

Aspects related to the grain size of iron samples sintered in hollow cathode discharge

Brunatto, Silvio Francisco

Universidade Federal do Paraná, 81531-990, Curitiba, PR, Brazil
brunatto@ufpr.br

Guimarães, Nicolas Virgilli

Universidade Federal do Paraná, 81531-990, Curitiba, PR, Brazil
brunatto@ufpr.br

Muzart, Joel Louis Rene

Universidade Federal de Santa Catarina, 88040-990, Florianópolis, SC, Brazil
muzart@materiais.ufsc.br

Abstract. *Metallurgical aspects of unalloyed iron sintered in hollow cathode discharge were studied, with special emphasis on the qualitative determination of the grain size. The average grain size was verified for iron samples sintered in different conditions: a) conventional sintering using a resistive heating furnace; and b) plasma sintering using hollow cathode discharge. Conventional sintering was carried out at 1423 K (1150°C) for 120 minutes, under a pre-purified H₂ flow at 101,33 kPa (760 Torr). For plasma sintering, two independent cathodes formed an annular hollow cathode discharge, and a pressed cylindrical sample of iron powder (99.75% pure), functioning as the central cathode, was placed concentrically inside an external cathode machined from a cylindrical AISI 310 stainless steel bar. The inter-cathode's radial space was 5.8 mm. Sintering was carried out at 1423 K (1150°C) for 120 minutes, under a gas mixture of 80% Ar and 20% H₂ flowing at $5 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$. The pressure of the gas mixture was kept constant at 400 Pa (3 Torr). The discharge was generated using a pulsed voltage power supply with a 200 μs period. Samples were characterized by optical microscopy confronting the morphology, size and shape of the grains obtained for the two sintering conditions. It was observed the average grain size for the sample sintered in plasma is very higher than that of the sample sintered conventionally. Besides, plasma sintering strongly affects the morphology and shape of the grain by increasing the grain growth mechanisms.*

Keywords: Hollow cathode discharge, Plasma sintering, Grain growth, Grain boundary.

1. Introduction

Abnormal glow discharges have been applied in various metallurgical processes, as plasma nitriding [1, 2] and more recently, plasma sintering [3, 4]. Electric discharges with annular cathode cavities lead to the effect known as hollow cathode discharge [5]. This discharge configuration has aroused in a growing technological interest, inasmuch as it can be utilised not only as an alternative processing technique of surface treatments but also in new applications and developments, being the case of hollow cathode discharge carburising [6], plasma nitriding combined with a hollow cathode discharge sputtering device [7], and hollow cathode discharge sputtering device for uniform large areas thin film deposition [8].

Based on the typical effect, a high ionisation rate [7, 10], of a direct current annular electric discharge, in abnormal regime, an efficient process for sinter compacted samples was developed. In addition, as a consequence of the high ionisation rate, an enhanced sputtering take place [9], which resulted, simultaneously to the sintering of the sample, in a modification of the chemical composition of the sample surface. In this system, a hollow cylinder made of AISI 310 stainless steel (the external cathode) was positioned concentrically in relation to the central cathode. The external cathode produced a plasma-confined geometry as well as a source of alloy elements, which by diffusion in the gas phase deposited on the sample surface.

Metallurgical aspects of unalloyed iron sintered in hollow cathode discharge were studied, with special emphasis on the determination of the grain size. The average grain size was verified for iron samples sintered in two different conditions: a) conventional sintering using a resistive heating furnace; and b) plasma sintering using hollow cathode discharge. This paper was divided in two parts. In the first one, special attention was given to the grain size characterization confronting the results obtained for the materials sintered in different conditions. In the second part, the results were discussed in terms of the literature contents, presenting a hypothesis to explain the grain growth mechanism.

2. Experimental and materials

The optic microscopy characterization was carried out with the objective to compare the grain size of the sintered materials in both the HCD technique and in the conventional technique. The HCD processed sample was sintered in the 1150 °C, during 60 min, with space $a = 5,8 \text{ mm}$, pressure of 3 Torr, flow of $5 \text{ cm}^3/\text{s}$ and external cathode machine-made from AISI 310 steel. The processed sample in conventional way was sintered in the same conditions of temperature and time, in resistive oven, inside of an alumina pipe. The atmosphere consisted of a flow of pre-purified H₂ to a pressure slightly higher than 760 Torr (1 atm), in accordance with procedure detailed in [11].

Figure 1 presents a schematic representation of the hollow cathode discharge experimental apparatus, with emphasis to the cathode-anode configuration in the vacuum chamber. A more detailed representation of the experimental apparatus can be found in previous works [12, 13].

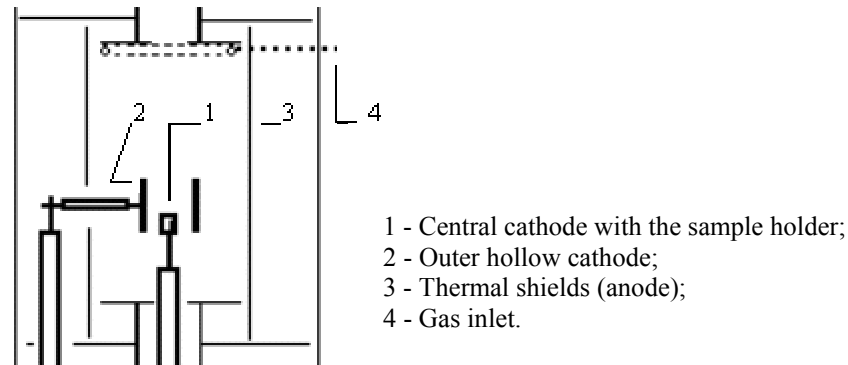


Figure 1 - Schematic representation of the experimental apparatus.

The discharge chamber was constituted by a stainless steel cylinder of 350 mm diameter and 380 mm height sealed with O-rings to steel plates on its bottom and top. The system was evacuated to a residual pressure of 1.33 Pa (10^{-2} torr) by a two-stage mechanical pump. The gas mixture of argon and hydrogen was adjusted by using two mass flow controllers of 8.33×10^{-6} and $3.33 \times 10^{-6} \text{ m}^3\text{s}^{-1}$ full scale, for Ar and H_2 gas respectively. The pressure in the vacuum chamber was adjusted by a manual valve and measured by using a capacitance manometer of 1.33×10^3 Pa (10 torr) full scale.

Samples of 9.5 mm diameter and 10 mm height were placed on an AISI 1008 carbon steel support (12 mm height) that worked as the central cathode. A cylindrical carbon steel part (3.5 mm height) was placed on the top of the sample, in order to generate a homogeneous annular discharge. The external cathode was machined from an AISI 310 stainless steel tube (atomic composition: 25% Cr, 16% Ni, 1.5% Mn, 1.5% Si, 0.03% C and balance of Fe) to an internal diameter of 21.2 mm, wall thickness of 2 mm and height of 25.4 mm. The inter-cathode distance was of 5.8 mm.

Both cathodes were negatively biased at the same voltage, using a square form pulsed power supply. The voltage was fixed to 565 V. To ensure a stable discharge, an electrical resistance was connected in series between the power supply and the plasma reactor. The power transferred to the plasma was adjusted by varying the time switched on (t_{on}) of the pulse. The pulse period used was 200 μs . The sample temperature was selected by adjusting the on/off time of the pulsed voltage. The temperature was measured by means of a chromel-alumel (type K of 1.5 mm diameter) thermocouple inserted 8 mm into the sample holder.

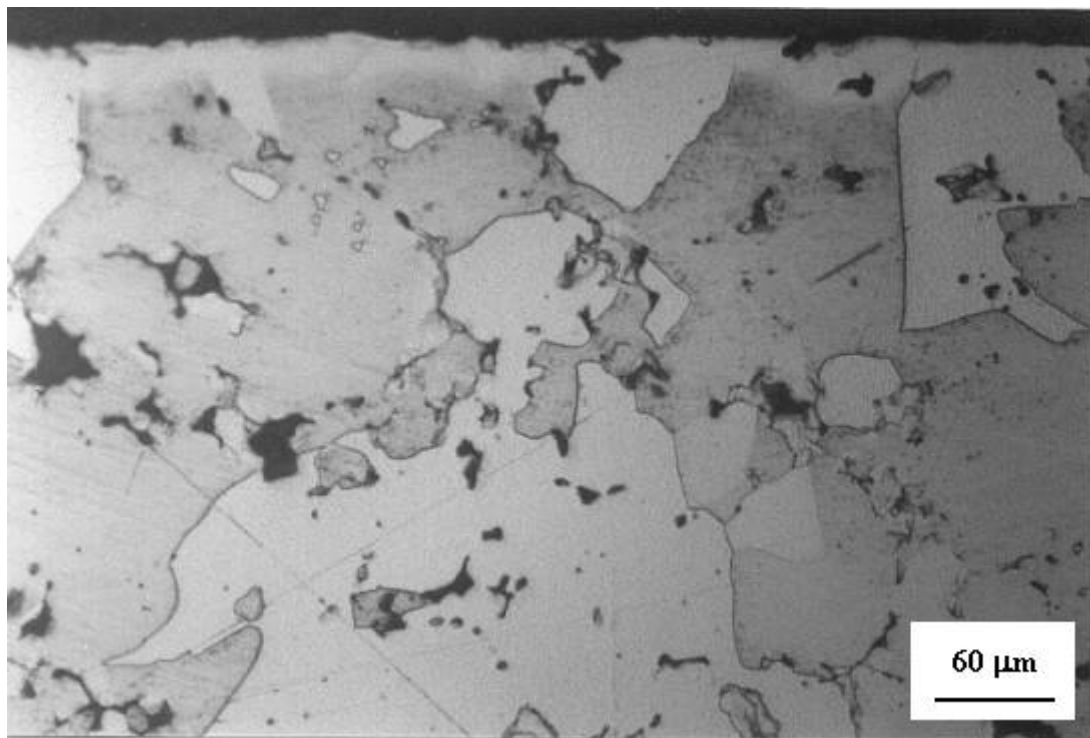
Samples of unalloyed iron were produced using Ancorsteel 1000C iron powder (99.75 wt. % pure). A double action press with moving die body was used to compact the samples which presented a green density of $7.0 \pm 0.1 \text{ g.cm}^{-3}$. The mass of the pressed samples typically was around 5.0 g. Mass loss on samples was measured with a 0.1 mg precision balance.

Sintering procedure was divided in three steps:

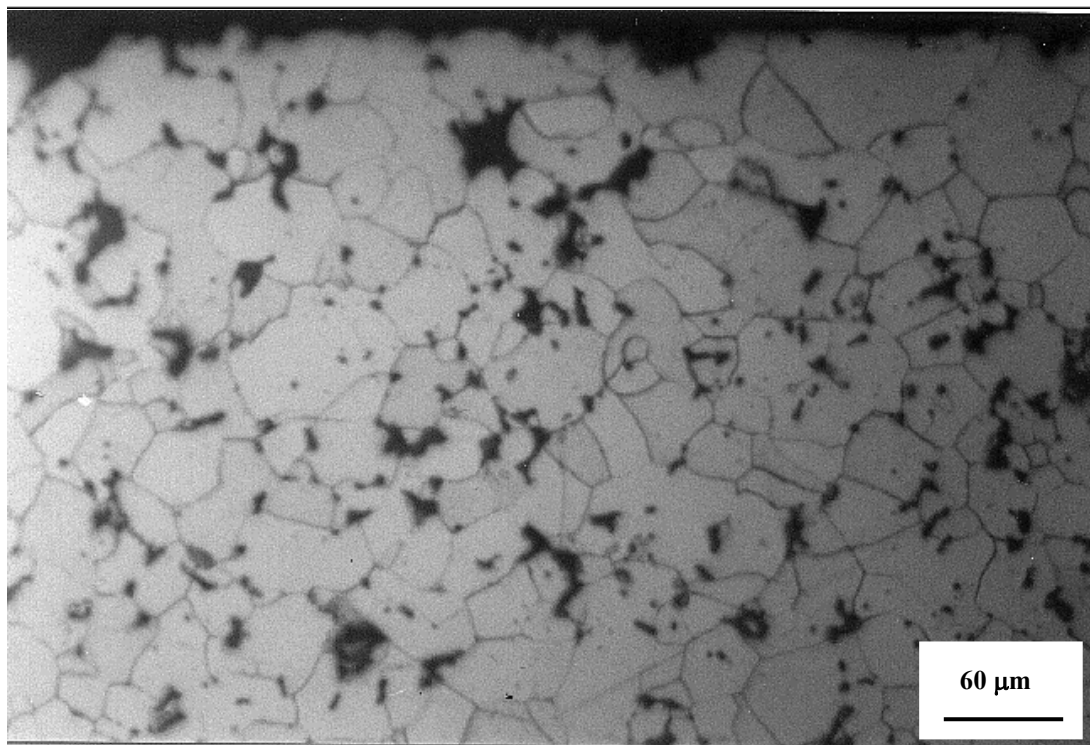
- a) sample cleaning under discharge at 723 K (450 °C), for 30 minutes, 133 Pa (1 torr) pressure and the resistance adjusted to 100 Ω ;
- b) sample heating at a heating rate of 0.42 K.s^{-1} (0.42 °C.s^{-1}) and sintering at 1423 K (1150 °C) using 400 Pa (3 Torr) pressure and resistance adjusted to 50 Ω ;
- c) sample cooling under a gas mixture flow.

3. Results and Discussions

Figure 2 show micrograph of the iron sample sintered in HCD (Fig. 2a) and of the iron sample that was processed in a conventional way (Fig. 2b). A strong grain growth mechanism in the sample processed in HCD can be evidenced. This behavior could be related to the activation of the sintering mechanisms when the plasma sintering technique is utilized [4]. Comparatively to the conventional process, it was observed in [4] a more effective pore rounding effect, for iron samples sintered in plasma. In the attempt to explain this result, the authors suggest a possible additional material transport mechanism improving the diffusion in the powder particles contact region of the compact ones (or, in the necks). Such mechanism would be attributed to the propagation of phonons along the material, being them produced by transference of momentum as a consequence of the sample bombardment for the plasma species. In that work no mention is made about the average grain size of the sintered materials. However, the hypothesis presented in [4] could be also valid in the attempt to explain the effect of the grain growth verified in the Figure 2(a).



(a)



(b)

Figure 2 - Micrographs of the iron sample cross section sintered in: (a) HCD; and (b) conventional way. Chemical attack: Nital-2%.

The understanding of this effect is slightly more complicated, being necessary to consider the possible metallurgical events that would lead to the attainment of a excessive grain growth.

Focusing the attention only in the metallurgical aspects, two studies could be important, being these studies complementary between themselves: a) one of them based on the mechanism of diffusion in the grain boundaries [14]; and the other, b) based on the grain boundaries disappearance during the sintering [15]. The theory formulated in this last work ([15]), using the model of two spheres in contact, demonstrates the possibility of disappearance of grain boundaries through two distinct ways. Initially, each particle contact results in a grain boundary due to the random orientation of the crystalline net from each particle. Such configuration corresponds to a place (the particles contact region) of minimum free energy, given that the grain boundary is located in a region whose area is minimum. In this condition, in the beginning of the sintering, the grain boundary is anchored not being able to move itself. The anchorage disappears when the particle contact ("neck") and consequently the respective grain boundary grow for an equal size to the one of the diameter of the lesser sphere, during the sintering evolution. In this point, where the size of the grain boundary coincides with the diameter of the lesser sphere, the boundary area becomes maximum and the system tends to minimize this energy excess. As a direct result, the de-anchorage of the grain boundary is attained. The boundary becomes free to move itself and the driving force for its movement to the long one of the crystalline net becomes the reduction of the grain boundary area [15]. The sintering evolution will continue until that the grain boundary disappears in the adjacent pore of the lesser particle or until that the related boundary meets and coalesces itself with one another grain boundary.

Considering the results of Figure 2, it could be expected the occurrence of the hypothesis based on the propagation of phonons [4] which would be responsible by improving the mechanism of disappearance of grain boundaries [15], for the simple activation of the superficial, inter-crystalline (in grain boundaries) and transcrystalline diffusion mechanisms. These assumptions would help to understand the verified abusive grain growth in the sample that was sintered in HCD. It is the suggestion, as subject for future works, the development of a study aiming at the best understanding of such effects and the quantitative determination of the average grain size of the sintered iron samples.

4. Conclusions

This work studied the metallurgical aspects of unalloyed iron sintered in hollow cathode discharge, with special emphasis on the qualitative determination of a grain size. The average grain size was verified for iron samples sintered in different conditions: a) conventional sintering using a resistive heating furnace; and b) plasma sintering using hollow cathode discharge. It was observed the average grain size for the sample sintered in plasma is very higher than that of the sample sintered conventionally. Besides, plasma sintering strongly affects the morphology and shape of the grain by increasing the grain growth mechanisms.

5. References

- [1] Shohet, J. L.: IEEE Transactions on Plasma Science, 1991, vol. 19, n. 5, pp. 725-33.
- [2] Hirvonen, J. P.; et alli: Surface and Coatings Technology, 1996, n. 84, pp. 600-04.
- [3] Muzart, J. L. R.; Batista, V. J.; Franco, C. V.; Klein, A. N.: Proceedings of Advances in Powder Metallurgy & Particulate Materials - 1997, MPIF, 1997, part 3, pp.77-84.
- [4] Batista, V. J.; Binder, R.; Klein, A. N.; Muzart, J. L. R.: The International Journal of Powder Metallurgy, 1998, vol. 34, n. 8, pp. 55-62.
- [5] Timanyuk, V. A.; Tkachenko, V. M.: Sov. Phys. Tech. Phys., 1989, vol. 34, n. 7, pp. 832-34.
- [6] Terakado, K.; et alli: Metallurgical and Materials Transactions A, 1996, vol. 27A, pp.401-05.
- [7] Benda, M.; Vlcek, J.; Cibulka, V.; Musil, J.: J. Vac. Sci. Technol. A, 1997, vol. 15, n. 5, pp. 2636-43.
- [8] Koch, H.; Friedrich, L. J.; et alli: J. Vac. Sci. Technol. A, 1991, vol. 9, n. 4, pp. 2374-77.
- [9] Chapman, B.: Glow Discharge Processes, John Wiley & Sons, New York, NY, 1980, 406 p.
- [10] Engel, A. v.: Ionized Gases, 2nd ed., American Institute of Physics, New York, NY, 1994, 325 p.
- [11] Brunatto, S.F.: Dissertação de Mestrado, 1993, CPGEM-UFSC.
- [12] Brunatto, S. F.; Kühn, I.; Muzart, J. L. R.: Materials Research, 2001, V. 4, n.4, pp. 245-250.
- [13] Brunatto, S. F.; Kühn, I.; Muzart, J. L. R.: Materials Science and Engineering A, 2003, V. 343, pp. 163-169.
- [14] Peterson, N. L.: International Metals Reviews, 1983, V. 28, n. 2, p. 65.
- [15] Berry R. S.; Bernholc, J. Salamon, P.: Appl. Phys. Lett., 1991, V. 58, n.6, pp. 595-597.