Can the use of pulsed direct current induce oscillation in the applied pressure during spark plasma sintering?

David Salamon, Mirva Eriksson, Mats Nygren and Zhijian Shen

Department of Materials and Environmental Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden
E-mail: mirva.eriksson@mmk.su.se

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Abstract
The spark plasma sintering (SPS) process is known for its rapid densification of metals and ceramics. The mechanism behind this rapid densification has been discussed during the last few decades and is yet uncertain. During our SPS experiments we noticed oscillations in the applied pressure, related to a change in electric current. In this study, we investigated the effect of pulsed electrical current on the applied mechanical pressure and related changes in temperature. We eliminated the effect of sample shrinkage in the SPS setup and used a transparent quartz die allowing direct observation of the sample. We found that the use of pulsed direct electric current in our apparatus induces pressure oscillations with the amplitude depending on the current density. While sintering Ti samples we observed temperature oscillations resulting from pressure oscillations, which we attribute to magnetic forces generated within the SPS apparatus. The described current–pressure–temperature relations might increase understanding of the SPS process.

Keywords: sintering, thermomechanical processing, SPS

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1. Introduction
Spark plasma sintering (SPS) has attracted increasing attention over the last decade. Technically, SPS is similar to conventional hot pressing, in which a sample is loaded inside a graphite die and a uniaxial pressure is applied during sintering. A schematic of an SPS setup is given in several of the references cited below. In a hot-pressing apparatus, furnace elements act as the heating source, whereas in SPS a pulsed direct current passes through the electrically conducting pressure die (sometimes also through the sample), thereby heating the sample. This enables very high heating rates (up to 1000 °C min⁻¹), allowing completion of the sintering cycle within a few minutes instead of hours, as required by a conventional hot press.

The benefit of SPS is claimed to be the decrease in the required sintering temperature. However, usually the temperature is measured on the surface of the die by a pyrometer or by a thermocouple inserted into the die. Both these methods are inaccurate, and the difference between the measured and actual temperatures depends on several factors such as the electrical and thermal properties of the sample; the size, shape and material of the die; the heating rate and pressure. Temperature gradients have been measured and modelled [1, 2]. The reported results demonstrate that the main benefit of the reduced temperature results from the increased temperature gradient. A current often has a positive effect on sintering, and electric current and an electric field improve sintering and reactions in applications other than SPS [3–6]. Electric current passing through the sintered sample can also improve the homogeneity of the microstructure of the sintered sample [7]. However, it is difficult to distinguish the effects of electric current and temperature during SPS experiments. The SPS mechanism
Figure 1. Experimental observation that a variation in current gives rise to a variation in the applied force (pressure). (a) The marked ripples in current is caused by an adjustment of the position of the pyrometer, which in turn gives rise to oscillations in the applied pressure. (b) When the current is manually switched off, its value typically increases for a few seconds before dropping to zero. This spike is associated with an increase in pressure (applied force). appears to be different for electrically insulating and conductive samples. Tomino et al calculated the current passing through an insulating Al₂O₃ sample [8] and found that it was close to zero, implying that no sparking occurs. Some conductive materials have shown sparking, and even formation of a plasma, but only at the onset of sintering and only at pressures below 20 MPa [9]. A recent in situ study showed no evidence of plasma in the SPS process [10]. The sintering behaviour does not appear to be affected by the electric pulse frequency [10, 11].

The motivation for this work is connected with our observations that a sudden change in the current during SPS experiments alters the applied pressure, as shown in figure 1. The ripple in the current in figure 1(a) is caused by an adjustment of the position of the pyrometer, which induces oscillations in the applied pressure. When the current is manually switched off in our SPS unit, the current typically increases for a few seconds before dropping to zero, as shown in figure 1(b). In this study, we have investigated the relation between the current and pressure (applied force), and how various on : off dc pulse settings affect the applied pressure.

2. Experimental procedure

We used two different SPS units fabricated by SPS Syntex Inc., Japan: Dr Sinter SPS 2050 and SPS-5.40MK-VI. In these units, the pulsed direct current is regulated by on : off settings that in turn determine the number of on and off periods of the direct current. Each pulse lasts 3.3 ms and has a 12 : 2 (39.6 : 6.6 ms) on : off ratio, as recommended by the manufacturer. The on : off settings 12 : 2, 10 : 9, 36 : 2 and 30 : 9 were used in the experiments described below. The on : off sequence was set before the start of each SPS run. During the experiments, the values of temperature, applied force, electric current, voltage and shrinkage were usually recorded in intervals of 1 s, but 0.1 and 6 s intervals were also used. Temperatures above 600°C were measured using an optical pyrometer, which was focused on a small hole in the surface of the graphite die or on the sample surface. The pressure in this SPS unit is applied by a hydraulic press with a moving lower ram. According to the manufacturer, the pressure in the Dr Sinter SPS 2050 unit is measured by a load cell with an accuracy of ±0.06 kN and a sampling rate of ∼15 times s⁻¹. All sintering experiments were carried out under low vacuum (5 Pa) with continuously running vacuum pumps. The power was regulated either manually or automatically, using the temperature feedback. The manually set output power did not vary with the on : off setting. The time evolution of the experiments with manually regulated power is described in table 1. The applied force (pressure) versus time program was always run in the manual mode and the hydraulic pressure was fixed at the beginning of the process. However, thermal expansion of the die and sample gave rise to an increase in the applied pressure during heating. The experiments presented below were performed in the Dr Sinter SPS 2050 unit unless stated otherwise.

We used two basic designs for the SPS die, which are shown in figure 2. In the ‘classical’ design (figure 2(a)), all parts are made from conductive graphite. The transparent SPS die design (figure 2(b)) included a quartz cylinder, which is not electrically conductive and therefore forces all current to pass through the sample. The quartz cylinder is optically transparent, which allows the observation of colour changes induced by the variation of current and pressure. The die parts are shown in figure 2(a).
Table 1. Steps of the manual regulation of power during the heating of sintering dies loaded with dense sialon ceramic blocks in two SPS units.

| Step | Dr Sinter 2050 SPS | SPS-5.40MK-VI |
|------|-------------------|---------------|
|      | Period of current | Power (%)      | Applied pressure |
|      | increase (min)    | (%)            | (kN)            |
| 1    | 0–0.5             | 7              | 36 (11.3)       |
| 2    | 2–2.5             | 10             | 36 (11.3)       |
| 3    | 4–4.5             | 15             | No regulation   |
| 4    | 10–10.5           | 20             | No regulation   |
| 5    | 15–15.5           | 25             | No regulation   |
| 6    | 20                | 0              | 0 MPa           |
|      | 0–0.3             | 2              | 36 (11.3)       |
|      | 2–2.3             | 4              | No regulation   |
|      | 4–4.3             | 6              | No regulation   |
|      | 10–10.3           | 8              | No regulation   |
|      | 10–1.3            | 10             | No regulation   |

Dense sialon ceramic blocks with a height of 6.5 or 26 mm were inserted into the graphite sintering die (inner diameter 20 mm). The blocks were annealed inside the die at 1400 °C, with a dwell time of 5 min and a pressure of 40 MPa in order to avoid deformation during subsequent experiments. After the annealing, the loaded graphite die remained inside the SPS apparatus during the entire set of experiments with the manual regulation of power.

The quartz die forces all pulsed current to flow through a conductive sample. Two grams of titanium powder (325 mesh) was pressed at 50 MPa to form pellets with diameter 12 mm and height 3.8 mm. These pellets were loaded into the sintering die (figure 2(b), diameter 12 mm) and a minimal mechanical pressure was applied. The sintering temperature was 800 °C and the dwell time was 2 min. The pyrometer was focused on the sample inside the quartz tube. The 12 : 2 and 10 : 9 on : off electric pulse settings were used for the SPS of titanium.

In another experiment, we used a conventional graphite die (containing a 6.5-mm-high presintered sialon specimen) and an on : off setting of 10 : 9. A pressure of 40 MPa was applied at room temperature. The temperature was then automatically raised to 600 °C within 4 min, and from this point onwards it was monitored and regulated using an optical pyrometer focused on the surface of the die. A heating rate of 200 °C min⁻¹ was used between 600 and 1400 °C and the holding time at 1400 °C was 5 min.

In another experiment we replaced the pressure die with a graphite punch 30 mm in diameter and 30 mm high, and applied the sintering conditions described in the previous paragraph.

3. Results

Data recorded during repeated and manually regulated SPS runs provided crucial evidence for the relation between current and pressure. Graphite dies loaded with dense sialon ceramic blocks were heated inside the Dr Sinter SPS 2050 chamber in five steps, using 7, 10, 15, 20 and 25% of the full power output and the pulse settings 12 : 2, 36 : 2, 30 : 9 and 10 : 9 (see table 1). The final temperature of the graphite die loaded with a short or high block (6.5 or 26 mm) was 1165–1176 or 1312–1337 °C, respectively, independent of the on : off setting. Figure 3(a) shows temperature profiles for various electric pulse settings. Note that 7 and 10% of the full power output were insufficient for reaching a temperature of 575 °C—the lowest temperature detectable with our pyrometer. Figure 3(b) shows the time evolution of current recorded every 1 s. It can be seen that at low input levels the different on : off settings yield almost the same current. However, the current decreases with increasing off time period.

The force recorded during the experiments whose temperature profiles are shown in figure 3 is plotted versus time in figure 4(a). During the first two steps, the pressure was allowed to increase owing to the thermal expansion of the pressure die, and at the end of step 2 it was manually adjusted.
Figure 4. Applied force as function of time during manually regulated SPS runs with various on : off settings. (a) Graphite die, sample height 26 mm. The white arrow indicates the time when the force was manually reduced (see text). Black arrows indicate peaks induced by an increase in the current due to a manual change in the input power. (b) Corresponding force traces recorded with different sampling intervals. The on : off setting is 12 : 2 in all cases.

to 36 MPa. No pressure adjustment took place during steps 3, 4 and 5. Note that the pressure oscillates for the 10 : 9 and 30 : 9 on : off settings, but not for the 12 : 2 on : off setting. The two black arrows indicate the moments when the input power was changed to 20 and 25%. The increase in current gives rise to a sudden increase in the applied force. Then, within a few seconds, the applied force stabilizes at a lower value for the 12 : 2 and 36 : 2 settings or continues oscillating around an average value for the 10 : 9 and 30 : 9 settings. The oscillation of the applied force is greatest for the 10 : 9 setting and is similar for the two studied sample heights (6.5 and 26 mm).

The amplitude of the pressure oscillations appeared to increase with the current. During the experiment with titanium powder, we did not observe pressure oscillations, but the current input was always below 200 A. However, we visually observed periodic oscillations of the temperature (colour) distribution, which were most prominent near the interface between the Ti powder and the punches, at the 10 : 9 setting, but not at the 12 : 2 setting.

The experiments with the manual regulation of power were performed in both SPS units using recording intervals of 0.1, 1 and 6 s. Figure 4(b) shows the force versus time plots for the different recording intervals using an on : off setting of 12 : 2 in the Dr Sinter SPS 2050 setup. Clear oscillations are seen for the 0.1 s recording interval but not for the 1 and 6 s recording intervals.

Figure 5 shows the applied force, temperature and current recorded every 6 s for the 26-mm-high sialon sample sintered with automatic power regulation and the 10 : 9 on : off setting. A heating rate of 200 °C min⁻¹ was used between 600 and 1400 °C and the holding time at 1400 °C was 5 min. The force versus time curve reveals that the thermal expansion of the die gives rise to a pressure increase. Regardless of the thermal expansion, the amplitude of the oscillating force increases with increasing current input. The pressure oscillations are barely noticeable at the beginning of the SPS run (approximately 120 s), which corresponds to a current of 300 A. The rapid increase in current owing to the use of a high heating rate (200 °C min⁻¹) enhanced the pressure oscillations. Their amplitude reached 0.7 kN during the dwell time (approximately 600 s), which corresponds to a current of 1410 A.

In one experiment the graphite die was replaced by a graphite punch with a 30 mm diameter and 30 mm height. The sintering conditions described in connection with figure 5 were applied to this punch. Pressure oscillations were observed (figure 6), and their amplitude increased with increasing current as in the previous experiment. Note that the current output was similar when using the sintering die (1600 A) and punch (1400 A), and thus the oscillating force is related to the SPS unit rather than the sample or sintering die.

Mechanical oscillations were also recorded in the second SPS unit in the case of manual regulation of power. The oscillations of the force with time at different on : off settings are shown in figure 6(b). Similarly to the results for the Dr Sinter SPS 2050 unit, the amplitude increases with increasing current and the frequency depends on the on : off setting.
confirms our previous observation shown in figure and the intensity of the applied current. This behaviour amplitude dependent on the on : off electric pulse sequence interferes with other forces. Punches vibrate with an mechanical pressure generated by the SPS hydraulic system current gives rise to pressure oscillations. The constant Our experiments demonstrate that the use of pulsed electric power, a sampling interval of 0.1 s and different on : off settings.

Figure 6. (a) Force versus time for a graphite punch and an on : off setting of 10 : 9, revealing a significant pressure oscillation (see text). (b) Force versus time plots recorded in the SPS-5.40MK-VI unit using a 6.5-mm-high sialon sample with manual regulation of the power, a sampling interval of 0.1 s and different on : off settings.

4. Discussion

Our experiments demonstrate that the use of pulsed electric current gives rise to pressure oscillations. The constant mechanical pressure generated by the SPS hydraulic system interferes with other forces. Punches vibrate with an amplitude dependent on the on : off electric pulse sequence and the intensity of the applied current. This behaviour confirms our previous observation shown in figure 1. Furthermore, in the case of Ti samples, the vibration of the punches induces temperature oscillations due to the change in electrical resistivity. An increase in resistivity due to the temporary decrease in contact pressure is clearly observed for the 10 : 9 pulse setting. The frequency and amplitude of the pulses crucially affect the contact resistance. The pulse frequency defines the time available for the system to react to pressure oscillations, and at high frequencies the local temperature change should be negligible. Temperature pulsations should not affect electrically insulating samples, but they can have an impact on the sintering die. A movement of the cylindrical die relatively to the punch during an SPS run changes the die–punch contact area, which might affect the temperature measurement. However, our experiments show that graphite dies loaded with dense sialon samples can be heated to the same final temperature regardless of the on : off setting (figure 3(a)). The height of a sample inside the graphite die plays a more significant role than the die electrical resistance—loading a short sample inside a sintering die increases the cylinder–punch contact area and decreases electrical resistivity. As a result, the measured temperature difference decreases by 150 ºC when the sample height is reduced from 26 to 6.5 mm. An SPS run is usually associated with shrinkage, which increases the demand for applied current. Similarly, the rapid heating of a sintering die can promote greater pressure oscillations. Pressure oscillation is critical for the stability of the SPS system in terms of electrical contacts. The changing amplitude of pulses with the input (see figure 5) can destabilize the SPS process, particularly at high electric currents. Electrical contact may be lost when the amplitude of pressure oscillations increases owing to a high current. If the source of the oscillating attraction/repulsion force is magnetic interaction within the SPS unit, then the magnetic force is only present when direct current is flowing through the system (on-state), and this interaction is related to the current density.

Our experiments were limited by the lack of an electrically conductive and transparent die, which would have allowed the direct observation of electrically insulating samples. Moreover, the frequency of SPS electric pulses (303 Hz, period 3.3 ms) was significantly higher than our maximum sampling frequency (10 Hz) and the human eye response (~24 Hz). However, if we count all on and off pulses together (e.g. the 10 : 9 setting corresponds to 33 + 29.7 ms), then the on : off pulses have frequencies of 7.8 (30 : 9), 8 (36 : 2), 15.9 (10 : 9) and 21.6 Hz (12 : 2). Figure 4 reveals that the 10 : 9 pulse setting (15.9 Hz) relates to a higher frequency of pressure oscillations than the 30 : 9 pulse setting (7.8 Hz). Nevertheless, the length of the off time has a significant effect on either the pressure oscillations or on our ability to record them, as demonstrated by the experiments with different recording times (figure 4(b)). Furthermore, a longer off time corresponds to more intense on pulses, both of which facilitate the recording of the pressure oscillations. In summary, more sensitive pressure sensors and shorter sampling times are needed for recording frequencies and amplitudes at short off times.

To the best of our knowledge, pressure oscillations have never been reported in SPS. A recent extensive review of the consolidation-synthesis of materials by electric current-activated/assisted sintering (ECAS) [12] did not mention any relation between the applied pressure and current. However, such phenomena can have significant consequences for the understanding of the SPS process. Our data indicate that the measured values of current depend on the on : off pulse setting. As shown in figure 3, the measured currents do not correspond to the input power, but the input power does determine the final temperature. Details of this problem have already been discussed [13]. We have verified the reproducibility of our data (see supplementary material available online at stacks.iop.org/STAM/13/015005/mmedia). However, it is not yet clear whether pressure oscillations are also present in SPS units fabricated by other manufacturers. Furthermore, the size of the sintering die is important—small
dies generally require less current to reach the target temperature, and the low input power leads to small pressure oscillations.

Pressure oscillation is also an important factor for the consolidation of particles, as dynamic pressing usually promotes their packing. Cyclic cold isostatic pressing [14, 15] homogenizes the microstructure faster than the application of constant pressure, and the homogenization efficiency increases with the number of cycles. Studies on the effect of pressure oscillations on the consolidation of particles will increase understanding of the mechanism of densification at low temperatures [16].

5. Conclusions

(1) In two different types of SPS apparatus, the use of pulsed direct current generates oscillations of the applied pressure.

(2) The pressure oscillations are generated by the apparatus itself and appear to be sample-related.

(3) The measured force contains two components: a static component generated by the hydraulic system, and an oscillating component, generated by pulsed direct electric current.

(4) The frequency and amplitude of pressure oscillations depend on the on : off setting and the current level.

(5) On : off settings with long off times (such as 10 : 9 and 30 : 9) result in stronger pressure oscillations than those with short off times (such as 36 : 2 and 12 : 2). The amplitude of the induced pressure oscillations also varies with the intensity of electric current pulses. The oscillation frequency appears to depend on the on : off setting, but further studies are needed to elucidate this relation.

(6) The above observations apply to the SPS systems produced by SPS Syntex Inc., Japan; they might not be valid for SPS units produced by other manufacturers.

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