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Influence of the Radial Spacing Between Cathodes on the Surface Composition of Iron Samples Sintered by Hollow Cathode Electric Discharge

S.F. Brunatto*[a], I. Kühn[b], J.L.R. Muzart[b]

[a]*Department of Mechanical Engineering, UFPR, 81531-990 Curitiba - PR, Brazil*
[b]*Department of Mechanical Engineering, UFSC, 88040-900 Florianópolis - SC, Brazil*

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The present work reports an investigation of the influence of the radial spacing between cathodes on the iron sintering process by hollow cathode electrical discharge, with surface enrichment of the alloying elements Cr and Ni. Pressed cylindrical samples of 9.5 mm diameter and density of 7.0 ± 0.1 g/cm^3 were prepared by compaction of Ancorsteel 1000C iron powder. These samples, constituting the central cathode, were positioned concentrically in the interior of an external cathode machined from a tube of stainless steel AISI 310 (containing: 25% Cr, 16% Ni, 1.5% Mn, 1.5% Si, 0.03% C and the remainder Fe). Sintering was done at 1150 °C, for 120 min, utilizing radial spacings between the central and hollow cathodes of 3, 6 and 9 mm and a gas mixture of 80% Ar and 20% H_2, with a flow rate of 5 cm^3/s at a pressure of 3 Torr. The electric discharge was generated using a pulsed voltage power source, with a period of 200 µs. The radial spacing had only a slight influence on the quantity of atoms of alloying elements deposited and diffused on the surface of the sample. Analysis with a microprobe showed the presence of chrome (up to 4.0%) and nickel (up to 3.0%, in at. %) at the surface of the samples. This surface enrichment can be attributed to the mechanism of sputtering of the metallic atoms present in the external cathode, with the deposition of these elements on the sample surface and consequent diffusion within the sample.

Keywords: *hollow cathode discharge, plasma sintering, sintered iron, surface deposition of alloying elements*

1. Introduction

Hollow cathode electric discharges are of great technological interest in many different applications, such as in light sources, surface treatments, atomic spectroscopy, plasmochemistry, lasers, cathode vaporization and the sintering of ceramic materials[1-5].

The phenomena occurring in plasma, and specifically, in hollow cathode electrical discharges, have been the motive for various fundamental studies[2]. The effect of the hollow cathode can be verified for different cathode geometries. For example, the effect can occur with cathodes having planar and parallel walls, cylindrical cavities or even annular cavities[6-9].

The effect of the hollow cathode in an annular cathodic cavity is an exponential increase in the density of the discharge current (or plasma). This increase occurs as a consequence of the trapping of electrons between the concentric cylindrical surfaces that comprise the cathodes. The trapping of the electrons, which results from the geometric confinement of the plasma in the annular cavity, causes a significant increase in the various collision processes between the discharge species (ions, electrons, atoms and neutral molecules), intensifying the ionisation reactions, excitation and relaxation. As a result there is also an increase in the quantity of the species (comprised basically of positive ions and neutral species) that impinge on the cathodic surfaces (connected to the negative of the power source). Two principal events result from this interaction between the plasma and the cathodic surface: a) the heating of the cathode to very high temperatures; and b) the sputtering effect, characterised by the tearing of metallic atoms from the cathodic surface, caused by the bombardment by the plasma species.

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e-mail: *brunatto@demec.ufpr.br

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Based on the typical effects of an annular electric discharge, in an abnormal regime, with a high rate of ionisation and the sputtering mechanism[3], a process was developed which permits, simultaneously, sintering and the alteration of the surface chemical composition of iron samples positioned as the central cathode in a hollow cathode system[9]. In this system, a hollow cylindrical cathode (the external cathode) is positioned concentrically in relation to the central cathode, and, besides acting to confine the geometry of the plasma, also acts as a source of alloying elements for the electric discharge, these elements depending exclusively on the material that constitutes the external cathode.

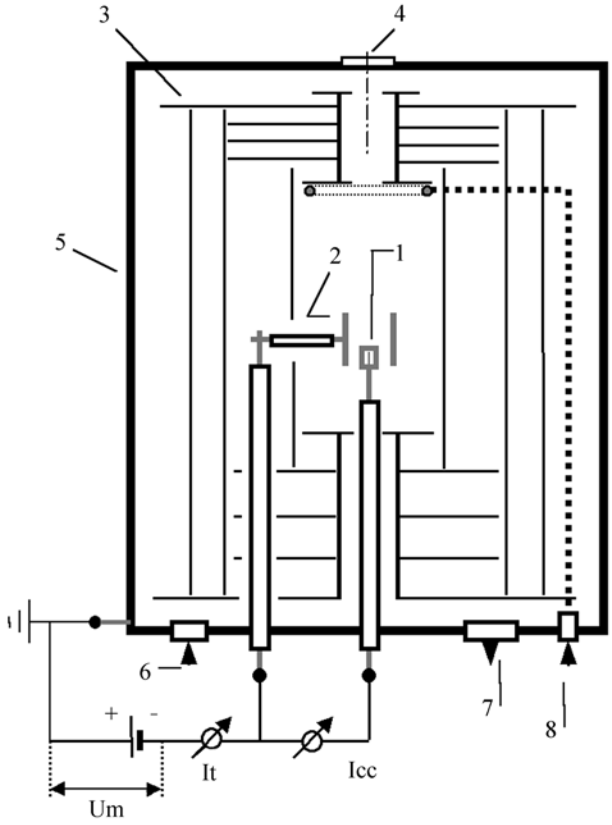
In this process, the attainment of high current densities, even at very low pressures (0.6 to 3 Torr), enables the heating of the material to temperatures adequate for sintering, through adjustment of the current, which depends on the potential applied to the electrodes. In addition, the sputtering effect intensifies with the applied potential, resulting in an increase in the offer of metallic atoms to the plasma. As a result there is a greater probability to enrich the surface of the sintered material, which constitutes the central cathode, with alloying elements originating from the external cathode.

The present work reports a study of the influence of the radial spacing between the cathodes on the iron sintering process, with simultaneous surface enrichment of the alloying elements Cr and Ni, by the process of hollow cathode electric discharge. Special attention is given to the quantity of the alloying elements deposited and diffused at the surface of the iron samples.

2. Experimental Procedure

Details of the experimental apparatus used in this study can be found in Fig. 1. The discharge chamber was built of stainless steel AISI 316, with a diameter of 350 mm and a height of 380 mm. The sample support was machined from low carbon steel AISI 1008. It had a diameter of 9.5 mm and a height of 12 mm, and was placed as the central cathode. The sintering temperature control was done with a k-type chromel-alumel thermocouple, inserted 8 mm into the sample holder. The external (hollow) cathode was machined from a tube of stainless steel AISI 310 (containing in atom%: 25% Cr, 16% Ni, 1.5% Mn, 1.5% Si, 0.03% C and the remainder Fe).

The electrical system was formed by three electrodes, being the two cathodes and an anode, and a power source. The anode, grounded and connected to the positive of the power source, was comprised of the reactor shell and a thermal shield consisting of stainless steel AISI 304 plates that surrounded both the cathodes. These plates were used to minimise the heat loss from the cathodic region during



1. Central cathode (sample holder with the inserted thermocouple);
2. Outer hollow cathode;
3. Thermal shield plates (anode);
4. Viewing window;
5. Discharge chamber (anode, grounded);
6. Measurement of absolute pressure (0-10 torr range);
7. Out to vacuum pump;
8. Inlet for flow of the gas mixture.

Um = measurement of average voltage;
Icc = measurement of central cathode electric current;
It = measurement of total electric current.

Figure 1. Simplified representation of the discharge chamber.

the process. The pulsed voltage power source had a period of 200 µs (time on + time off). The power supplied to the process was controlled via the time of the on pulse.

Due to the fact that the study was done with a power source without stabilisation of the input voltage, the experiments were subject to fluctuations in the voltage of the electric network (maximum fluctuations of 380 V ± 5% were observed). A resistance in series was placed between the discharge chamber and the power source to minimise the risks of an arcing discharge regime. This resistance controlled the peak voltage supplied to the cathodes. The cathodes were submitted to the same potential difference, through an electrical connection in parallel.

The discharge chamber design allows the possibility of independent mounting of the central and external cathodes, with the absence of mechanical contact, in order to allow the measurement of the individual electric currents in the cathodes.

Pure iron was selected as the material to be processed as the central cathode, given that it has a considerable solubility for many alloying elements and has an enormous range of applications in metallurgy. The choice of stainless steel AISI 310 (in atom %: 24.50% Cr, 16.20% Ni, 1.50% Mn, 1.50% Si, 0.03% C, the remainder being Fe) as the material of the external cathode guaranteed the presence of a large quantity of alloying elements, while being a material widely available and easily machined to produce the cathodes.

The reactor cleaning procedure, after it was opened for the mounting of the experimental cathodes, was divided in two steps:

- cleaning of the cathodes, of refractory components and iron samples, in petroleum ether under ultrasound for 15 min;
- attainment of a vacuum of 10^{-2} Torr, with at least two flushings, under flow of argon and hydrogen (gases of purity of 99.999%);

For the sintering process, cylindrical samples of iron, obtained from Ancorsteel 1000C powder, with an estimated purity of 99.75 wt%, were pressed to a diameter of 9.5 mm and a height of 10.0 mm (both ± 0,1 mm) with a density of 7.0 ± 0.1 g/cm^3, without zinc stearate. Sinterings were done for a period of 120 min, at a temperature of 1150 °C, with a flow of 5 cm^3/s of a gaseous mixture of 80% Ar and 20% H_2, at a pressure of 3 Torr. The external cathodes had their internal diameters machined so as to guarantee three distinct values for the radial spacing between the cathodes, 3.2, 5.8 and 9.2 mm. The peak voltage of the pulse at the outlet of the power source was 565 ± 4 V.

The procedure for sintering the pressed iron sample involved four steps:

- pre-discharge at 450 °C for 30 min, at a pressure of 1 Torr, with the resistance adjusted to 100 Ω;
- adjustment of the pressure to 3 Torr and of the resistance to 50 Ω, with heating to the sintering temperature at a rate of 25 ± 5 °C/min;
- sintering at 1150 °C with the resistance adjusted to 50 Ω; and
- cooling under flow of the gas mixture.

The sintered samples were characterised by scanning electron microscopy and by energy dispersive X-ray microprobe analysis, without the use of specific chemical standards. Characterisations were done on the lateral surface of the cylindrical samples with the aim of identifying the changes in chemical composition at the surface exposed to the ionic bombardment. In addition, the concentration profiles of chrome and nickel were determined in transverse sections of the samples prepared by standard procedures for metallography. They were determined using a 5 x 40 µm^2 area of electron beam scanning. The chemical analyses were repeated at steps of 5 µm. In the concentration profile graphs the measurements are presented as average values obtained at the middle of each step (at 2.5 µm). A quadratic curve was fitted to the data and the areas under the curve was calculated by integration in order to determine the influence of the radial spacing between the cathodes on the quantity of alloying atoms deposited and diffused within the sample material.

For the determination of surface chemical composition, the results presented are the average of nine analyses done on different positions on the lateral surface of the samples. The analyses were realised using a 700 x 900 µm^2 area of electron beam scanning. In the case of the amount of Cr and Ni at the sample surface, the 95% confidence intervals were less than ±0.20 atom% for each of the three different conditions studied. Measurements made by the microprobe present an experimental error of 0.30 atom% for substitutional alloy elements (like Cr and Ni).

Furthermore, it must be emphasised that if identical conditions of processing are guaranteed, differences of up to 15% for the degree of surface enrichment with alloying elements can be observed. This is related to the characteristics of the hollow cathode discharge, which is highly sensitive to small differences in the cleanliness of the atmosphere and the geometry of the discharge chamber, amongst other factors.

3. Results and Discussion

Figure 2 shows the effect of the radial spacing between cathodes on the average process variables obtained during the final 20 min of the sintering processing step at 1150 °C. These results show a more intense hollow cathode effect for smaller radial spacings, as expected, which is evidenced by the lower "pulse on" times (t_{ON} = 24 µs) at a radial spacing of 3.2 mm. To maintain the sintering temperature at 1150 °C with the other spacings, it was necessary to use large values of t_{ON} (39 and 65 µs for 5.8 and 9.2 mm, respectively), resulting in larger values for the current of the external cathode (I_{CE}). This behaviour is due to the increase in the rate of ionisation with t_{ON}. It must be clear that the average voltage effectively applied in the process is directly related to t_{ON}. On the other hand, the currents were very similar for the central cathode, for all three of the radial spacings (158 ± 4 mA). This result is as expected, since the sample temperature is a function of the central cathode current density. Current densities of the order of 20 mA/cm^2 were obtained at the sintering temperature of 1150 °C, for all three conditions studied (the central cathode area effectively exposed to the electrical discharge of the hollow cathode used in the calculation of the current density was 7.8 cm^2).

Figure 3 shows the chemical spectra of the sample sintered with a radial spacing of 3.2 mm. The analyses were done for two distinct positions on the sample, on the base (Fig. 3a) and on the lateral surface (Fig. 3b). As the base and top of the sample are not exposed to the annular discharge, both these faces have the initial chemical composition of the compact, or, in other words, approximately 100% iron. In contrast, the lateral surface of the sample, exposed to the hollow cathode electrical discharge, was enriched in alloying elements originating from the external cathode, namely chrome and nickel. After sintering the surface contained 3.60 at.% Cr (3.35 wt.% Cr) and 2.50 at.% Ni (2.65 wt.% Ni).

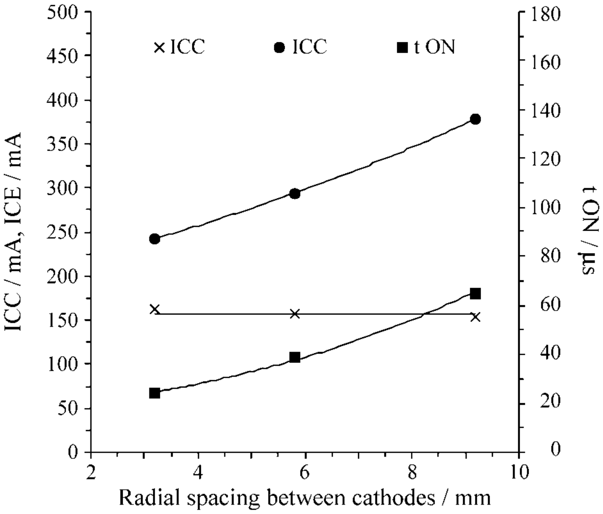


Figure 2. Average values, during the final 20 min of sintering, of the processing variables as a function of the radial spacing between cathodes.

Figure 4 shows the concentration profiles for Cr and Ni, for the iron samples sintered at radial spacings between cathodes of a) 3.2 mm, b) 5.8 mm and c) 9.2 mm. Shown also are the approximate quantities of alloying elements deposited and diffused to the interior of each sample, with these values being obtained by integration of the area under curves fitted to each concentration profile.

For all three sintering conditions the quantities of Cr deposited were greater than those of Ni. The same occurred in relation to the depth of diffusion of these elements below the surfaces of the samples. This is probably due to the quantity of chrome atoms in the electrical discharge being greater than that of Ni. This arises from the sputtering mechanism, which depends on the composition of the external cathode, given that the sputtering coefficients of the metals Fe, Cr and Ni are quite similar.

Further, in accordance with Fick's laws, the observed shallow diffusion of Ni could be expected due to the smaller concentration gradient of this element in relation to that of Cr (Fig. 4). The Fick's laws state that the diffusion depth is proportional to the concentration gradient of the alloying element. In this case, a lower concentration of an alloying

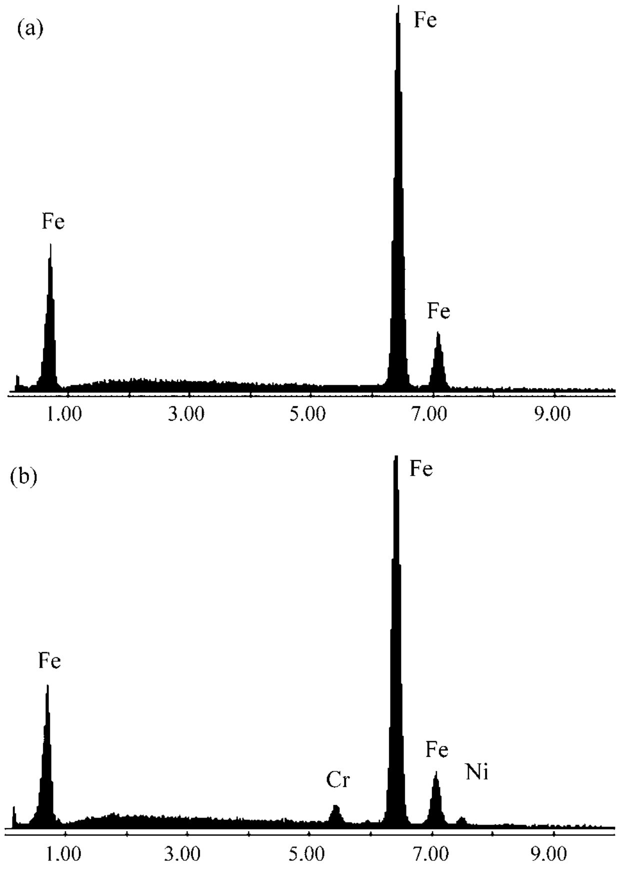
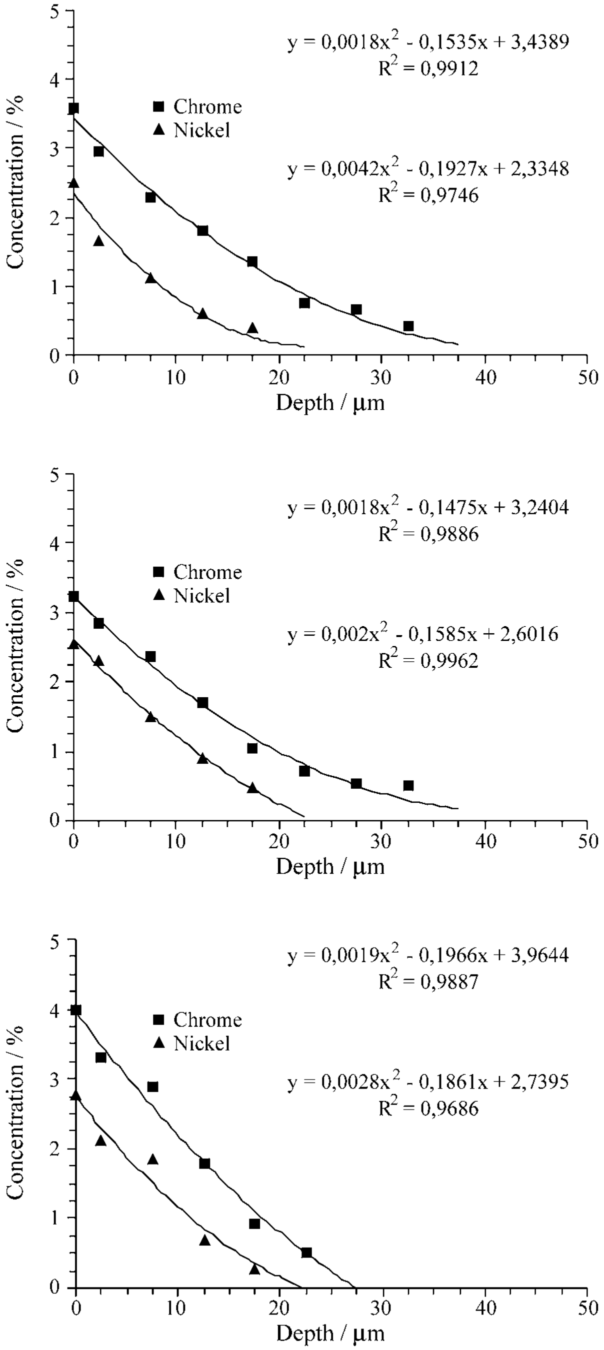


Figure 3. Chemical spectra of samples processed with a radial spacing between the cathodes of 3.2 mm: a) spectrum from the base of the sample; and b) spectrum from the lateral surface of the sample.

element on the surface of the material means that the depth of diffusion will be smaller.

Also to be considered are the individual diffusion coefficients of Ni and Cr in Fe-γ, given that for the quantities of Cr and Ni deposited, the sintering of the surface of the sample tends to occur in the austenitic field, such as occurs in the bulk of the material[10]. These diffusion coefficients, at a temperature of 1150 °C, are 1.5×10^{-11} for nickel and 4.1×10^{-11} for chrome [11]. Therefore it can be expected that atoms of Ni, upon being deposited on the surface of the iron samples, diffuse into the austenite 3 times more slowly than atoms of Cr, tending to suffer a process of re-sputtering to a much greater degree (given that the central cathode also suffers a strong bombardment). Disregarding any additional effect of combined diffusion of Ni and Cr, given that the latter tends to diffuse more easily, the results in Fig. 4



Area under the chrome concentration profile (µm . at %):

$$\int_0^{37.5} 0.0018x^2 - 0.1535x + 3.4389\,dx = 52.67$$

Area under the nickel concentration profile (µm . at %):

$$\int_0^{22.5} 0.0042x^2 - 0.1927x + 2.3348\,dx = 19.703$$

(a)

Area under the chrome concentration profile (µm . at %):

$$\int_0^{37.5} 0.0018x^2 - 0.1475x + 3.2404\,dx = 49.445$$

Area under the nickel concentration profile (µm . at %):

$$\int_0^{22.5} 0.002x^2 - 0.1585x + 2.6016\,dx = 26.009$$

(b)

Area under the chrome concentration profile (µm . at %):

$$\int_0^{27.5} 0.0019x^2 - 0.1966x + 3.9644\,dx = 47.853$$

Area under the nickel concentration profile (µm . at %):

$$\int_0^{22.5} 0.0028x^2 - 0.1861x + 2.7395\,dx = 25.163$$

(c)

Figure 4. Concentration profiles of Cr and Ni, with the corresponding fitted equations and calculated areas indicated, for iron samples processed with radial spacings between cathodes of: a) 3.2 m; b) 5.8 mm and c) 9.2 mm.

(a, b, c) seem quite reasonable: for all three conditions studied there was always a smaller diffusion depth for Ni. The profiles show a presence of traces of Cr to depths of up to 35 µm and of Ni to depths of up to 20 µm.

It is important to note that the process used has particular characteristics which tend to activate surface diffusion of the atoms that are deposited on the sample. In fact, the increase in surface diffusion of metal atoms as a consequence of the surface ion bombardment in plasma processing has motivated many studies[12,13]. In the present work the intense ionisation of the hollow cathode electrical discharge results in a heavy bombardment of ions and neutral species, promoting strong interactions between the plasma and the surface of the sample, besides a strong heating of the central cathode. The evolution of the metallurgical sintering process of iron compacts is itself evidence of these two effects.

Returning to Fig. 4 (a, b, c), the calculations of the areas under the concentration profiles indicated the approximate evolution of the quantity of atoms of Cr and Ni deposited and diffused in the samples. The average (± standard error) for the three conditions for Cr was 50.0 ± 2.5 atom%.µm and for Ni it was 23.5 ± 3.5 atom%.µm. Considering only the surface chemical compositions of the iron samples, the average values for the chemical analyses indicated the presence of 3.60 ± 0.15, 3.30 ± 0.05 and 4.00 ± 0.05 atom% Cr and 2.50 ± 0.15, 2.55 ± 0.10 and 2.80 ± 0.20 atom% Ni, for radial spacings of 3.2, 5.8 and 9.2 mm, respectively. Analysis of these results allows the affirmation that the radial spacing between cathodes has only a small effect on the process of surface enrichment, given that the quantities of alloying elements were very similar for the three radial spacings used and that the observed differences in the average values for the surface compositions are not significant, considering the likely level of systematic error in the measurements (0.30 atom%). This result is directly related to the intense ionisation and sputtering, typical of hollow cathode electrical discharge, and therefore, of discharges with annular geometry.

4. Conclusions

This work aimed to study the influence of the radial spacing between cathodes on the surface characteristics of iron samples sintered by hollow cathode electrical discharge, with special attention being given to the quantity of alloying elements (Cr and Ni) deposited and diffused at the surfaces of these samples.

The work showed the viability of simultaneous sintering of iron with a considerable surface enrichment of alloying elements, thus making the process potentially important for the optimisation of the surface properties of sintered components.

The radial spacing between cathodes had only little influence on the quantity of alloying elements deposited and diffused on the surfaces of the samples, which is directly related to the basic characteristics of hollow cathode electrical discharge. On the other hand, this parameter does have an effect on the power that must be supplied to maintain the samples at the sintering temperature, which is best evidenced by the decrease in the time of the on pulse, the average voltage and the total electric current as the radial spacing between cathodes is decreased.

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