The influence of DC pulse current pattern on the different materials properties of samples obtained by spark plasma sintering

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Abstract. Spark plasma sintering (SPS) also known as pulsed electric current sintering (PECS) or field-assisted sintering technique (FAST), belongs to a class of powder metallurgy techniques. The fundamental of this technique is appeared over last 50 years ago, but modern SPS technique is appeared within the last 20 years depending on this principle. The variation of this factor is so extensive for each material that only a few papers have been devoted to this research. This review paper summarizes the latest research findings with respect to experimental procedures, densification behaviors, microstructural characteristics, and mechanical properties of various materials synthesized using SPS, mainly highlighting the influence of the electric DC pulse current on the relative density, mechanical and tribological properties of various materials during sintering.
Keywords: Spark plasma Sintering (SPS), DC pulse current pattern (t_{on}:t_{off}).

1. Introduction

Spark Plasma Sintering (SPS) is one of the most advanced nanopowder consolidation methods, which applies a uniaxial pressure and heat between the raw powder and the matrix using high heating rates (from 100 to 1000 °C/min). The heat required for sintering is generally generated by Joule heating when a determined pulsed direct current passes through the graphite matrix, in addition, part of the heat is generated thanks to the electrical discharges and the high temperature plasma inside the nanopowder. Plasma is considered to be generated by spark discharges in the gap or at the point of contact between the material particles when the pulse current is applied. The temperature in the spark discharge zones is in the order of about 1000 °C, which leads to local melting and/or evaporation of the raw material in very short periods of time. This leads the formation of a neck in the contact zones between the powder particles due to the mass transfer process [1–8]. For this reason, the study of the influence of the pulse current form on the mechanical properties of sintered samples is a very interesting field of research, which requires a lot of attention due to its practical application. Unfortunately, only few research groups are worked in this field, and they established some dependence for the sintering of specific materials under certain conditions. For instance, Xie et al. [9], showed that the frequency is a factor that influences on the homogenous temperature distribution through sintering raw powder, but it has not influence on the sintered sample material properties. On the other hand, a pulsed DC current during sintering can generate very high heating and cooling rates, which enhance the diffusion mechanism of the raw material, which in turn permit the grain growth control process, and leads to a combined improvement of different material properties that include high-temperature strength and good mechanical properties such as density, toughness, flexural strength and good surface stability at the high-temperature environment [10].

2. Effect of pulse current pattern

2.1 Characteristic parameters of electric pulse currents

The type of electrical current used is one of the main features in Spark Plasma Sintering (SPS) techniques. Depending on the SPS machine and its manufacturer the SPS processing system can apply one of three different types of electrical current such as alternating current (AC), direct current (DC), and pulsed DC. Fig.1 shows the forms of previously listed currents (Fig.1a, 1b, 1c) with the inclusion of a peculiar form (Fig.1d) [11]. As the Fig.1a shows, DC flows at a constant rate in one direction and it is completely characterized by the current intensity (*I*). When the intensity of the DC does not change over time this current is named Steady Current. Unlike DC, the AC (Fig.1b) oscillates and

shifts direction at a fixed frequency, and it is characterized by the maximum current intensity (I_{max}) and frequency (ω). The usual waveform of AC used in SPS processing is a sine wave. Fig.1c shows the pulsed DC form, in which additional parameters are used for its complete description, such as pulse duration (t_{pulse}), on- and off-time (t_{on} and t_{off}, respectively), and maximum current (I_{max}). Finally, Fig.1d schematically shows an electric current, in which the electric current is applied in two stages. In the first one, there is a pulsed electric current while, in the second stage, a Steady Current is followed. The first stage is well defined by the maximum current I_{max}, the on-time (t_{on}) and the off-time (t_{off}), while the second stage is described by the current intensity I. In addition to these parameters, the stages relative duration t_I and t_{II}, should be given.
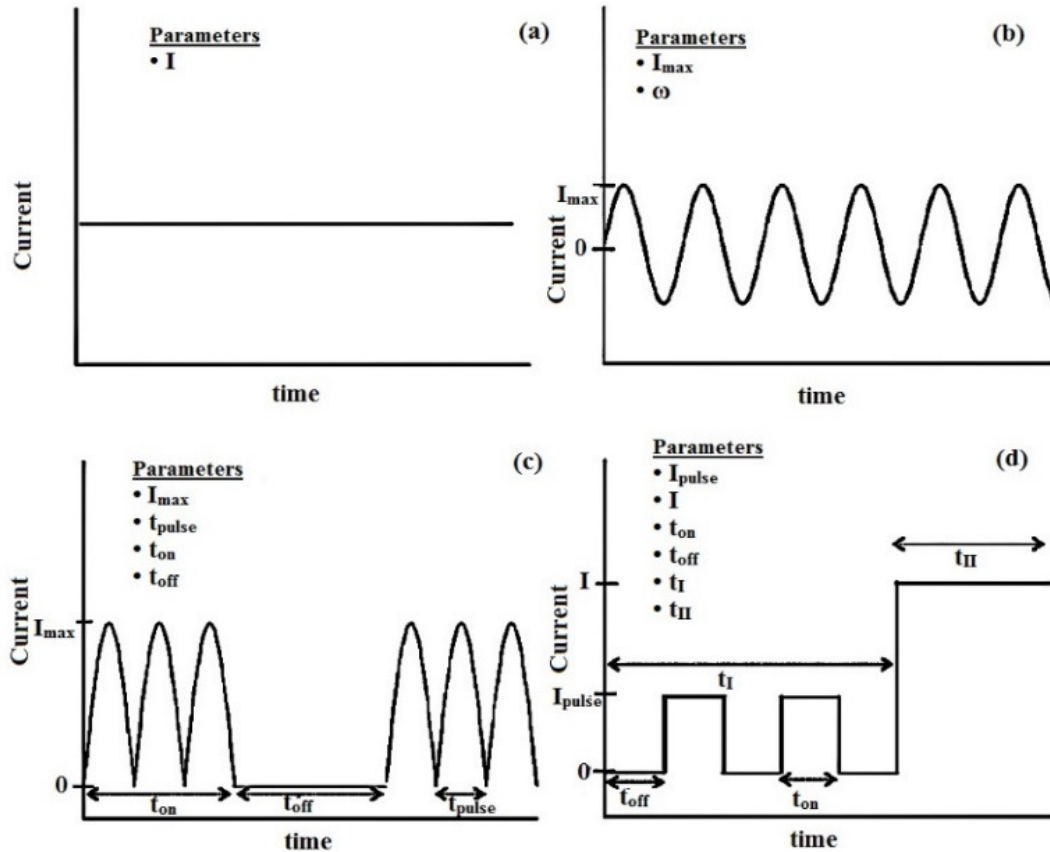

Fig.1. Typical electric current waveforms imposed in the SPS process: (a) DC, (b) AC, (c) pulsed DC, (d) two stages current (pulsed DC+DC) [11].

These types of electrical currents could be applied in SPS processing, but the most widely used is pulsed DC, which is created by a pulse generator that can control the ON-OFF pulse parameters, thanks to its application providing a high heating rate in the contact areas between adjacent micro and nanoparticles. It is important to indicate that most works on SPS are published without a complete description and an exact definition of the parameters necessary to correctly characterize the applied electric current. So, the current forms presented in Fig.1 should not be considered as unique since different combinations of current forms and/or pulses having different shape may have been applied in published works without explicitly reporting the corresponding details.

3. Influence of current pulses pattern on the sample properties

Dang et al. [12] investigated the influence of various current pulses pattern (t_{on}:t_{off}) of 12:2, 2:6 (300Hz) pulse generator and 40:10, 10:20 (16 Hz) inverter. For both cases, the sintering temperature

was in the range from 1100 °C to 1400 °C during 5 minutes and at a uniaxial pressure 30 MPa in a vacuum during SPS process of alumina (Al_2O_3). The results of this study show that the current pulses pattern and the frequency do not influence on the densification process. In other work, Lagos et al. [13] applied a steady direct current density (4 and 5 kA/cm^2) during the SPS in order to obtain samples of WC with 6 and 10 wt% of Co in 500 ms. These parameters conducted to a very fast sintering that permits carry out the process without any protective atmosphere and inhibits the grain growth, which increase the material hardness.

Chakraborty et al. [14] also studied the influence of pulse current pattern on the sintered material density by SPS. In their work, various DC pulses current pattern from (t_{on}:t_{off}) (10:1, 10:5, 10:10, 10:15, 50:5, 50:25, 50:50, 100:5, 100;50, 100:100) were applied on ZrB_2 (conducting ceramic) under argon atmosphere and a pressure of 35MPa in order to reach the sintering temperature of 2100 °C with a holding time of 15 min. The authors reported that the maximum relative density was achieved (98.65%, measured by the Archimedes method) was achieved in DC pulse current, where the duration of the ON and OFF pulse was 50 ms and 5 ms, respectively. Moreover, the mechanical properties of as sintered ZrB_2 samples were Vickers hardness – 16.64 GPa, Fracture toughness – 4.69 MPa·m$^{0.5}$. However, the relative density of the ZrB_2 ceramic obtained by constant DC was obviously lower, Table 1.

Table 1. Relative density (RD), hardness (HV) and fracture toughness (K_{IC}) of ZrB_2 prepared under various pulse current pattern of SPS at 2100 °C for 15 min dwell time [14]

Sample №	Pulse current (t_{on}:t_{off}) (ms)	Relative Density (%)	Hardness (GPa)		K_{IC} (MPa·m$^{0.5}$)	
			1 kgf	500 gf	1 kgf	500 gf
1	Direct current	98.58	15.69±1.33	17.05±1.40	4.02±0.32	2.98±0.31
2	10:1	97.41	15.32±1.29	17.21±1.29	4.40±0.37	2.57±0.30
3	10:5	98.25	16.14±1.42	17.31±1.28	3.40±0.35	2.15±0.33
4	10:10	98.30	15.88±1.34	17.20±1.32	2.77±0.39	3.35±0.29
5	10:15	96.12	15.39±1.22	15.71±1.33	2.75±0.41	3.08±0.31
6	50:5	98.65	16.64±1.48	17.83±1.42	4.69±0.43	3.92±0.33
7	50:25	97.91	16.50±1.38	17.46±1.44	3.52±0.39	2.57±0.30
8	50:50	98.05	16.09±1.29	17.14±1.40	3.43±0.37	2.24±0.28
9	100:5	98.03	16.02±1.31	17.67±1.35	2.98±0.32	2.89±0.25
10	100:50	97.87	16.25±1.32	17.64±1.33	3.80±0.38	2.16±0.29
11	100:100	98.10	16.29±1.30	17.54±1.34	4.31±0.34	3.67±0.30

Maniere et al. [15] studied the influence of DC pulses current pattern (t_{on}:t_{off}) (12:2, 9:5, and 7:7) on the current intensity used to densification both conducting manganese (Mn) and insulating alumina (Al_2O_3) powders. The authors indicated that a reduction in the pulse on-time required a higher intensity in order to achieve the expected temperature, especially for manganese. Their results show that DC pulses current on sintering of conducting powdered materials and the pulse frequency has no obvious influence on both conducting and insulating materials (Fig.2 and 3).

Bernardo et al. [16] studied the influence of the DC electric current patterns (AC and DC) on the microstructure of bulk $BiFeO_3$ and Ti-doped $BiFeO_3$. The results indicated that DC sintering could induce heterogeneous microstructures due to current localization and thermal gradients inside the specimens. In contrast, these macroscopic defects were avoided in the AC sintering process. The AC processing led to symmetrical and highly homogeneous microstructures within the entire specimen.

Lalet et al. [17] researched the relative density of a carbon fiber-reinforced aluminum matrix (Al-CF) composite fabricated by SPS in various pulse current pattern (t_{on}:t_{off}) (24:1, 12:2, 6:4, 3:3), pressure at 50 MPa, the heating rate of 40 °C/min at maximum temperature 600 °C, dwell time was 10 min for samples with 80 µm CF, 40 min for samples 80 and 500 µm CF and 80 min for samples with 500 µm CF. The samples of powders were prepared by mixing 50 vol% of carbon fibers (CF), where the first type was 80 µm long CF and the second one was 500 µm long CF. The results of

relative density are shown in Fig.4. The Al-CF samples were annealed at 650 °C for 6 h under argon atmosphere and the thermal expansion behaviors.
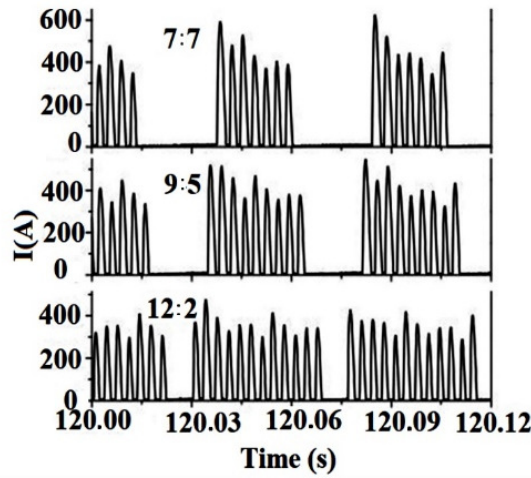

Fig.2. Effect of pulses current pattern – the current pulse intensity at various current pattern (12:2, 9:5 and 7:7) [15].
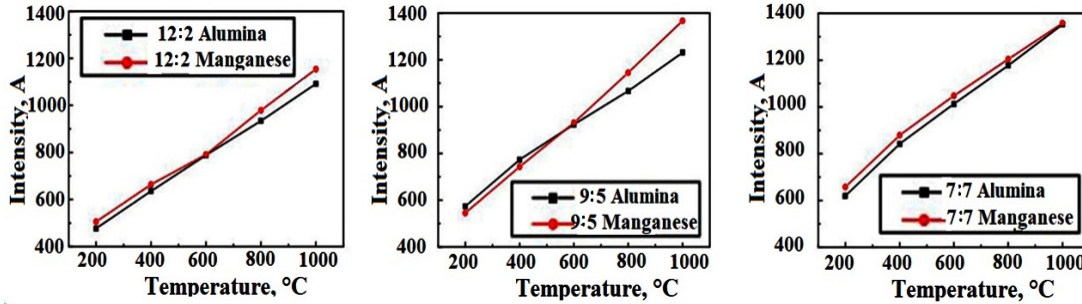

Fig.3. Effect of pulses current pattern – I_{max} measured in various pulse current pattern and temperatures [15].

Tamburini et al. [18] studied the influence of a DC pulsing current on the reactivity between Si wafer and Mo foils. They are used for this study pulse current pattern (t_{on}:t_{off}) (2:8, 8:2, 12:2 and 7:7), temperature at 1070, 1170 and 1270 °C. The effect of pulsing on the solid-state reactivity rather between two flat foils (Mo and Si). Their results show that the direction of current and pulse current pattern do not influence on the thickness of the product layer (Fig.5) and the grain growth of products is formed at 1070, 1170 , 1270 °C and is independent on the pulse current pattern.
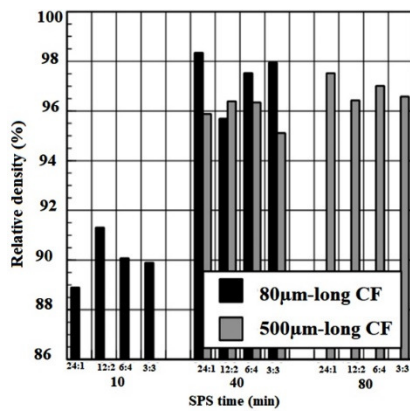

Fig.4. The relative densities of Al-CF 50 vol% composites fabricated by SPS with various pulse current patterns [17].
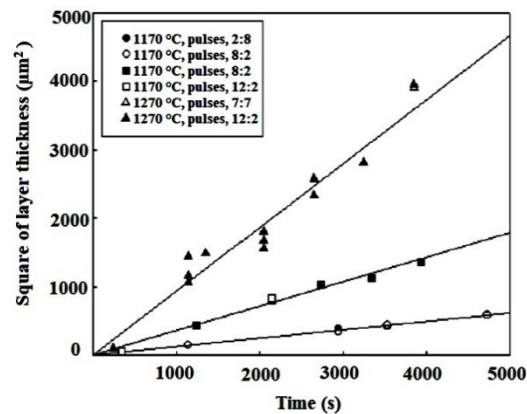
Fig.5. The growth of $MoSi_2$ layer in the SPS at different temperatures and under different pulse patterns [18].

In the scientific literature, Sairam et al. [19] studied the influence of pulse current parameters on the consolidation and mechanical properties of boron carbide (B$_4$C). In this study, samples were sintered with DC pulse current pattern 5:5 (t_{on}:t_{off}), a uniaxial pressure of 50 MPa, and the sintering temperature was in the range from 1100 °C to 1800 °C. The theoretical density of boron carbide samples was obtained at a temperature 1800 °C and holding time 15 minutes, which is a lower temperature compared to conventional sintering methods (2000 °C and 12 minutes of exposure time), in which a relative density of 95% of the theoretical one is achieved.

Analysis of the sintered material showed that the grain size was in the range from 2 to 6 µm. This means that the SPS process itself effectively inhibits grain growth, which leads to an increase in the hardness of sintered samples from 0.2 GPa to 37.2 GPa, when the density of the sintered sample increases from 65% to almost the theoretical value. Near the theoretical density, B$_4$C samples have a fracture toughness of 2.8 MPa·m$^{0.5}$ and this value increases with decreasing sample density to a maximum value of 5.8 MPa·m$^{0.5}$, which corresponds to a relative density of 91%. Moreover, the elastic modulus increases with increasing density and reaches a maximum value of 570 GPa at 100% of the relative density of boron carbide. The research data are shown in Table 2 and Table 3.

Table 2. DC pulse parameters and mechanical properties of sintered boron carbide [19]

T, (°C)	dwell, (min)	P, (MPa)	DC pulse parameters, (ms)	Relative density, (%)	HV, (GPa)	E, (GPa)	K_{IC}, (MPa·m$^{0.5}$)
1100	15	50	5:5	65	0.2	19	–
1200	15	50	5:5	65.8	0.2	39	–
1300	15	50	5:5	66.5	0.4	45	–
1400	15	50	5:5	70.5	0.9	74	–
1500	15	50	5:5	71.8	2.4	105	–
1600	15	50	5:5	81.8	6.7	138	–
1700	15	50	5:5	94.4	32	418	4.3
1800	5	50	5:5	91	25.7	403	5.8
1800	10	50	5:5	96	33.3	447	3.1
1800	15	50	5:5	100	37.2	570	2.8

T – sintering Temperature; dwell – holding time; P – uniaxial pressure; HV – Vickers Hardness; E – modulus of elasticity; K_{IC} – fracture toughness.

Moreover, Montes et al. [20] demonstrated that the DC mode was advantageous for the consolidation of pure metals (e.g Fe, Ti) at their lab scale. The influence of pulse current pattern on the sintered material density was investigated by Tang et al. [21]. They studied the consolidation of oxidized tungsten carbides powders by SPS using different DC pulses current patterns (constant DC at 1600 °C and pulse DC at 1820 °C), heating rate at 200 °C/min and holding time at 10 and 6 min, respectively. Their results show that the DC pulses current patterns is the only way to obtain a nearly full density of severely oxidized WC ceramic and improvement of the toughness and hardness.

Table 3. The Effect of pulse frequency on densification of boron carbide [19]

T, (°C)	dwell, (min)	P, (MPa)	DC pulse parameters, (ms)	Relative density, (%)
1600	15	50	100:1	81
1600	15	50	50:1	81.5
1600	15	50	10:1	82.7
1600	15	50	5:5	81.8

T – sintering Temperature; dwell – holding time; P – uniaxial pressure.

Zuo et al. [22] studied the influence of current parameters on the density of a sintered Si$_3$N$_4$-TiN. For the work, they are used selected continuous electric current (Continuous DC, 0 Hz) power and pulsed electric current power (Pulsed DC, 10:5), a temperature 1750 °C with a heating rate

100 °C/min and a holding time of 10 minutes, at a pressure 35 MPa. As a result, it was found that all composite samples reached a high density at the same heating cycle, but with a strikingly different degree of transformation of the α-β phases and the final microstructure. Moreover, it has been proved that the liquid phase formation temperatures and particle rearrangement depend on the size and content of TiN particles, this confirms the hypothesis of local heating and activation of the electric wetting mechanism by liquid sintering of ceramics based on Si_3N_4.

Locci et al. [23] investigated the effect of current pattern during the spark plasma sintering (SPS) of electrically conductive aluminum powders. Their results showed when the pulse current is passing through the sintering powder the final density of sample is about 5% higher than conventional sintering sample. Sun et al. [24] investigated the effect of DC pulse current parameters on the samples $[Fe_{0.8}Co_{0.2}B_{0.05}Si_{0.2}]_{96}Nb_4$. They are used in this paper temperature at 520 °C, pressure at 600 MPa, various DC pulse current pattern (t_{on}:t_{off}) (2:9; 2:2 and 12:2). Their results show that the high mechanical properties have achieved at pulse current 2:9. During sintering the smaller pulse current pattern 2:9 pattern can make the particle boundary regions to obtain a high energy to consolidate the Fe-based amorphous alloy powders and moreover, the larger cooling time can play a significant role on avoiding crystallization of amorphous alloy in sintering process.

4. Conclusion

SPS is the most effective method for consolidation and mechanical and physical properties of metal and ceramic materials, including composites and nanocomposites. The advantages in SPS process, the DC pulse current heating can generate high heating and cooling rates, enhance diffusion mechanism, controlling the grain growth process, high reproduction, easy process control on the SPS apparatus etc., allow to achieve increased physical and mechanical properties of various composites. However, during the analysis of literature in this field very few papers were found. In SPS processing, the influence of DC pulse current parameters (DC, AC, pulsed DC and two stages current (pulsed DC+DC)) has achieved high density at the same heating cycle, but the materials differ in the final microstructure and different phase transformations of composites.

Acknowledgments

5. References

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