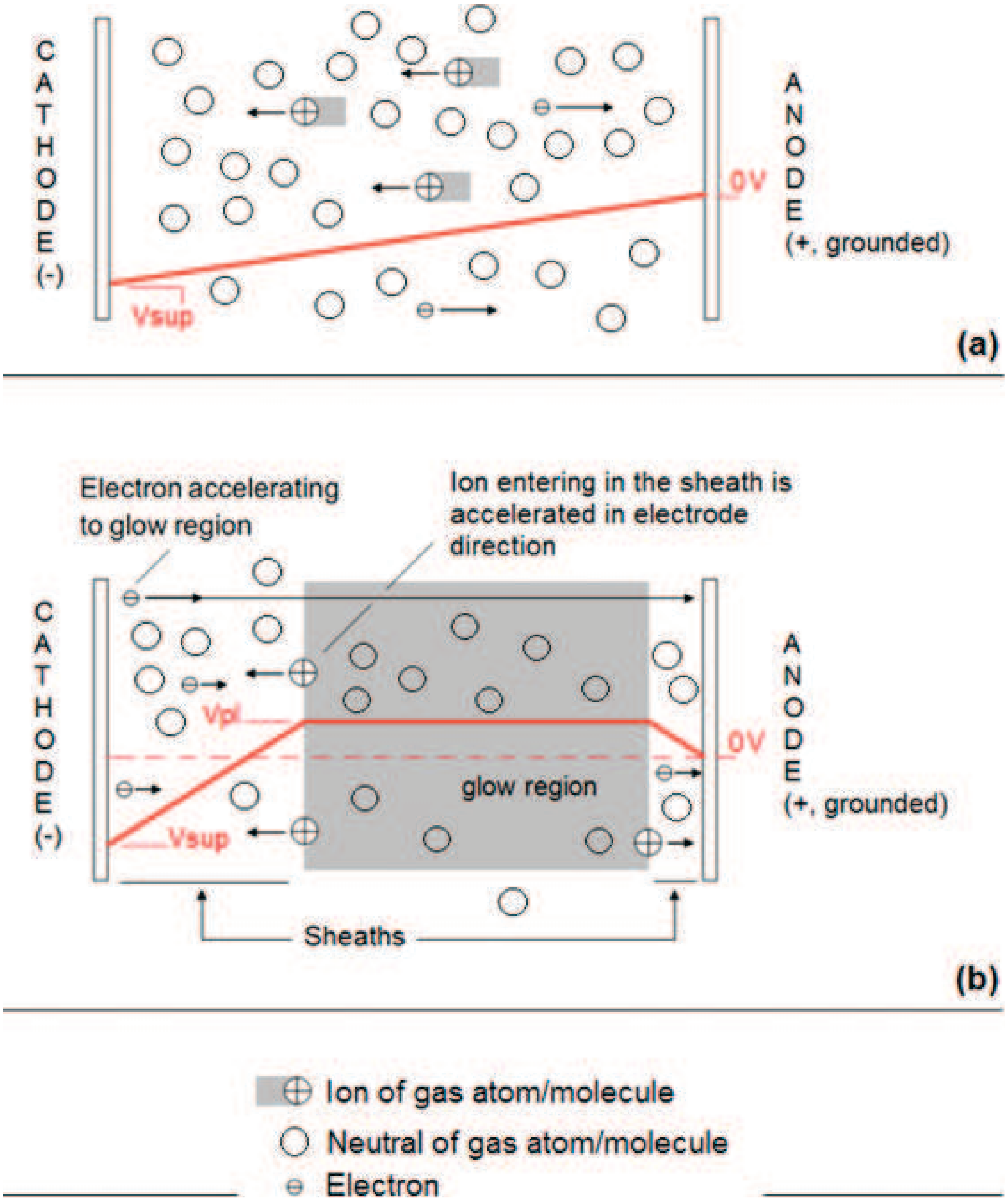

Figure 3. Discharge potential distribution between the electrodes of a typical electrical system used in dc plasma process: (a) before the glow discharge (plasma) to be established and (b) after the obtainment of plasma.

that in **Figure 3(b)**. In **Figure 3(a)**, the scheme of a gas at low pressure and the respective electrodes of a typical electrical system used in dc glow discharge chambers are shown. It is to be noted that ions and electrons of the gas, initially present at very low number density (around 10^3 cm^{-3}), are accelerated by the electrical field imposed by the power supply. For a specific potential and sufficient low pressure, the dielectric gas breakdown is achieved, phenomena governed by Paschen's law [7], and a glow discharge (thus the plasma) is established, changing the potential distribution along the discharge to that presented in **Figure 3(b)** due to the generation of a significant number of charged species. In abnormal glow regime, the glow region is approximately equipotential (negligible electrical field), presenting a positive potential, known as plasma potential (V_{pl}), on the order of +10 V [1], and the electrical field, which before breakdown was approximately linear between the electrodes, becomes restricted next to both the cathode and anode sheaths. The ions produced by ionization collisions (with high-energy electrons) that randomly reach the glow region-sheath interfaces are accelerated to the respective electrodes and can make additional collisions with neutral species, resulting, for example, in the known charge-exchange collisions in the sheath [1]. This is an important kind of collision, since fast (high kinetic energy) neutrals driven to the electrode surfaces are produced by this mean, explaining why not only fast ions bombard such surfaces but also fast neutrals.

Figure 3(b) corresponds to the usual kind of glow discharge used in dc plasma sintering process usually termed as the cathode configuration [5, 6], where the part to be sintered acts as the cathode of the discharge. There are two distinct regions with considerable electrical fields along the discharge, the cathode fall where the potential varies from the plasma potential down to the negative potential imposed by the power supply (V_{sup}), and the anode fall where the potential varies from the plasma potential down to zero at the grounded electrode, where the part could also be placed to undergo the sintering process.

At this point it is important to introduce the reader for the different ways or techniques for which a part can be sintered under dc plasma environmental.

2.2. The different techniques of dc plasma sintering

Some different possibilities or techniques (discharge configuration) to carry out the plasma sintering process can be listed as follows:

- Case 1: Sintering of parts in the cathode configuration in cold-wall chambers (without auxiliary resistive heating);
- Case 2: Sintering of parts in the hollow cathode discharge (HCD) configuration in cold-wall chambers (without auxiliary resistive heating);
- Case 3: Sintering of parts in the anode (or floating potential) configuration in cold-wall chambers (without auxiliary resistive heating); and
- Case 4: Sintering of parts in any of the aforementioned configurations in hot-wall chambers (with auxiliary resistive heating).

For the first case, here termed as the cathode configuration in cold-wall chambers, the heating of the part at temperatures high enough for the sintering purpose (around 1100–1250°C, for iron parts) is achieved exclusively by the plasma fast species bombardment. For this case, if the gas mixture is composed of 80% Ar + 20% H_2, pressure usually varies in the range of 10–30

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Torr (1333–3999 Pa), considering pulse voltages of 600–700 V [11–16]. This condition, i.e., for parts acting as the cathode of the plasma device, is illustrated in **Figure 3(b)**.

The second case is the hollow cathode discharge [8], as shown in **Figure 4** that is a special kind of dc abnormal glow discharge, for which the same principles of the cathode configuration (see **Figure 3b**) are also valid. But in this configuration, by considering that both the cathode walls present a same potential, the potential distribution along the discharge is changed, being comprised by two similar electrical field regions next to each cathode surface, and the

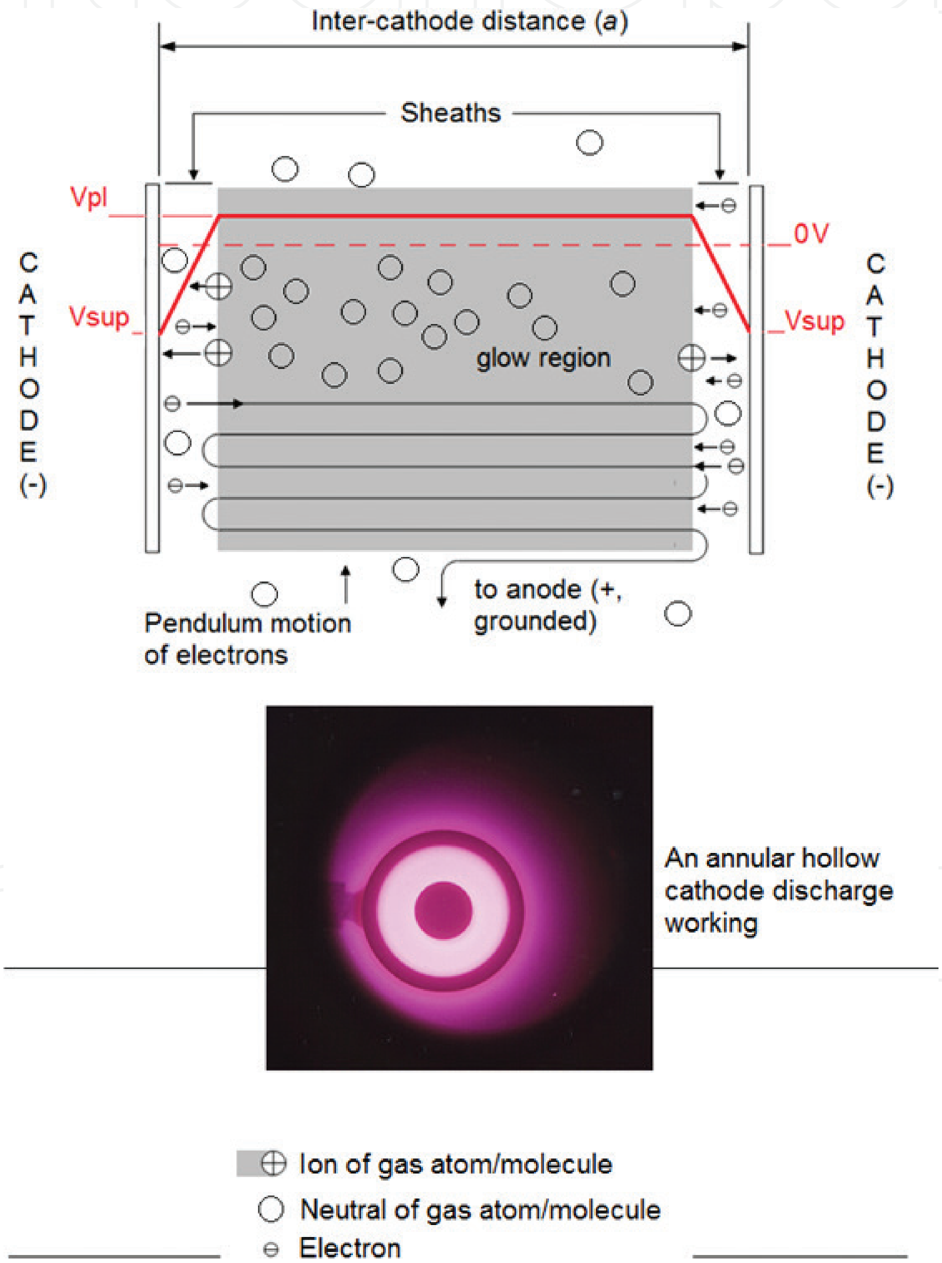

Figure 4. Discharge potential distribution at the hollow cathode discharge configuration and photo of an annular glow discharge (here, the hollow cathode effect is evidenced by the more intense light brighter than that verified outside the outer cathode (referred to the central one), which is also surrounded by plasma (in this case, presenting a less intense light bright)).

glow region that is virtually field-free. In this case, the grounded anode reference is outside from the hollow cathode region (not shown in **Figure 4**).

For the hollow cathode configuration, considering the same gas mixture, sintering temperatures can be attained by using lower gas pressures or voltage than those used in cathode configuration. In hollow cathode configuration, for a gas mixture composed of 80% Ar + 20% H_2, the pressure range usually varies from 1 (133 Pa) to 9 (1200 Pa) Torr, considering pulse voltages on the order of 450 V [5, 6, 17–23]. Here, the heating of the part to the sintering temperature is carried out by the fast plasma species bombardment, and the part to be sintered acts as one cathode of the formed hollow cathode discharge. This situation is illustrated in the bottom of **Figure 4**, in which cylindrical parts to be sintered act as the inner cathode of a typical annular hollow cathode discharge, as presented in references [17–23]. It is to be noted that, for this configuration, plasma is much more ionized than that obtained in cathode configuration. This is due to the electron pendulum motion between the cathode falls that repulse electrons, keeping most of them arrested inside the discharge, thus increasing the collision probability and the ionization rate. As a reference, in a hollow cathode discharge, the current densities can be two orders of magnitude higher than that of a conventional discharge [7].

For the third case, parts are placed in the anode or in the floating potential (electrically insulated) so that no significant heating will be produced by plasma fast species bombardment. In this case, the discharge cathode is heated, and the part is mainly heated by radiation of the "hot cathode." In addition, the very chemical-active plasma environment acts in the part surface, but the physical effects related to the fast species bombardment are strongly reduced.

Finally, all configurations presented here can be applied in a hot-wall chamber so that the heating effect can be partially supplied by an auxiliary-resistive heating system (the fourth case). For example, in sintering of parts in the cathode configuration in hot-wall chambers, the part heating can be performed by the fast plasma species bombardment as well as by the heat transferred from the auxiliary-resistive heating system. In this case, the main role of the plasma is creating a highly reactive atmosphere, as chemically as physically, by means of excited-species-enriched environment. The use of an auxiliary-resistive heating system makes possible to decrease the high risk of plasma instabilities when high power input is necessary to perform sintering. In addition, it tends to reduce the texturing effects caused by sputtering, an effect which is typical of surfaces sintered in cathode configuration, as presented in [5]. In the anode/floating potential configuration [5, 6], the heating is due to the heat transferred by radiation from the cathode walls heated by plasma species bombardment and by using an auxiliary-resistive heating system. In this case, the relatively intense fast plasma species (ions and neutrals) bombardment verified for parts acting as cathode does not occur, and the parts sintered in anode do not present significant texturing effect caused by sputtering.

Additionally, the anode configuration (with or without hot wall) also makes possible to perform simultaneous sputtering-deposition treatment with the sintering process. For this situation, atoms sputtered from the (hot) cathode wall can be deposited on the anode (and/or floating part) surface, being that surface alloying is also expected to occur, depending on the composition of each electrode as well as the plasma parameters. This configuration has also been used to perform the debinding of powder injection molding (PIM) parts [5, 6, 24–28]. It is worth to be mentioned that the anode configuration comprises the very well-established hybrid sintering furnace (or hybrid dc plasma reactor) designed for plasma-assisted debinding and the sintering of powder injection molded parts [24–28]. This system has already been used in industrial production of PIM parts. If it is the interest, the reader can access the furnace scheme presented in reference [5].

Independently from the chosen configuration, the dc plasma sintering procedure is frequently divided into four steps. For the case of iron parts, the first step is the cleaning of the parts usually under a H_2 + Ar (or pure H_2) glow discharge at 723 K (450°C) for 30 min, using 133 Pa (1–3 Torr) pressure. The three other steps are the heating stage of the parts to be sintered at moderate heating rates up to the sintering temperature, the sintering stage, and, finally, the cooling stage under the used gas mixture flow. Such procedure is valid for all above mentioned dc plasma sintering techniques. As a general rule, cathodes are negatively biased at pulse voltage of at least 450 V, but they can be set up to about 1000 V, generally using square form pulsed power supply with frequency ranging from 1 kHz up to few hundreds of kHz. The choice of the pulse voltage and duty cycle depends on the sintering technique and on the discharge parameters like the gas mixture and pressure, besides others. In addition, for the case of hot-wall chamber, the desired power to be transferred to the plasma can be chosen by setting the auxiliary heating system parameters (keeping in mind the sintering temperature to be attained).

3. Plasma environment and chemical-potential setting in sintering

Figure 5 shows typical scheme of a sintering contact between two particles (scheme adapted from Thümmler and Oberacker [29]) but here subjected to the dc plasma environment. In that case [29], the main sintering mechanisms occurring in metals under the total absence of plasma environment, excepting the plastic flow, are presented and carefully discussed, namely, superficial diffusion (way 1), evaporation and recondensation (way 2), volume diffusion (way 3), and grain-boundary diffusion (way 4), as presented in **Figure 5**.

Under the plasma environment, for particles next to the surface, the sputtering [1, 2, 4, 8–10, 30–36] caused by the fast plasma species bombarding the cathode surface becomes important, since it leads the density of sputtered metal atoms to be increased in the plasma phase, thus acting directly on the enhancement of the evaporation and recondensation mechanism (way 2). Moreover, the superficial diffusion mechanism (way 1) tends to be strongly incremented by the fast plasma bombardment, as well as the volume diffusion mechanism (way 3) at the surface, since the vacancy density next to the surface tends to be increased, as one of the possible events of the plasma-surface (interface) interaction (see **Figure 6**). Finally, as a result of the use of high-purity hydrogen in the gas mixture, associated with the hydrogen dissociation in the plasma environment, the oxide-reduction

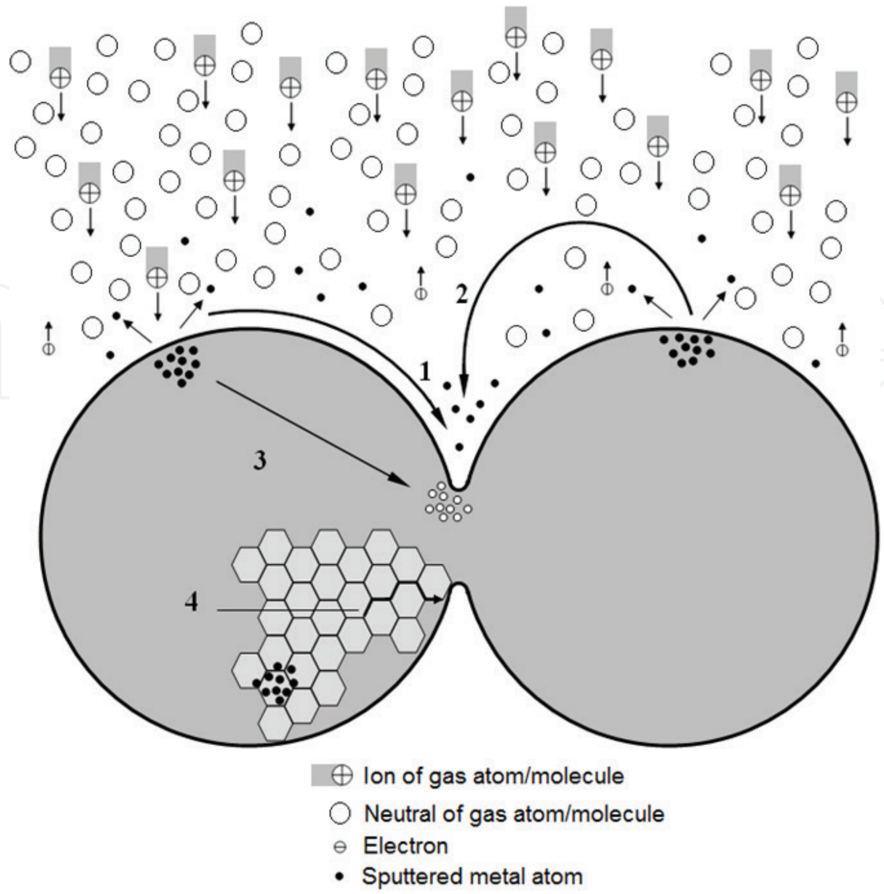

Figure 5. Scheme of a sintering contact between two particles (scheme adapted from Thümmler and Oberacker [29]), subjected to the dc plasma environment, showing the main sintering mechanisms, excepting the plastic flow: superficial diffusion (way 1), evaporation and recondensation (way 2), volume diffusion (way 3), and grain-boundary diffusion (way 4).

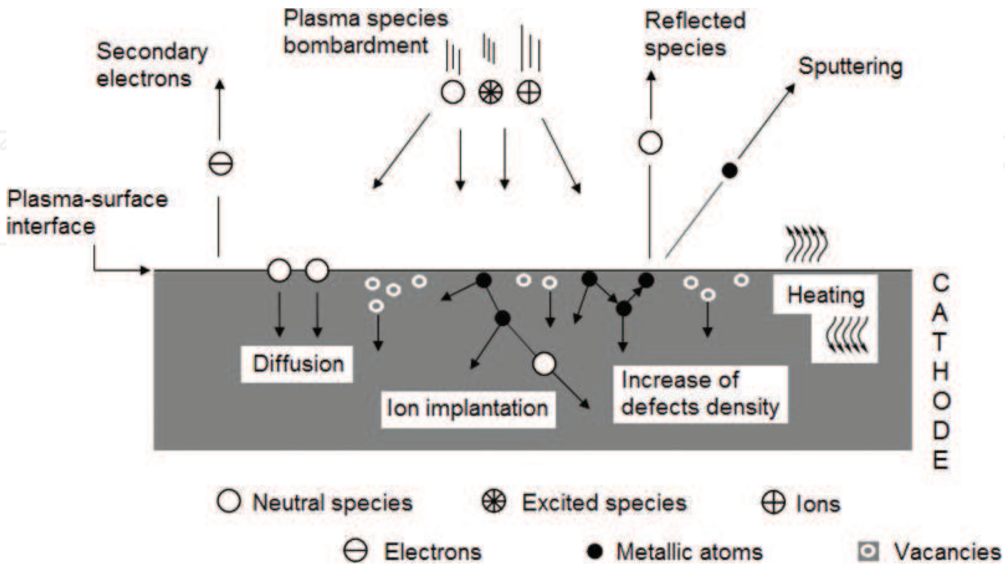

Figure 6. Typical events of the plasma-surface interface interaction (adapted from [1, 5, 6]).

effect is higher than in conventional processes, and the grain-boundary diffusion (way 4) tends to be also increased. It would be due to a supposed higher cleanness (based on the oxygen-free boundaries) attained in grain-boundary sites (particle contact). If the reader is interested, diffusion in solids is very well treated in [37].

Figure 6 shows the typical events of the plasma-surface interface interaction. The main events occurring more significantly in the cathode (part) surface, where the species energy is the highest, can be listed as follows [1, 5, 6]:

- Composition changes and chemical reactions as a result from the use of reactive gas species in the plasma (for all cases of dc plasma sintering techniques considered before) as well as of atoms sputtered from another cathode (it is supposed to be viable for the cases 2 and 3, only) being deposited in the part surface and diffusing into the substrate bulk;
- Ion implantation, as a result of the use of high pulse voltages, more probable in the hollow cathode discharge, due to the presence of fast species of higher energy for this particular configuration;
- Increase of the punctual defect density (like vacancies, interstitial, and/or substitutional atoms) in the first atomic layers of the substrate;
- Reflection of impingent plasma species;
- Emission of secondary electrons, which play important role in the discharge maintenance, since they are accelerated by the potential fall of the cathode sheath into the glow region, acquiring high energy;
- Sputtering, consisting of surface (metal and/or nonmetal) atoms torn off from its original surface as a result of the high-energy plasma species bombardment; and
- Heating of the cathode, as a result of the momentum transfer as the high kinetic energy species bombard its surface.

It is worth to be mentioned that in dc plasma sintering process one of the main roles of the plasma is providing a highly reductive atmosphere compared to conventional sintering furnaces. In this way, the smaller the oxygen species density in plasma, the higher is its oxide-reduction potential. Regarding the residual air pressure inside the vacuum chamber, it is to be noted that the oxygen partial pressure (P_{O2}) must be controlled and kept to low values, usually much lower than 0.27 Pa (0.21×10^{-2} Torr, the usual residual pressure of primary vacuum systems). In this case, certifying that stanch gas lines are present, by reducing leakage points all over the plasma installation, is imperative for a good sintering process. In addition, since all the dc plasma sintering techniques considered here are carried out under gas flow, gas-washing procedure of the vacuum chamber, by intercalating the evacuation/high-purity gas filling of it, makes possible to additionally decrease the P_{O2} of the referred system.

At this point, the use of the parameter gas flow regarding the plasma environment should be stressed to the good understanding of the reader. A correct gas mixture flow to the plasma sintering treatment is important since the gas flow is responsible by changing the gas species in the vacuum chamber. As different oxygen sources can be present in the plasma sintering environment like oxygen-based species (e.g., H_2O) adsorbed in the anode walls (internal to the vacuum chamber), oxides (present as oxide film on the powder particles) in the part to be sintered, and in organic compounds (like stearates used to lubricate the metal powder particles before the compaction step of the pressed part), the use of an adequate flow can prevent a possible chemical-potential change of the atmosphere from reductive to oxidant due to impurities being incorporated to the atmosphere. In previous work [23], the influence of the gas mixture flow on the processing parameters of hollow cathode discharge iron sintering was studied, and it was shown that by using a flow of 2×10^{-6} N m^3 s^{-1}, the stainless steel external cathode was completely oxidized, but by using a flow of 5×10^{-6} N m^3 s^{-1}, a clean and bright-aspect surface was achieved after the iron part sintering in the central cathode. It is worth to be mentioned that these values are only valid for the experimental apparatus and samples used in [23].

Regarding the gas utilized in plasma sintering processes, besides hydrogen (H_2), which is a strong oxide reductor usually present in sintering gas mixtures, Ar is mainly used for the heating purpose. This is because its relatively high atomic mass makes the energy transfer for elastic collisions to the treating material more effective, resulting in heating of the metal part to be sintered. The hydrogen, since it is a strong reductive gas, is important to convert oxides into metal, considering that oxide layers are present in metal particles.

Finally, another important step to be considered in the dc plasma sintering process is the plasma cleaning stage before sintering. The cleaning stage is usually carried out using the same Ar + H_2 sintering gas mixture, or eventually in a pure H_2 predischarge at low pressure (normally at 3 Torr), before the isothermal sintering stage. It is aimed, in the cleaning stage, eliminating the undesired influence of microarcs, which can be originated from the plasma species bombarding organic molecules present in electrode surfaces, and can be responsible by leading the discharge regime change from the abnormal to arc. This step has also an important role on the degassing of the plasma chamber wall, reducing contamination by such species in the sintering step.

Now that the reader is familiar with plasma, to illustrate some important effects of plasma on the sintering process, in the next section, some results on plasma heating and surface modification during plasma sintering will be presented.

4. Plasma heating

Figure 7(a, b, c) shows different heating curves for cylindrical iron cathode (10 mm diameter × 25.4 mm height) presented in the bottom of **Figure 4** for different conditions by varying the discharge configuration (with and without hollow cathode effect) and plasma parameters. **Figure 7(a)** shows the temperatures attained by varying the switched-on time (equivalent to the duty cycle) at the hollow cathode discharge (HCD) configuration for different pressures. **Figure 7(b)** presents the temperatures attained by varying the cathode pulse voltage (Vp) and the switched-on time for both the cathode and HCD (for an inter-cathode distance a = 6 mm) configurations, and the same is presented in **Figure 7(c)** but for intercathode distance a = 9 mm. The indicated temperatures in **Figure 7**(**a**, **b** and **c**) were measured in the abovementioned cathode (usually termed as the central cathode of the

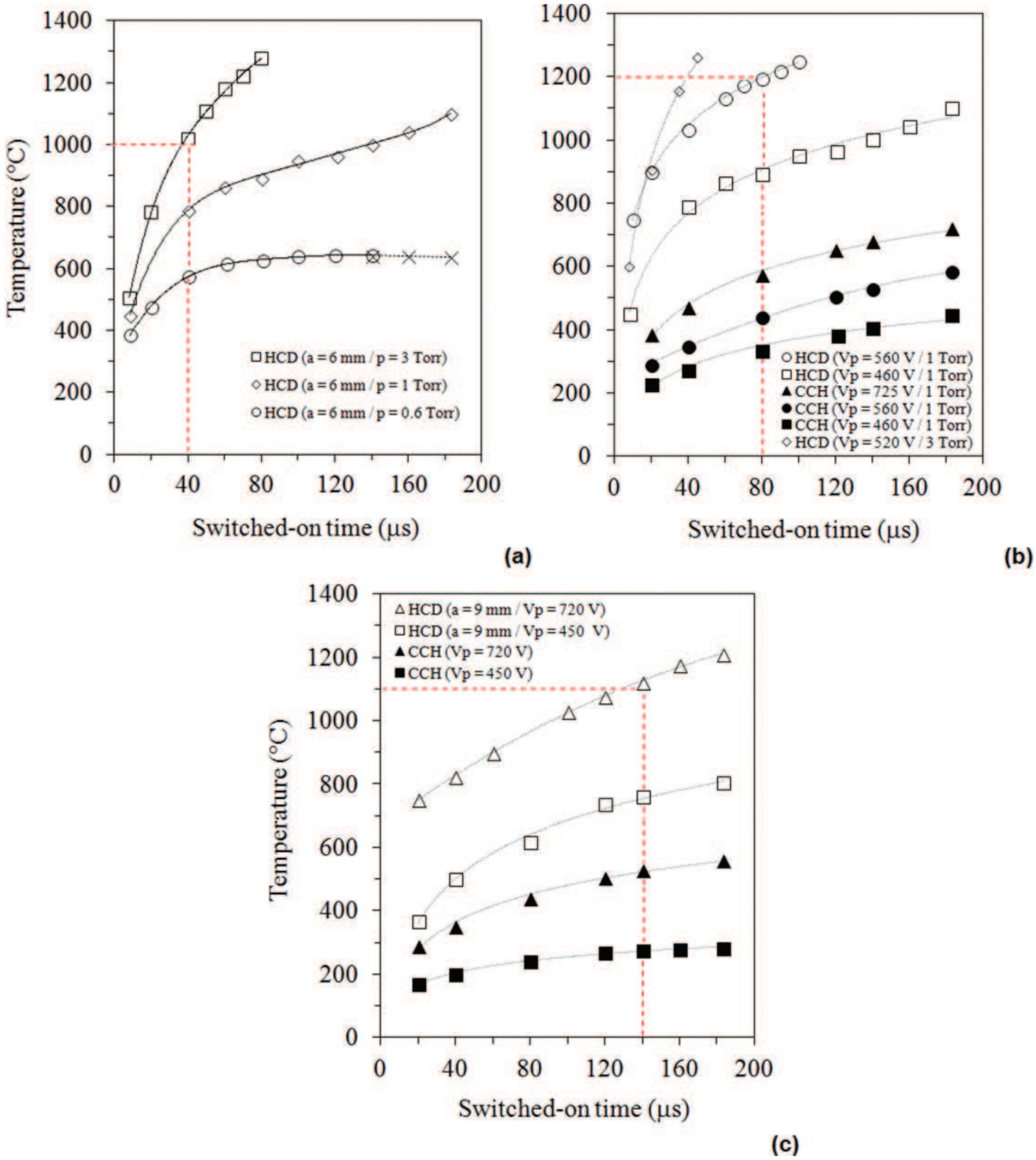

Figure 7. Different heating curves of cylindrical iron cathodes (10 mm diameter × 25.4 mm height) as functions of switched-on time (equivalent to the duty cycle) for different glow discharge configurations to dc plasma sintering purpose, for (a) hollow cathode discharge (*HCD*) (inter-cathode distance a = 6 mm) configuration as a function of the pressure, (b) both the cathode (*CCH*) and hollow cathode discharge (*HCD*) configurations at different cathode pulse voltages (Vp) and inter-cathode distance of 6 mm, and (c) the same at inter-cathode distance a = 9 mm, respectively.

hollow cathode configuration) by inserting a thermocouple inside it. For the cathode configuration, the cylindrical external (hollow) cathode was simply removed, thus leading to a heating condition where only one cathode (the central one) was present in the discharge. For more details, the reader can access the references [17–23]. In all cases, temperature increment can be expected as the switched-on time of the power supply, and thus the mean power transferred to the plasma is increased.

Considering other aspects, **Figure 7(a)** results also show the effect of the gas pressure on the cathode heating. Results indicate that the higher the pressure the higher is the ionization of the annular glow discharge, thus, the temperature achieved in the cathode. In the example shown using dashed red lines, for a specific switched-on time of 40 μs, considering square wave period of 200 μs (duty cycle of 20%), temperatures around 550, 750, and 1000°C are obtained for 0.6, 1.0, and 3.0 Torr pressures, respectively. At 0.6 Torr pressure, an annular glow discharge of instable operation is attained (indicated by the dashed black line for switched-on time ranging from 140 to 190 μs), being not adequate for the sintering purpose. This result agrees well with the expected for the product *ap* (*a* = inter-cathode distance and *p* = pressure), coming from more basic plasma studies, for which a stable hollow cathode discharge occurs for products *ap* ranging from 0.375 to 3.75 cm Torr [31]. Note that for a = 6 mm and p = 0.6 Torr, a product *ap* equal to 0.36 cm Torr is attained, which falls out of the proposed range for a stable condition. At 1 Torr, a duty cycle of 90% (maximum enabled by the power supply) has been used aiming to attain temperature high enough to perform iron sintering (~1100°C). And, for 3 Torr, the maximum temperature measurable by the K-type thermocouple was attained before the maximum duty cycle enabled by the power supply (~1250°C at 80 μs).

Figure 7(**b** and **c**) aims to put in evidence the role of the applied pulse voltage (Vp) on the cathode heating effect as well as the occurrence or not of the hollow cathode effect. It is evidenced that, as expected, the higher the voltage the higher is the temperature achieved in the cathode if considered the same configuration. On the other hand, considering the occurrence or not of hollow cathode effect, at 1 Torr pressure and *a* = 6 mm, for example, by using a 560 V pulse voltage, for a specific switched-on time of 80 μs, and considering a square wave period of 200 μs (duty cycle of 40%, see **Figure 7b**), the cathode temperature is increased from about 420°C, at the cathode configuration heating (*CCH*) to 1200°C, at the hollow cathode discharge (*HCD*). Finally, at 0.6 Torr pressure and *a* = 9 mm, for example, by using a 720 V pulse voltage, for a specific switched-on time of 140 μs, and considering a square wave period of 200 μs (duty cycle of 70%, see **Figure 7c**), the cathode temperature is increased from about 500°C, at the cathode configuration heating (*CCH*) to 1100°C, at the hollow cathode discharge (*HCD*). Being the interest, the reader can access additional details about the HCD in references [17–23].

In brief, from all results presented in **Figure 7**(**a**, **b** and **c**) as a general orientation regarding the cathode plasma heating, the use of higher pressures, pulse voltages, and duty cycles leads to higher glow discharge ionization with consequent higher current and dissipated power and thus the cathode heating to be improved, making possible to achieve temperatures high enough to sinter several metals. If the cathode configuration is considered only, in the absence of the hollow cathode effect, the use of pressures around 10–30 Torr is necessary to attain sintering temperatures for iron components, as confirmed in [11–16], whereas pressures around 3–10 Torr are enough in the HCD, as shown in **Figure 7**(**a**, **b** and **c**).

5. Surface-related phenomena for plasma-sintered parts

Figure 8(**a–d**) shows, for comparison purpose, SEM micrographs of the top (subjected to *HCD*) and bottom (non-subjected to *HCD*) of a cylindrical green (pressed) iron (Ancorsteel 1000C iron powder) sample (**Figure 8a** and **c**, respectively) sintered in the central cathode of a hollow cathode discharge (HCD), using external stainless steel cathode ((**Figure 8b** and **d**, respectively). In this case, sintering was performed at 1150°C, during 2 hours, using inter-cathode distance of 6 mm, with a flow of 5×10^{-6} N m^3 s^{-1}, in 80% Ar + 20% H_2 gas mixture, and a pressure of 3 Torr. It is to be noted that in **Figure 8**(**b** and **d**), showing the surface condition after sintering, SEM micrographs were taken in the same positions of **Figure 8**(**a** and **c**), indicating the surface condition of the pressed iron sample, before sintering. The top of the sample was exposed to the plasma (as shown in **Figure 9**) aiming to put in evidence how effective the mass transport is affected by the discharge (plasma environment). Additionally to **Figure 8** (**a–d**) micrographs, **Figure 10** shows the Cr and Ni concentration profiles obtained in the originally pure iron-pressed sample surface, as a result of the deposition of metal atoms sputtered from the external cathode made of stainless steel on the pure iron sample top. All results shown in **Figures 8(a–d)** and **10** confirm the role of the sputtering, typically enhanced in *HCD*, in intensifying the mass transport in plasma phase and sample surface (as shown in **Figure 5** near the particle surfaces), thus improving the sintering mechanisms of the superficial diffusion (way 1) and the evaporation and recondensation (way 2). In this case, the role of the sputtering has supposedly increased the metal atoms density in plasma phase, which tends to recondense (or to be deposited) next to the surfaces subjected to the intense fast plasma species bombardment, preferentially in concave areas. Note that by confronting the iron sample bottom surface (non-subjected to the plasma species bombardment) in a same position in its green (before sintering) and sintered states (**Figure 8c** and **d**, respectively), apparently no additional surface densification was verified. This fact confirms that the sample bottom was sintered through the known mechanisms expected for the conventional sintering (as shown in [29]). Nevertheless, contrarily, for the top surface (subjected to the plasma species bombardment), important surface densification was achieved, which is confirmed by comparing the iron sample top surface (before plasma species bombardment) in a same position in its green and sintered states (**Figure 8a** and **b**, respectively). In this case, the sample top was sintered with increased superficial diffusion (way 1), and the evaporation and recondensation (way 2) improved by sputtering-depositing mechanism occurring in plasma (as shown in **Figure 5**) that conclude this discussion.

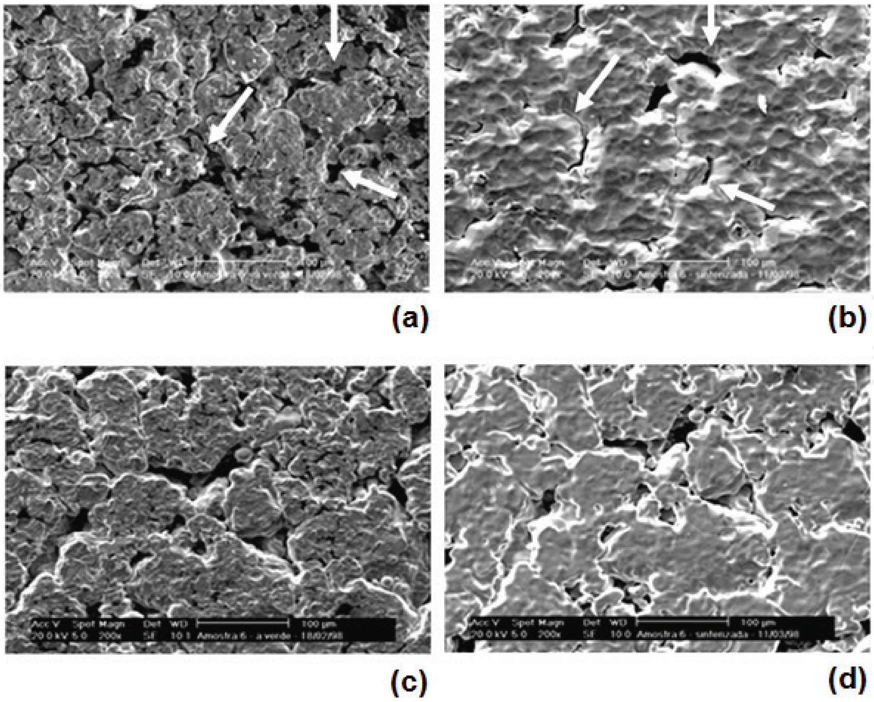

Figure 8. SEM micrographs of the (a and b) top surface (subjected to *HCD*) and (c and d) bottom (nonsubjected to *HCD*) of a cylindrical iron sample (Ancorsteel 1000C iron powder), before (a and c) and after (b and d) sintering, respectively (white arrows indicate identical positions of a same sample, before and after the sintering).

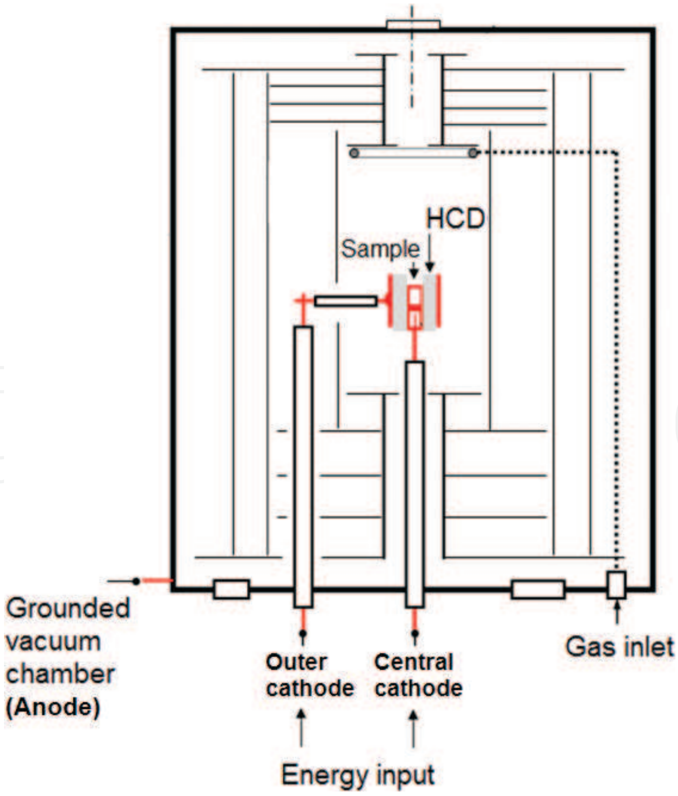

Figure 9. Scheme of *HCD* sintering experiment used to put in evidence the sintering mechanism here termed sputtering-deposition mechanism, occurring in dc plasma sintering system.

http://dx.doi.org/10.5772/66870

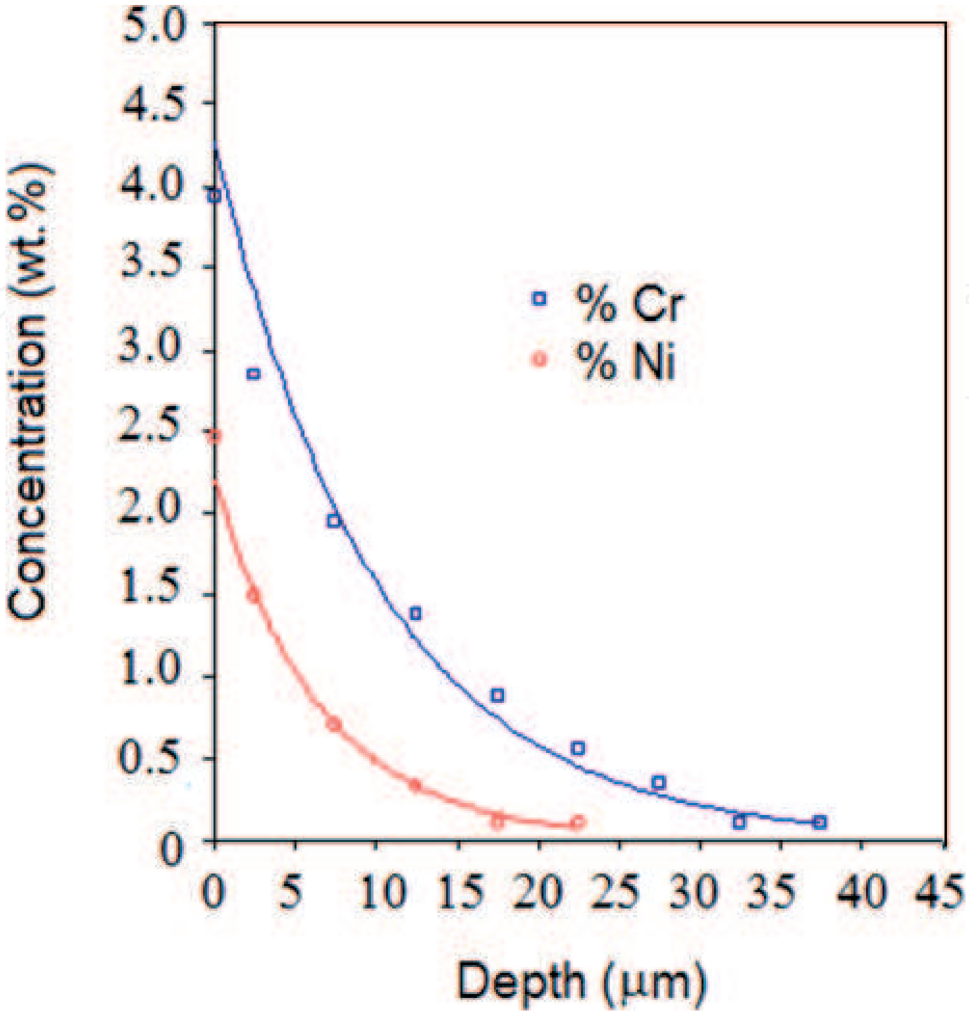

Figure 10. EDS measured Cr and Ni concentration depth profiles obtained in the sintered pure iron sample top surface, as a result of the deposition of metal atoms sputtered from the external stainless steel cathode, subjected to hollow cathode effect.

6. DC plasma sintering advantages over the conventional sintering

Considering all the presented phenomena involved in dc plasma sintering, it is expected that this process can present important technological advantage over "conventional sintering." As presented in [5, 6], some advantages of the dc plasma-assisted sintering process in respect to conventional sintering technique, as a consequence of the plasma species bombardment, besides other physicochemical phenomena, could be listed as follows:

- Possibility of surface diffusion increment;
- Possibility of surface texturing obtainment (see **Figure 8b** results) and eventual surface densification of the sintered part;
- Easy obtainment of highly reductive environment, enabling sintering of metals that tend to form very stable oxides (like Ti and stainless steels);

- Possibility of surface alloying of the sintered part carried out simultaneously to the part sintering, due to the sputtering-depositing effects (i.e., the enrichment of the part surface with alloying elements); and
- Finally, possibility of carrying out thermochemical treatments (such as nitriding, carburizing, and/or carbonitriding) that can be simultaneously performed in the sintering thermal cycle (as presented in reference [38]), or just after the sintering, in a single loading processing, by readjusting temperature and gas mixture, introducing reactive gases like nitrogen (N_2) and/or carbon (e.g., by means of the use of CH_4).

7. Final remarks

In this work, dc plasma-assisted sintering of metal parts is shown as a promising and relatively new research and development field in PM. The main aim of this work was to introduce the reader to the main applications of the dc plasma sintering process in the referred field. To achieve this goal, the present chapter was divided in a brief introduction and sections in which the bases of the abnormal glow discharge regime (dc plasma) were carefully treated, showing the main particularities of this new and “fascinating glow world” of dc plasma applied to the sintering of metal parts. Finally, the main techniques of dc plasma sintering, thermodynamic fundamentals of the plasma environment, aspects of the plasma heating, and plasma-surface-related phenomena of sintered parts were successfully treated, making possible to the reader to achieve a good understanding on the great potentialities of the dc plasma sintering process applied to the powder metallurgy.

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