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PLASMA SINTERING OF UNALLOYED IRON: INFLUENCE OF ELECTRODE GEOMETRY

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ABSTRACT

Unalloyed iron samples were sintered in DC plasma formed by hydrogen and argon using the following electrode geometries: anode with and without metallic protector. Water atomized iron powder was compacted at 600 MPa and sintered in plasma atmosphere in order to investigate respectively the microstructure changes on the surface and in the bulk of the samples with temperatures varying from 740 to 1100ºC. The samples when sintered on anode with metallic protector geometry presented deposition of manganese and sulphur found out in the materials used to construct the electrodes. With regard to microstructural characterization, the samples showed large and irregular grains different from those processed in resistance furnace.

1. INTRODUCTION

Abnormal glow discharge in a mixture of hydrogen and argon gases having an ionization degree ranging from $\eta=10^{-4}$ to $\eta=10^{-6}$ has been used to sinter compacted metallic powder. This technique is called plasma sintering [1-5]. The bulk of powders is transformed in a specific shape and consolidated by compaction [6]. The sintering process, regardless of the technique used, is a thermal treatment for bonding particles into a coherent, predominantly solid structure via mass transport events that often occur on the atomic scale, promoting strength and lower system energy as explained by German [7]. The heat is provided by abnormal glow discharge and it depends on how the sample is positioned on the electrodes. As discussed by Chapman [8] the heat is fed by the ion, neutral and electron bombardment or just by cathode irradiation according to sample position adopted in the electrode geometry enabling the sintering process.
Glow discharge is a cold plasma can assist metallurgic process such as, chemical and physical vapor deposition, etching, nitriding or nitrocarburizing, oxide reduction, surface enrichment by sputtering and surface cleaning [9-14]. In these applications, the reactive species generated in the plasma are able to produce an activated process where the ion, neutral atom or electron bombardment reach the target heating the substrate for the desired objective. According to Chapman [8] the abnormal glow discharge is characterized when the electrode is negatively biased promoting a glow region around the cathode due to a specific gas under low pressure. There is an electric field in the cathode sheath where ions are strongly accelerated. Collisions between ions and atoms or molecules of the gas discharge in the cathode sheath resulted in a flow of fast neutrals and ions toward the cathode. On the other hand, there is another electric field in the anode sheath but less intensive than the cathode sheath. The electrons produced by collisions in the glow discharge are taken to a grounded electrode reaching the sample positioned on the anode.
Hence, a mixture of argon and hydrogen has been used to produce an abnormal glow discharge and then sintering unalloyed iron with the sample placed on a holder which worked as anode with metallic protector and anode without metallic protector to avoid any kind of bombardment.

2. EXPERIMENTAL

The plasma sintering apparatus is shown in Figure 1. The reactor consists of a steel cylinder with 300 mm in diameter and 300 mm in height, sealed by O-rings and closed at both ends by steel plates. Connections for 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. The gas mixture consisting of 80% argon (99.999% pure) and 20% hydrogen (99.998% pure) was adjusted using two mass flow controllers whose full-scale value was 8.3 x 10^{-6} m^3s^{-1} (500 sccm) and the total gas flow was set to 4 x 10^{-6} m^3s^{-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.

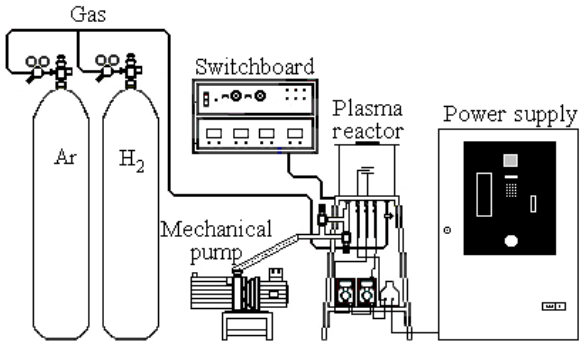

Figure 1 - Experimental apparatus.

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The samples were produced by water atomization obtaining irregular powder DC177 from Höganäs Brazil Ltda. In order to characterize the microstructure of the bulk samples and on the surface, the iron powder with a large size distribution was mixed with 0.6% wt of zinc stearate and compacted to a pressure of 600 MPa using a double action compacter. The samples with 9.5 mm in diameter and 6 mm high were placed on a steel AISI 1020 support working on anode with metallic protector and anode without metallic protector geometries as shown in Figure 2(a) and 2(b), respectively.

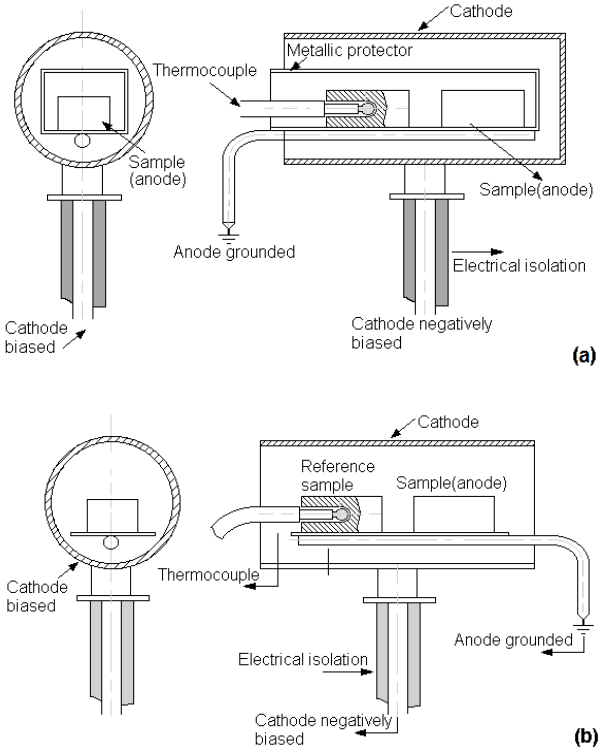


Figure 2 - Schematic representation of the electrodes geometries: anode with metallic protector (a); anode without metallic protector (b).

To study the samples surface working on the first geometry, the process has been carried out for 30 minutes at 900, 1000 and 1100ºC using a power source of 5 kW, which generated a square waveform pulse voltage varying from 400 to 700 V. The process temperature was adjusted by varying the gas pressure from 733 Pa (5,5 Torr) to 2400 Pa (18 Torr) and maintaining time switched on (Ton) fixed for each plasma sintering. In order to investigate growth and mobility of the grains in the austenitic and ferritic phases, the sintering process was carried out in three different level of temperatures (740, 850 and 950ºC) using anode without metallic protector geometry. The pulse voltage of 600 V was used maintaining the time switched on (Ton) fixed for every level of temperature. The sample was processed twice at a level of 950ºC: first it was put into glow discharge for 20 minutes; and second the same sample was reheated again to 950ºC, remaining just for 30 minutes. In both situations, the samples were cooled with plasma turned off. Concerning to the ferritic phase, the samples of unalloyed iron were processed at 740 and 850ºC both during 45 minutes. These temperatures in the ferritic field have been chosen because they were above and below Curie temperature (770ºC). For all electrode geometries a cylinder of sintered iron 9.5 mm in diameter and 6 mm height symmetrically placed near 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. Delubing was performed in a resistance furnace at a temperature of 500ºC for 30 minutes in hydrogen atmosphere. The Carl Zeiss-Jean microscope was used to perform the optical microscopy of the cross-sectioned samples, polishing with alumina 0,3μm and etching with 2% nitric acid in order to identify the ferritic microestruture using 500× magnification. In order to find the same region in unalloyed iron that was processed twice at 950ºC, the sample was polished and etched to characterize the microstructure doing a indentation in a ferritic grain. Later, the same sample was reheated to 950ºC again for 30 minutes and finally it was reprepared to find the same micro region that was previously marked by indentation as shown in Figures 5(a) and (b).

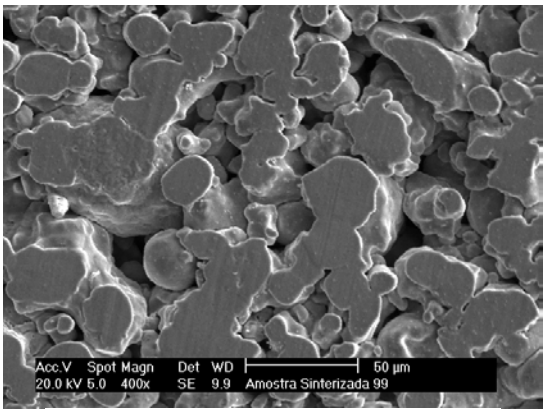
3. RESULTS AND DISCUSSION

During experimental procedures with unalloyed iron sintered in plasma atmosphere, some interesting phenomena took place with the samples due to different parameters involved in the process. For example, the temperature ranged from 900 to 1100ºC; Ton also ranged from 60 to 145 μs; pulse voltage varied from 400 to 700 V; and finally gas pressure was adjusted by consequence about these parameters. As will be shown in the following the results were relevant because they have presented different aspects when compared with conventional way to process unalloyed iron.

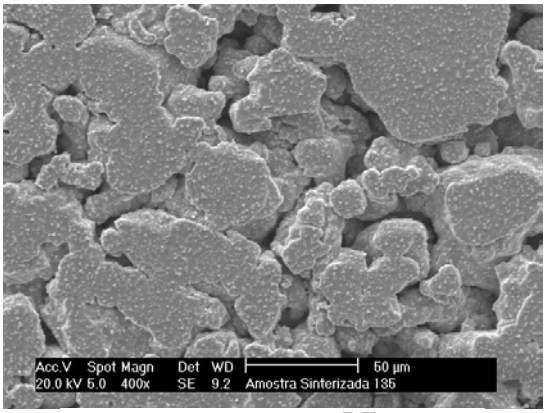
3.1 Samples sintered on the furnace plasma geometry

Micrographs shown in Figure 3 refer to samples sintered in a plasma atmosphere by using anode with metallic protector geometry at conditions 1, 2 and 3, respectively, to Figures 3(a), 3(b) and 3(c) as illustrated in Table 1. The unalloyed samples sintered in this geometry presented satisfactory results as described by Lourenço [15]. However, when some samples were sintered in the conditions cited on Table 1, they have presented interesting physical aspects. Evidently, the viability about the sintering process in this geometry was not committed. The samples sintered in the conditions 1, 2 e 3 presented depositions of metal impurities as shown in Figures 3(a), 3(b) and 3(c). The chemical analysis done on the sample surface indicated that elements like Mn, S e Si were present near glow discharge. This effect was observed to three levels of temperature 900, 1000 and mainly 1100ºC presenting large quantity. These elements are found in AISI 1020 materials with significant quantity in their grain boundaries This steel grade has been used to build the electrode

geometries to sinter the samples in plasma atmosphere. In this geometry, anode with metallic protector, the samples are heated just by radiation coming from cathode because they are protected by metallic shield as shown in Figure 2(a). Thus, the ions and neutral atoms of gas mixture are accelerated towards cathode extracting elements, such as Fe, Mn, S and Si and others that constitute these materials. As the diffusivity of these elements in grain boundaries is pretty high, then the concentration of them on the sample surface is not worthless. The samples put out in this geometry have lower temperature and as a result, the vapor pressure also is low, facilitating the deposition these elements. Impurities like manganese have vapor pressure about 20 Pa (0,15 Torr) at 1100ºC and sulphur with value higher than manganese around 14 Pa (0,10 Torr) at 150 ºC tend to evaporate from high to low temperature regions where the samples are placed. Micrographs presented in Figure 3 showed that the amount of these elements is proportional to temperature of sintering process, mainly manganese and suphur. At 900ºC, the sample surface have low roughness and low amount of these impurities was detected. At 1000ºC and much more at 1100ºC, the presence of small particles on the samples surface were observed with significant increase of manganese and sulphur peaks. The chemical analysis done just in a small particle placed in a sample processed at 1100ºC, as shown in Figure 4, has revealed expressive high manganese and sulphur peaks when compared with unalloyed iron peak. Probably, this effect indicates these particles are formed by manganese sulfide (MnS).



(a)



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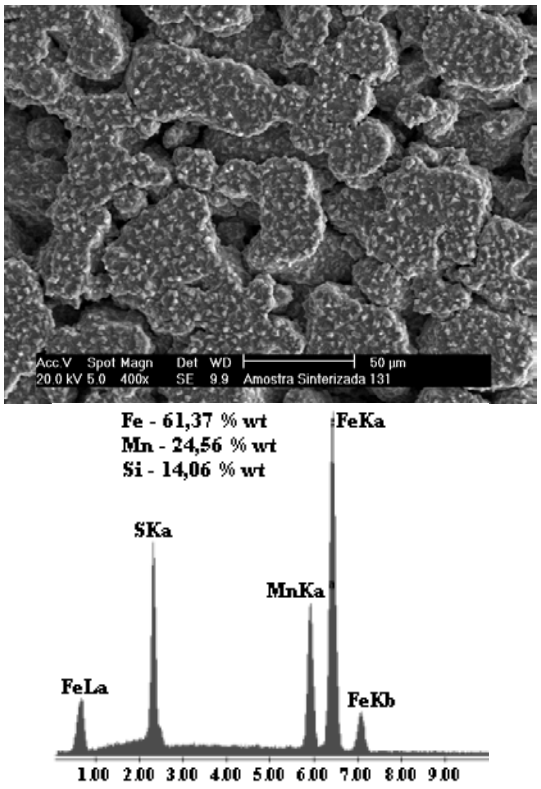


(c)

Figure 3 - Micrographs of surface samples sintered on the anode with metallic protector geometry at 900ºC (a); 1000°C (b); and 1100°C (c).

3.2 Bulk investigation

Micrographs of the unalloyed iron sample sintered in plasma atmosphere at 950ºC for 20 minutes (a) and the same one that was reheated again to 950ºC for 30 minutes, using the same conditions as before (b) are presented in Figure 5. The images were carried out in the same region in order to follow the ferritic microstructure that was sintered in the austenitic phase. The experiment was done by marking an indentation after the first metallographic preparation. Micrographs of the unalloyed iron sintered in plasma atmosphere at 850ºC, Figure 5(c), and another one at 740ºC, Figure 5(d), to characterize the microstructure in the ferritic phase after holding for 45 minutes. The conditions to this study are shown in Table 2. The micrographs processed in the austenitic field (a) and (b) have relevant differences as compared with those sintered in ferritic phase (c) and (d).

Table 1 - Plasma sintering parameters using furnace plasma geometry

	Voltage (V)	T (ºC)	t_{on} (µs)	Pressure (Pa/Torr)
Condition 1	400±10	900	110	2400 / 18
Condition 2	700±10	1000	110	760 / 5,7
Condition 3	700±10	1100	140	733 / 5,5

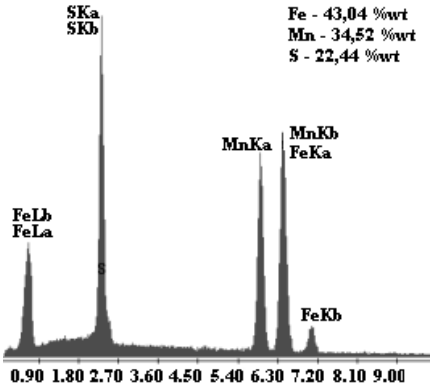
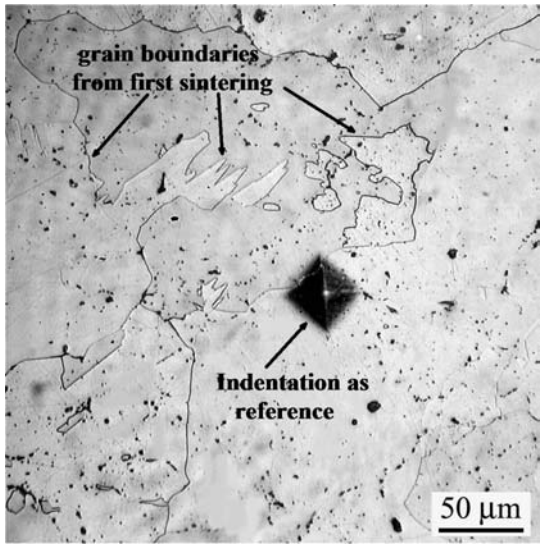


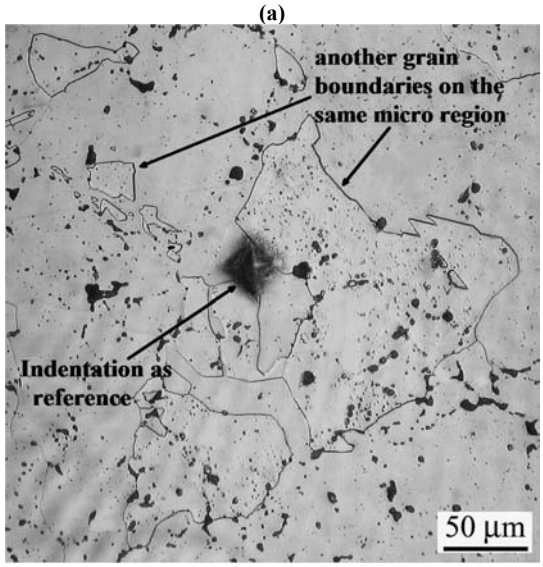
Figure 4 - Chemistry analysis done in a small particle placed in a sample surface processed at 1100ºC.

Table 2: Plasma sintering parameters using confined anode-cathode geometry

	Voltage (V)	T (ºC)	t_{on} (µs)	Pressure (Pa/Torr)
Condition 1	600±10	950 (first)	145	533 / 4,0
Condition 2	600±10	950 (second)	145	533 / 4,0
Condition 3	600±10	850	100	533 / 4,0
Condition 4	600±10	740	60	533 / 4,0



(a)



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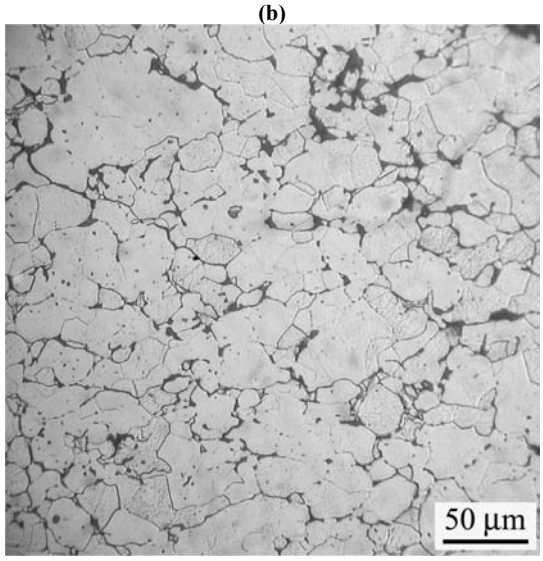
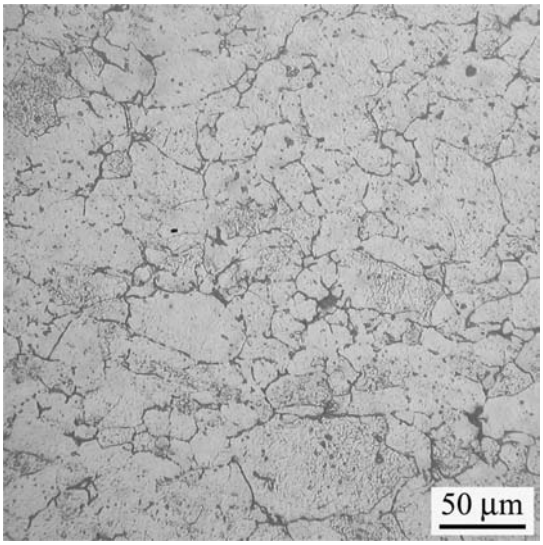


(c)



(d)

Figure 5 - Micrographs of samples sintered on anode without metallic protector: at 950ºC for 20 minutes (a); at 950ºC for 30 minutes (b); at 850ºC for 45 minutes (c); and at 740ºC for 45 minutes (d).

The difference between the micrographs of the samples sintered in the austenitic phase was expressive in terms of size, characteristic and mobility of the grains. On the other hand those processed in the ferritic phase presented small and equiaxed grains like the samples sintered in resistance furnace as shown in the micrograph of Figure 6. Several authors tried to explain such effects but without any conclusive explanation.

The first theory discussed by Batista [2] and Brunatto [16] explained that the large grains are attributed to phonons due to ions bombardment from cathode electrode, promoting shock waves into the crystalline reticulate. These ions can reach the target with energy around 60 to 90 eV as discussed by Budtz-Jorgensen [17] and Peter [18]. According to Chapman [8] the plasma effects interact just in the sample surface measuring some atomic layers by being impossible to transform into the bulk like images shown in Figures 5(a) and 5(b). The theory about phonons is discarded because during sintering in anode with metallic protector without any kind of bombardment, the grains went on growing.

Lourenço [15] claimed that some external potential must happenduring plasma sintering in the austenitic phase to contribute for such microstructural evolution, presented here as the second hypothesis. As discussed by Tsurekawa [19] there are different external influence to interfere in the size and boundary grain mobility as electrical field, ultra sonic vibration, solute concentration and magnetic field. Among these, only the magnetic field acts during plasma sintering owing to current passing through the cathode and grounded anode generating a magnetic field in line with a Biot-Sarvat law dependence. Indeed, according to Choi [20] the austenitic phase is more magnetically susceptible than ferritic phase, that is, it is less unstable in the presence of the magnetic field. The sequence of micrographs (a) and (b) of Figure 5, in the same place of the sample with significant changes, denotes that new grains took place in a short time (between 20 and 30 minutes) contributing to affirm that some event happened during plasma sintering, being probably a magnetic field. Austenitic/ferritic phase transformation probably did not contribute to such microstructural changes because grain nucleation is not so intensive because the plasma was turned off during the cooling of the samples. In accordance with Watanabe [21] the influence in phase transformation is more significant in magnetic field presence. In fact, some samples were cooled in the presence of plasma atmosphere and thus, presented the same characteristics. At high temperature the boundary grains are able to migrate under some external influence consuming grains and expanding other ones. Then its surface specific will be decreased when they are magnetically oriented in accordance with susceptibility propriety as discussed by Molodov [22] and Chen [23]. It is not sure whether these grain boundaries in micrographs in Figs 5(a) and 5(b) are the same. On the other hand, it is easy to realize the relevant microstructural changes, probably influenced by the magnetic field during plasma sintering and only in the austenitic phase. This subject has been also treated by Sheikh-Ali et al [24] when they performed an annealing under magnetic field in zinc observing the occurrence of intensive boundary migration after 5 minutes while there was not mobility in other samples processed in normal conditions (resistive furnace). Tsurekawa [25] sintered in a magnetic field iron carbonyl at above and below Curie temperature (770º) finding normal and equiaxed grains like these samples processed in a resistive furnace. Then the micrographs in Figure 5, whose samples were sintered below (c) and above Curie temperature (d) for 45 minutes, also presented normal and regular grains like those processed in a conventional system, as shown in micrograph of Figure 6. As discussed by Choi et al [20] the ferritic phase loses its magnetization above Curie temperature but it continues stable until it transforms in austenitic phase at 912ºC. Thus, the results in the ferritic phase are in agreement to the results published earlier. However, the assumption above described is not conclusive to explain de origin about these large grains.

Another assumption about these larger grains was recently discussed by Pavanati [26]. He argued through the premise that grains were not revealed using nitric acid (2% nital) as chemistry reagent because it becomes inefficient without impurities in the unalloyed iron samples. These impurities, mainly found at the grain boundaries, were eliminated due to plasma atmosphere compound with argon and hydrogen. He supposed that the presence of hydrogen could lead the elimination of these impurities placed at some grain boundaries. Therefore, the grains with lower level of impurities have higher mobility, and initiate abnormal growth like these shown in Figures 5(a) and 5(b). Furthermore, he also reported about the influence of austenitic/ferritic phase transformation. As the austenitic/ferritic phase transformation occurs by means of nucleation and growth, he claimed that large grains were formed in the absence of plasma, when the plasma was turned off. It is supposed that grain growth occurs in the austenitic phase and after austenitic/ferritic phase transformation, the grains become small but

larger than ferritic phase processed in resistance furnace. This effect about grain boundaries happens just with unalloyed iron, while that alloyed iron sintered in plasma did not exhibit abnormally grown grains

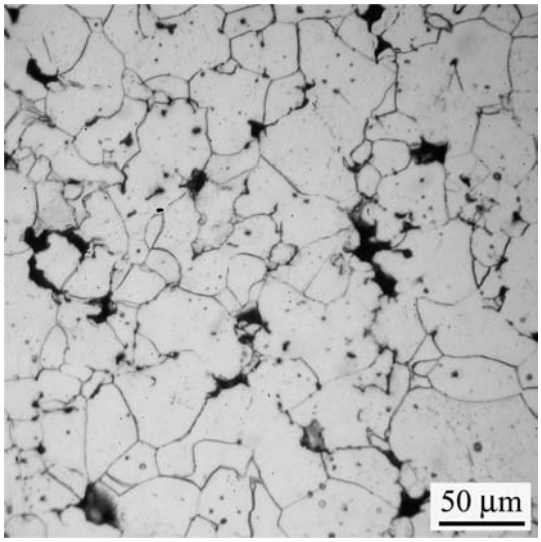


Figure 6 - Micrographs of sample sintered in resistance furnace at 1100ºC.

4. CONCLUSIONS

- The samples sintered in plasma atmosphere presented satisfactory results to any electrode geometry used, regardless of the effects discussed in this work;
- Some samples presented on their outer side deposition, such as manganese and sulphur found out in the materials of electrode geometries extracted from cathode.
- The characteristic microstructure of unalloyed iron sintered in a plasma atmosphere presented large and irregular grains that differed from those processed in a resistive furnace.
- Three theories about the origin of these coarse grains were presented but without any conclusive explanation.

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