

THE EFFECT OF PULSE AND VOLTAGE ON UNALLOYED IRON SURFACE DURING SINTERING ON THE CATHODE OF GLOW DISCHARGE

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ABSTRACT

Atomized iron powder was compacted at 500 MPa and sintered in a plasma atmosphere with the purpose to investigate the effects occurred on the surface of the samples with temperatures varying from 900 to 1100°C, voltage ranging from 400 to 700 V with time switched on (T_{on}) of 80, 110 and 140 μ s for each voltage level. These samples were sintered in DC plasma compound of hydrogen and argon using the cathode geometry. The samples have also been processed in a conventional system just for comparative effects. They have presented a significant atomic mobility on the surface promoting a decreasing porosity to a voltage level around 700 V. However, when some samples were sintered at 400 V with low T_{on} their surfaces presented a cluster of iron atoms in a spherical shape due to low kinetic energy of ions striking the samples.

1. INTRODUCTION

The cathode plays an important role in materials sputtering (atomic pulverization) due to be a target of energetic ions coming from glow discharge, in addition to being a source of electron production to the plasma maintenance. Little experimental data have been made available since Davis Vanderslice's work published in 1960's [1] about energy ion distribution bombarding the cathode. It was assumed that maybe due to the assembling these works, they have become difficult to carry out goods results. On the other hand, theoretical works simulating energy ion distribution were published [2-5]. From 1990's until the current days some experimental data have appeared, for example, the works cited in [6,7-12]. Some experimental results of energy ion distribution in different conditions of electric discharge will be presented below.

Peter et al. [9,10] have approximately measured the energy of H^+ and Ar^+ at 100 and 90 eV, respectively, in its maximum intensity for an electric discharge of 1.67×10^{-6} m³/s of H_2 , 1.67×10^{-6} m³/s of N_2 and 3.34×10^{-7} m³/s of air with pressure of 200 Pa (1.5 Torr), voltage of 500 and 400 V, and current around 0.1 A using a pulsed power source. They have used this discharge for the nitriding metallurgic process. Mason et al. [5] have developed a theoretical model to calculate the energy of fast neutral atoms bom-

barding the cathode. This subject has been treated by few researchers because the greater interest has been always given to the energy about ions only. The fast neutral atoms are formed by symmetrical charge transference in the cathode sheath continuing towards cathode with the same energy about ion that originated it. They have affirmed that most of the erosion in the cathode has been probably caused by fast neutral atoms and not by ions, although its energy could be slightly smaller, varying from 40 to 60 eV, rather than ions energy around 68 eV. These values have been analytically calculated in a discharge of pure argon in the following conditions: gas pressure varying from 67 to 133 Pa (from 0.5 to 1 Torr); current from 0,4 to 1 mA; and voltage applied to the cathode of 800 V. Straaten et al. [6] have measured the energy ions distribution of the X^+ , X^{2+} , X^{2+} , M^+ and MX^+ bombarding the cathode. The letter X represents the gases used in the electrical discharge (Ar and Ne) and letter M, material of cathode (Al, Cu, Mo and Ta). The conditions about the electrical discharge used by the authors have been the following: gas pressure from 10 to 100 Pa (from 0.075 to 0.75 Torr), current ranging from 1 to 5 mA and voltage varying from 500 to 1500 V. It was noticed that Ar^{2+} presented a wide peak with energy ranging from 70 to 600 eV. The Ar^{2+} originated in the glow discharge crosses the cathode sheath with few or no collision reaching the cathode with maximum energy. The energy distribution about Ar^+ and Ar^{2+} has presented narrow peaks with energy around 70 eV due to their high cross section. In terms of quantity the Ar^+ was present 10 times greater than Ar^{2+} and 100 times than Ar^{2+} . Straaten et al. [6] have also noticed that the cathode was significant bombarded by ions coming from its proper material. The Cu^+ with approximately 20% of the flow of Ar^+ reached the cathode with energy between 150 and 650 eV. Most of the ions formed by cathode material M^+ were originated in the glow discharge with energy loss lesser than energy of Ar^+ since it has few collisions by symmetrical charge transference. Budtz-Jorgensen et al. [13] have proved in experimental works that ArH^+ has had significant contribution for sputtering phenomena when compared with Ar^+ . These measures of sputtering rate have been made in a cathode of stainless steel and iron, with different compositions of Ar/H_2 but they have been always done with the voltage at 300 V, time switched on (T_{on}) at 100 μ s and gas pressure at 58.67 Pa (0.44 Torr). Budtz-Jorgensen et al. [13] have concluded that the role of hydro-

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gen in the cathode erosion in these electrical discharges was mainly owing to chemical sputtering. It was also verified that the greater rate of physicist sputtering was originated by ArH^+ for the gas mixture set out at 20% H_2 and 80%Ar. For an amount of 5% of H_2 into argon had a significant formation of the Ar^+ with energy around 80 eV. When the H_2 was increased more than 5% there was a reduction of Ar^+ and consequently ArH^+ was raised. Both ions have presented a similar energy distribution around 80 eV. According to Budtz-Jorgensen et al. [13] the ArH^+ dissociation is the main source of Ar^+ in the cathode sheath. Budtz-Jorgensen et al. [14] have carried out through other experiments using gold and aluminum cathodes with discharge of Ar/ H_2 at 20 Pa (0.15 Torr), time switched on (T_{on}) at 100 μs and voltage on the cathode at 300 V. When they have used the gold cathode, it was verified that the hydrogen addition into pure argon has increased significantly the atomic pulverization about this material. It was not attributed to chemical sputtering because the gold is not reactive. In this sense, the physical sputtering dominated the process by wide formation of ArH^+ when hydrogen was added in the discharge with sputtering rate optimized to a composition of 20% H_2 and 80%Ar. Regarding the aluminum cathode with the same conditions used before, it was necessary much more hydrogen in the discharge due to have greater importance of chemical sputtering than a physical one. The ions Ar^{2+} have dominated the physical sputtering because the increase of hydrogen did not influence the kind of atomic pulverization. In this case there was a necessity to supply ions of hydrogen to react to Al_2O_3 through chemical reaction.

In this current paper, several unalloyed iron samples were sintered using DC plasma when they were put on cathode. This technique was already used by different authors in order to do the same metallurgic process [15-19].

2. EXPERIMENTAL AND MATERIAIS

O texto propriamente dito deverá ser digitado em fonte tipo The plasma sintering apparatus is shown in Figure 1. The reactor consisted of a steel cylinder 300 mm in diameter and 300 mm in height, sealed by o-rings and closed at both ends by steel plates. Connections for a gas inlet, vacuum pump, pressure sensor and electrodes, electrically insulated, were connected to the steel plates. Prior to sintering, the system was pumped down by a two-stage mechanical pump until a residual pressure of less than 1.3 Pa was reached. The gas mixture consisting of 80% argon (99.999% pure) and 20% hydrogen (99.998% pure) was adjusted using two datametrics mass flow controllers whose full-scale value was $8.3 \times 10^{-6} \text{ m}^3\text{s}^{-1}$ (500 sccm) and the total gas flow was set to $4 \times 10^{-6} \text{ m}^3\text{s}^{-1}$ (240 sccm). The pressure in the vacuum chamber was adjusted and measured with accuracy better than 2% by a manual valve and measured using an Edward capacitance manometer of 13300 Pa (100 Torr) full-scale. The samples were produced by water atomization obtaining irregular powder DC177 from Höganäs Brazil Ltda. In or-

der to investigate the surface of the samples, this iron powder was sieved resulting in particle size with narrow distribution ranging from 43 to 63 μm . Then the powder was mixed with 0.6% wt of zinc stearate and compacted to a pressure of 500 MPa using a double action. The delubing was performed in a resistance furnace at a temperature of 500°C for 30 minutes in a hydrogen atmosphere. This condition was chosen to facilitate the study of surface porosity. The samples with 9.5 mm in diameter and 6 mm height were placed on a steel AISI 1020 support working on the cathode geometry as shown in Figure 2. Plasma sintering for this study was carried out for 30 minutes at 900, 1000 and 1100°C using a power source of 5 kW, which generated a square waveform pulse voltage varying from 400 to 700 V and the time switched on (T_{on}) of the pulse period ranging from 10 to 250 μs . All sintering process was held at 400, 500, 600 and 700 V being used T_{on} at 80, 110 and 140 μs for each voltage. These parameters have been used for the levels of temperature of 900, 1000 and 1100°C. The process temperature was adjusted by varying the gas pressure and maintaining T_{on} and voltage fixed for each plasma sintering as shown in Table 1. A cylinder of sintered unalloyed iron at 9.5 mm in diameter and 6 mm height symmetrically placed near to the sample was used for temperature measurements. The type K thermocouple was protected with a stainless steel cover, 1.5 mm in diameter, electrically insulated with Al_2O_3 and inserted 5 mm into the reference sample.

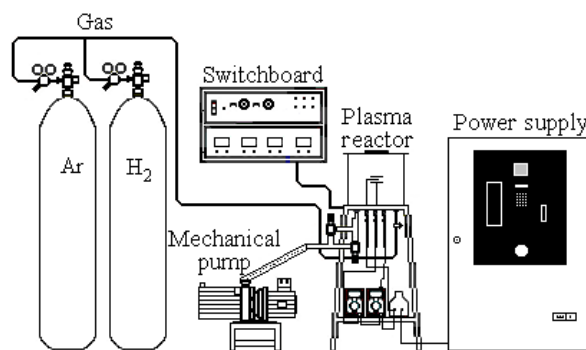


Figure 1 - Experimental apparatus.

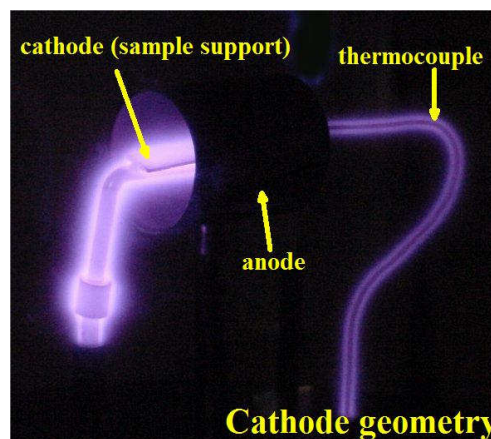


Figure 2 - Schematic representation of cathode geometry.

Table 1 - Gas pressure in (Pa/Torr) used during plasma sintering

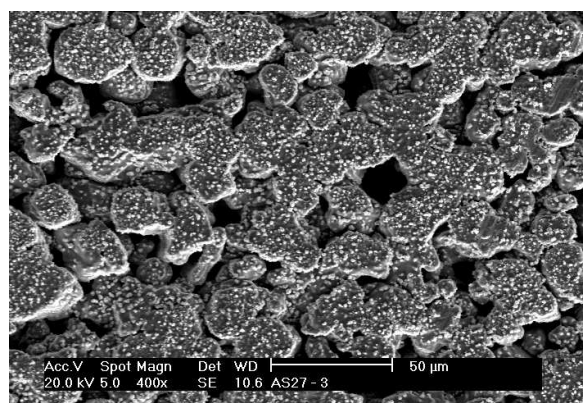
	400 V			500 V		
	80 μ s	110 μ s	140 μ s	80 μ s	110 μ s	140 μ s
900°C	1270/9.5	1076/8.1	931/7	783/5.9	692/5.2	619/4.6
1000°C	2544/19.1	1469/11	1360/10.2	1325/9.9	925/6.9	816/6.1
1100°C	2721/20.4	1653/12.4	1343/10.1	1320/9.9	969/7.3	839/6.3
	600 V			700 V		
	80 μ s	110 μ s	140 μ s	80 μ s	110 μ s	140 μ s
900°C	564/4.2	488/3.7	437/3.3	448/3.4	428/3.2	372/2.8
1000°C	735/5.5	657/4.9	609/4.6	584/4.4	535/4	491/3.7
1100°C	789/5.9	659/4.9	624/4.7	599/4.5	512/3.8	476/3.6

Surface micrographs of the sintered samples were obtained by using a scanning electron microscope in order to evaluate the efficiency about sintering process only on the surface of them. The SE (secondary electron) pictures for the image analyses were taken using a 400x magnification.

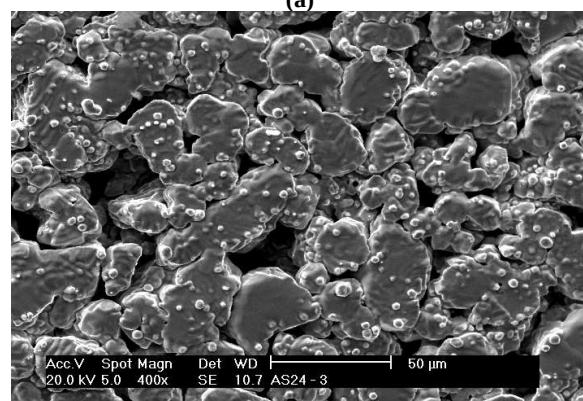
3. RESULTS AND DISCUSSION

Micrographs shown in Figure 3 were sintered in a plasma atmosphere using cathode geometry during 30 minutes at 900°C, 400 V and Ton at 80, 110 and 140 μ s, respectively, to Figures 3(a), 3(b), and 3(c). Clustering of iron atoms was formed in small spherical shape which was dependent upon the voltage and Ton used. A significant amount of these small clusters have been observed together for the sample sintered at 400 V and Ton at 80 μ s according to micrograph shown in Figure 3(a). When the voltage was increased to a level of 700 V maintaining Ton at 80 μ s, fewer clusters of iron atoms in spherical shape have been visualized on their surfaces and became cleaner when it was raised to 140 μ s. These effects are shown in micrographs of the Figures 4(a), 4(b), and 4(c) also sintered for 30 minutes at 900°C, 700 V and respectively Ton at 80, 110 and 140 μ s. The same conditions of sintering have been repeated for temperatures of 1000°C and 1100°C whose parameters are shown in Table 1. A chemical analysis focused in a small particle of the sintered sample has revealed that it was compound essentially of by iron according to Figure 5.

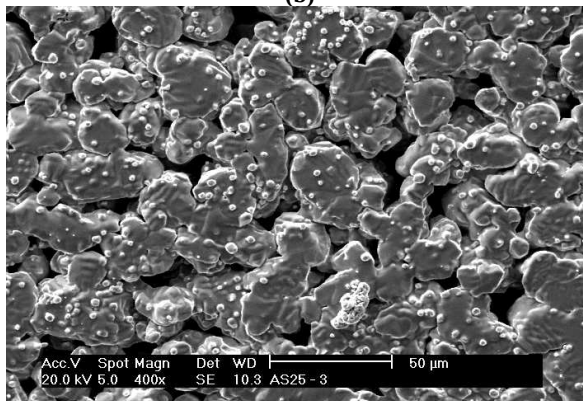
Surface diffusion, grain boundary diffusion and volume diffusion are the three main mechanisms of material transport in a sintering process purely in solid state as discussed by Thümmel and German [20,21]. However, another kind of diffusion, vaporization and re-condensation, can occur depending on the vapor pressure of the processed material. The vaporization and re-condensation could be worthless when these samples of unalloyed iron were sintered in a conventional system, though, this mechanism could be activated when the samples were sintered in the DC plasma by adopting cathode geometry. By using DC plasma technique, ions that arrive at the interface between the glow region and the cathode sheath are strongly accelerated towards the cathode.



(a)



(b)



(c)

Figure 3 - Micrograph of surface sample sintered on the cathode geometry at 900°C, 400 V and 80 μ s (a), 110 μ s (b) and 140 μ s (c).

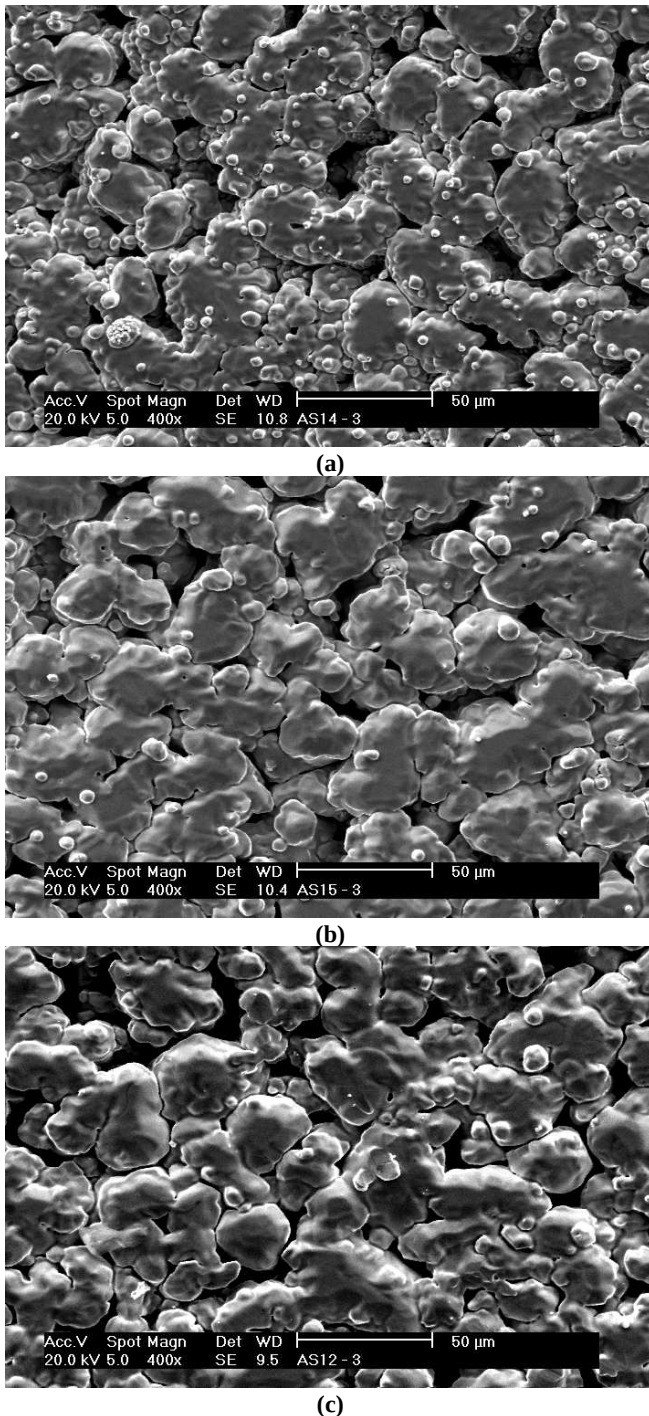


Figure 4 - Micrograph of surface sample sintered on the cathode geometry at 900°C, 700 V and 80 μ s (a), 110 μ s (b) and 140 μ s (c).

According to the theoretical foundation used in this work, the flow of ions have energy about 50 to 100 eV using very low gas pressures around 10 to 300 Pa (from 0.075 to 1.5 Torr). At usual gas pressures used in this work that have ranged between 372 and 2721 Pa (2.8 and 20.4 Torr) this level of energy tends to diminish. In accordance to Chapman [22] the kinetic energy of ions striking the sample surface is a direct function of the electric field in the cathode

sheath and inversely proportional to the gas pressure. These ions which bombard the cathode, promote three main effects: heating, sputtering of atoms from the cathode and kinetic energy transference to the atoms of the surface [22].

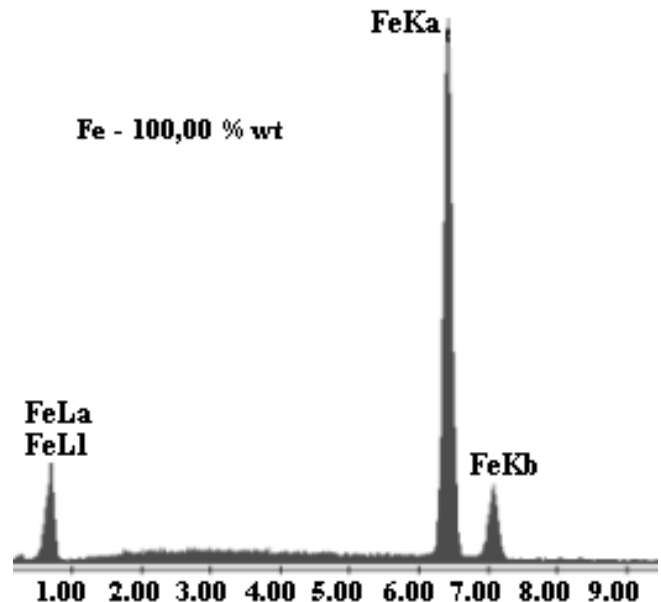


Figure 5 - Chemical analysis focused on a small spherical particle of the samples sintered at 900°C and 400 V.

When the pressure was adjusted to 1270 Pa at 400 V and 80 μ s the number of collisions with atoms was higher than when the pressure was maintained at 372 Pa at 700 V and 140 μ s. As a consequence, the amount about the cluster of iron was higher in the former case than when compared with latter one. As the energy of ions bombarding the cathode increased, consequently bigger the mobility of iron atoms on the sample surface, activating the vaporization and re-condensation diffusion. Due to sputtering, a high concentration of iron atoms that occurred in the gas phase, followed by an increasing of condensation that evidently was dependent on kinetic energy. This condensation of atoms occurs preferentially on the concave surface where vapor pressure is lower. In an opposite way, it was easier to extract an iron atom from the convex part where the vapor pressure is the highest. Nevertheless, some atoms arising from the cathode reach the glow discharge and consequently become ions by collisions with electrons coming back to the cathode with high energy. Thus, when several iron atoms in the vapor phase condensate on the sample surface with low kinetic energy and temperature, they tend to form a cluster because of their low mobility and diffusion, mainly at 900°C and pressure adjusted at 1270 Pa. In this way a cluster of iron atoms was formed without neck formation between a pair of particles because the combination among temperature (900°C), voltage (400 V) and T_{on} (80 μ s) was not interesting. This effect has significantly decreased when voltage pulse rises to 700 V and gas pressure falls to 372 Pa, even though maintaining the process at

900°C. In fact, when the voltage was increased, the ion energy that bombard the sample surface has become significantly higher in order to promote an activated diffusion including the loss of particles identification that defines the second sintering stage according to Thummler and German [20,21]. This effect is well visualized in micrograph of Figure 4(c). On the other hand when the process temperature was raised to 1000 and mainly 1100°C, as well as the maintenance gas pressure around 500 Pa (4 Torr), voltage at 700 V with Ton in 140 μ s, the effect discussed above has disappeared owing to significant increase of temperature. The combination of high voltage and temperature resulted in surface sealing as shown in Figure 6 and mainly 7 contributing to the porosity sealing [23]. The effect of temperature was not so significant because when the samples were sintered in conventional system, no porosity sealing was observed even at 1100°C as shown in micrograph of Figure 8.

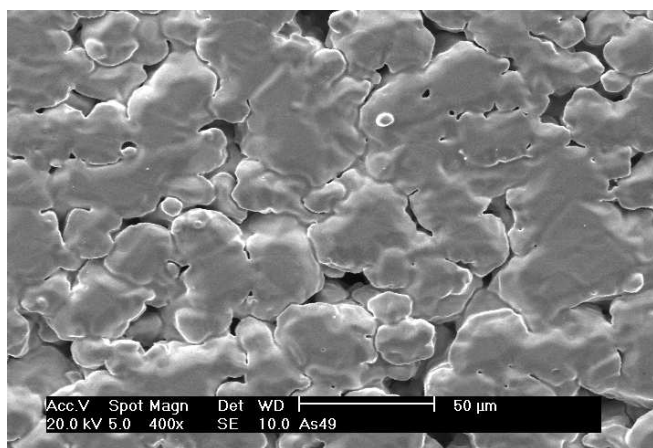


Figure 6 - Micrograph of surface sample sintered on the cathode geometry at 1000°C, 700 V and 140 μ s.

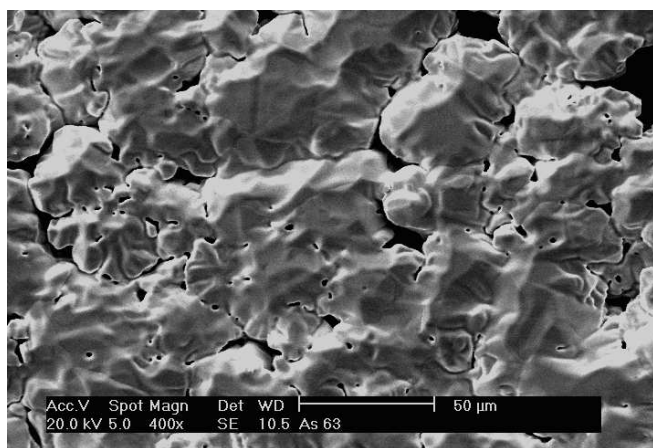


Figure 7 - Micrograph of surface sample sintered on the cathode geometry at 1100°C, 700 V and 140 μ s.

In short, the kinetic energy of ions bombarding samples was so important to close the porosity of them. Therefore, ions extract iron atoms from the convex part because the vapor pressure is higher and deposit them in a concave one by opposite effect and this way the sealing is verified in according to images shown in Figure 7.

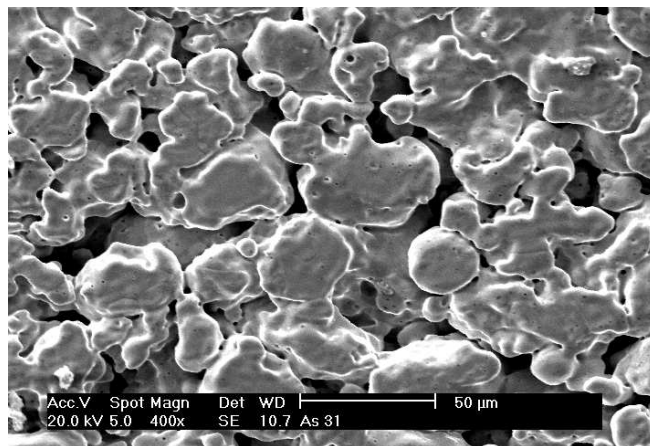


Figure 8 - Micrographs of sample sintered in conventional system at 1100°C.

4. CONCLUSIONS

The samples sintered on the cathode geometry have presented a cluster of iron atoms in spherical shape when they were processed at 900°C, 400 V and Ton was set at 80 μ s. However, this effect slightly disappeared when the voltage was increased to level of 600 and 700 V using Ton at 140 μ s, even maintaining the same process temperature. This is due to exclusively, to ion energy bombarding the sample surface promoting activated diffusion. Nonetheless, when the process temperature was increased to 1000 and 1100°C, maintaining voltage at 700 V with Ton in 140 μ s, the effect about iron cluster completely disappeared, owing to relevant increase of atomic diffusion including the elimination of surface porosity.

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