

Pasquale Cavaliere *Editor*

# Spark Plasma Sintering of Materials

Advances in Processing and Applications

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# Preface

From the two last decades, elaboration techniques based on the use of high current intensities, among which the SPS technique is probably the most popular, have attracted considerable interest. Spark plasma sintering (SPS) is the process of consolidating powder (metallic or ceramic) constrained in a die (most often graphite) through the application of large amounts of pulsed DC electrical current.

Unlike conventional sintering, the SPS process affords rapid heating rates and reduced sintering temperatures that suppress microstructural coarsening. It has been demonstrated that the surface oxides at interparticle contact points can be mitigated by SPS. The SPS method has recently made significant advancements in materials science and materials processing thanks to its capability of fast and efficient densification of a great variety of materials and the suitability of the equipment for conducting solid-state syntheses and syntheses, in which liquid phases can form within limited volumes locally at the contacts between particles.

Spark plasma sintering (SPS) has garnered considerable attention for its ability to retain nanocrystalline microstructures and create materials with interesting functional properties. This is in part due to its ability to process materials at lower temperatures and in shorter amounts of time compared to conventional techniques, making SPS a true nonequilibrium processing technique. Decades of research have led to SPS finding success in nearly every category of material and property. SPS is uniquely positioned to take advantage of grain boundary strengthening due to its ability to process materials to high density with minimal grain growth.

Several scientists continue to develop the spark plasma sintering technology to fulfill the needs of high-performance applications. This book outlines current knowledge in SPS by reviewing the major fundamentals of the process and its features and applications, as well, provides an overview of recent and emerging developments in the process and the future potential of this technology. Despite SPS is still an emerging technology, investigations and applications have been widely reported in previous works, attracting great attentions from both scientific and industrial communities. Existing works mainly focused on applications, product properties, processing parameters optimization, and materials performances. So far, a systematic summarization and review on these topics is still lacking. In the

present book, the different aspects of this emerging technology are addressed in the context of technology, materials, and applications. There are fundamental aspects of the SPS process that are not heavily researched but can be improved in order to enhance SPS transition into manufacturing. Many of these areas, including tooling design, tooling material, powder conditions, and current waveform, are evaluated in the present book to determine how changes could be used to improve the SPS process.

The book provides the SPS fundamentals and applications based on studies belonging to scientists from 12 countries and 40 universities and research centers. The book chapters focus on process fundamentals, nanocomposites, ceramics and hard metals, thermoelectric and magnetic materials, Ni- and Ti-based alloys, and high entropy alloys.

My special acknowledgments to the passion and cooperation of all the authors and reviewers who made possible the realization of the book and the reduction of the publication time with their hard work and prompt responses.

My special thanks to the professionalism of the editorial office assistants. Finally, I would like to dedicate the work to my brother, Andrea.

Lecce, Italy

Pasquale Cavaliere

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**Part I**  
**Process Fundamentals**

# Spark Plasma Sintering: Process Fundamentals



Pasquale Cavaliere, B. Sadeghi, and A. Shabani

## 1 Introduction

Sintering refers to the process of firing and consolidating powders at temperatures lower than their melting point, where diffusional mass transport leads to bonding between particles and the formation of a dense body. Bulk samples could be produced through sintering by using various powder materials. Generally, sintering can be done using various methods such as conventional sintering, microwave sintering, hot press (HP), hot isostatic press (HIP) and spark-plasma sintering (SPS). SPS is an emerging powder consolidating technique that provides significant advantages in the processing of high-temperature materials with poor deformability into configurations that were previously unattainable. It is known as a low-voltage, direct current, pulsed current-activated pressure technique. It can be applied to produce bulk samples that start from a broad range of powders (pure metals, alloys, ceramics and so on). During sintering, external pressure and an electric field are applied simultaneously to enhance the densification of the powder compacts. It is worth noting that SPS is similar to HP, but the main difference is in the procedure that produces heat and transmits it to the sintered material. In contrast to HP, which uses an external heating source, in SPS a pulsed direct current is allowed to pass through the conductive die and through the sample. So, the pulsed direct current produces an electric field during the sintering process. Therefore, the powders are heated from both outside and inside.

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In SPS, because no coarsening and grain growth is allowed, high relative densities are reached in a very short time, and nano-sized powders can be sintered without considerable grain growth, something that is not possible in a conventional sintering process.

Several theories have been proposed for physically modelling the SPS process; among them micro-spark/plasma theory is the most popular. In this theory, when spark discharge appears in the gap between the particles of a material, a local high-temperature state occurs as a result of the spark. Thus, during the SPS process, vaporization occurs and the powder particle surfaces melt; constricted shapes or “necks” form gradually around the contact area between the particles. Plastic transformation progresses during sintering, resulting in a sintered compact of over 99% density. Because only the surface temperature of the particles rises rapidly by self-heating, particle growth of the starting powder materials is controlled.

Spark-plasma sintering technique was first developed in 1930, but at that time the technology was not good enough to be commercialized. In 1980, the technique was developed further and various search laboratories—especially in Japan—began to use it. Sintering under electric current was first mentioned in a US patent published in 1913. The patent aimed to protect pressure- and current-assisted sintering system in a vacuum. More than 50 years—and about 20 additional patents—later, Kiyoshi Inoue invented “spark sintering”, which is based on pulsed current; however, its commercialization was not a great success. In the late 1970s, even before Lockheed Missile and Space Co. bought parts of Inoue’s work, the same technique had been used to produce near-net-shape products, very large components, functionally graded materials (FGMs) and non-equilibrium composites. But, there was little documentation of the process’ successful implementation in industry. After Inoue’s patents expired in the early 1990s, Japanese companies (in particular Sumitomo Coal Mining Co., Ltd.) began to produce SPS machines. Later, FCT Systeme GmbH, in Germany, and Thermal Technology LLC, Inc., in the USA, began producing similar equipment based on pulsed direct current. Nowadays, several companies in China, Korea and Japan offer FAST/SPS set-ups, and the number of FAST/SPS devices installed globally is estimated at 1750 (accounting for two-thirds of the industry).

## 2 SPS Components

Spark Plasma Sintering equipment is required to rapidly sinter conductive, non-conductive and/or composite powder materials to the required level of density, including full density. Rapid sintering/densification should take place by the generation of plasma due to sparking between the particles. Details of the SPS components follow.

## 2.1 *Furnace Cum Pressing Chamber*

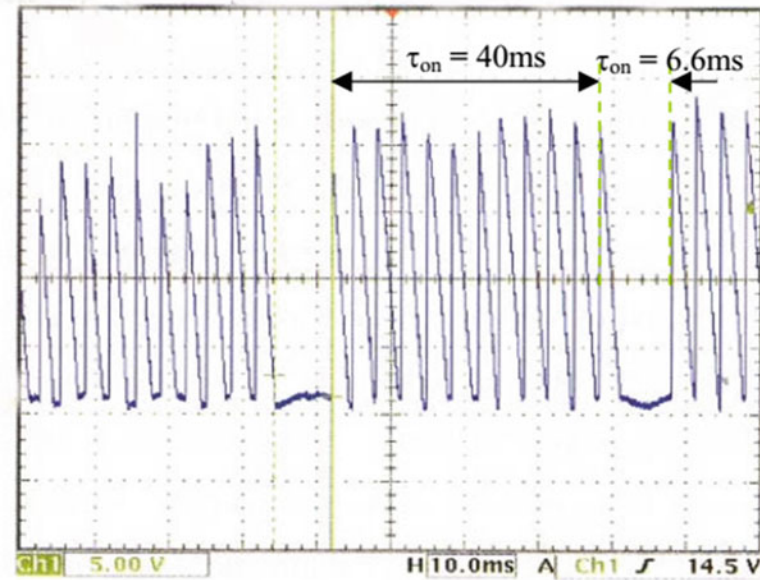
Whole sintering operation will take place inside a furnace cum pressing chamber. The chamber should be capable of sintering the powder in various atmospheres such as vacuum, nitrogen or any inert atmosphere. It should withstand a vacuum of  $1 \times 10^{-4}$  mbar (at least in cold conditions) and a sintering temperature as high as 2200 °C. The size of the chamber should be sufficient to accommodate the largest mould set without obstruction. It should consist of:

- Stainless steel chamber
- Water-cooled, double-walled vacuum chamber
- Front-loading type
- Ports for viewing and placing pyrometer.
- Two additional blind flanges for installation of additional devices and gauges
- Inert gas inlet and air admittance
- An additional glass window for positioning lamp outside the chamber.

## 2.2 *Power Supply for Furnace*

The power supply to the furnace should be sufficient to reach a temperature of up to 2200 °C in vacuum/argon/nitrogen atmosphere at a heating rate variable of up to at least 800 °C/min. The input power supply should be 415 VAC  $\pm$ 10%, 50 Hz.

- Output DC pulse current (Fig. 1): Variable up to a minimum 8000 A (higher amperage up to 10,000 A is desirable), DC waveform (ON and OFF time) should be manually adjustable and programmable with a PC.
- Pulse duration: Programmable within a range from 5 to 255 ms. A higher range is acceptable. Figure 6 shows the ON-OFF pulsed DC used during the entire sintering cycle, with a standard on-off time relation of 12:2. Also, the ON pulses can be programmed from 1 to 99, whereas consecutive OFF pulses are limited to a maximum of 9. In most SPS machine catalogs, the manufacturer recommends a pulse sequence of 12:2 and that OFF pulses not exceed ON pulses. It is worth noting the height of the pulses varies, and, occasionally, the number of pulses can differ from the programmed sequence.
- Range of temperature: Selectable at any range from room temperature to 2200 °C; a higher range is acceptable. The temperature should be manually adjustable and programmable with a PC.
- Ammeter and voltmeter to read average output amps and volts.
- Heating rate variable up to 1000 °C/min. A higher rate is desirable. However, both the maximum temperature and heating rate are limited by the size of the die. However, a higher current is needed to heat a larger die to the same temperature level achieved by a smaller die. Additionally, the higher heating rates cause heterogeneous distribution of the temperature into the die and sample.



**Fig. 1** DC pulsed current applied during sintering

- The power supply along with the mould design should be such that the temperature variation along a sample of 30 mm in diameter at a given set temperature should not exceed  $\pm 5^\circ\text{C}$ .

### 2.3 Vacuum Pumping System

A vacuum pumping system should be attached for evacuating the chamber and must be capable of attaining the following vacuum levels:

- Ultimate vacuum level: Minimum  $5 \times 10^{-2}$  mbar, higher vacuum as high as  $10^{-4}$  mbar is preferable.
- Overall leak rate in the chamber:  $< 5 \times 10^{-3}$  mbar-l/s.
- Manually operated roughing valve, plumbing system to connect chamber to the pump, O rings, seals, connector, etc.
- Safety devices/interlocks: The unit should have safety devices/interlocks for the safety of the machine/operator like:
  - Water pressure flow switch
  - Automatic safety valve for releasing the pressure in case of emergency
- Vacuum-measuring gauge and gauge-heads: Digital display meter programmable with a PC.

## ***2.4 Pressing System***

A hydraulically (preferably) controlled pressing system should be provided to compact the powder at the desired pressure inside the furnace chamber. The pressure can be applied and released very quickly, and very high pressures compared to conventional HP can be used.

- Overall force: 25-ton-force or equivalent (~250 kN).
- The pressing frame should be mounted on four rigid posts to align the upper and lower ram.
- Both rams (anvil/piston) should be adequately water cooled to withstand the sintering temperature of 2200 °C in graphite die.
- The pressing cylinder should be driven servo-hydraulically and monitored manually as well as through programmable software using a PC for setting at a desired level of force value. Hydraulic power supply should include pump, oil reservoir, filters, etc.
- A pressure gauge should be provided for observing instantaneous compaction pressure.

## ***2.5 Water Circulation System***

Double-walled vacuum chamber, upper ram (anvil) and lower ram (piston), power feeder, electronics, etc. should have adequate water and air cooling for safe operation of equipment.

## ***2.6 Gas Inlet System***

A gas inlet system should be provided to purge the inert/nitrogen or other gas inside the chamber, and the gas inlet should be controlled using a solenoid valve and measured using a flow meter. Appropriate plumbing should be provided.

## ***2.7 Control and Instrumentation***

The input power (voltage and current), vacuum level, hydraulic press, closed cycle water circulation system and all safety interlocks should be controlled through the control console. The complete operation should be manually operated as well as automated through a PC using proper application software.

## 2.8 *Temperature Measurement Tools*

Temperature should be monitored at different places of the die using both thermocouple and IR pyrometer. For both cases, the observed temperature should be interfaced with a PC to record it. At least one of the temperature measurements should be very close (within 5 mm) to the centre axis of the sample. Appropriate thermocouples (K type) and an IR pyrometer for different ranges of temperatures should be provided. The accuracy of measurement for either case should be within  $\pm 0.2\%$ . The IR pyrometer should measure and control the temperature within the range of 700–2200 °C.

Provision should be made to measure temperature at other places such as anvil and piston using appropriate thermocouples.

## 2.9 *Mould Sets*

One set of moulds consists of die and punch. Mould sets of high density graphite or tungsten carbide should be provided to obtain the different sintered specimen sizes.

## 3 *SPS Mechanisms*

Figure 2 shows a comparison between SPS and conventional sintering methods. HP and SPS have some similarities, i.e. loading of powder mixture into die, applying external pressure and holding it during sintering process. However, there is a remarkable difference in the nature and the ‘how’ of the generation of heat in both techniques. In SPS, unlike in HP that uses an external heating source, a pulsed direct current is passed through the graphite die and, in appropriate cases, also through the sample. Therefore, in SPS the sample is heated from both outside and inside (self-heating). It is of interest to note that the sintering temperature can be a few hundred degrees lower than what is typically used in a conventional sintering process such as HP.

Generally, spark plasma sintering is carried out in four main stages as shown in Fig. 2. Removing gases and creating vacuum is the first stage. Applying pressure during the second stage is followed by resistance heating in the third stage and, finally, cooling in the fourth stage (Saheb et al. 2012) (Fig. 3).

SPS is an under-pressure sintering technique based on electrical discharge of pulsed DC between the space of the powder particles and the generation of the spark. The propagation of the pulsed current occurs across particle surfaces as shown in Fig. 4.

When the spark generates into empty spaces or contact points of the powder particles, the local heat generated in the discharge column results in temporary

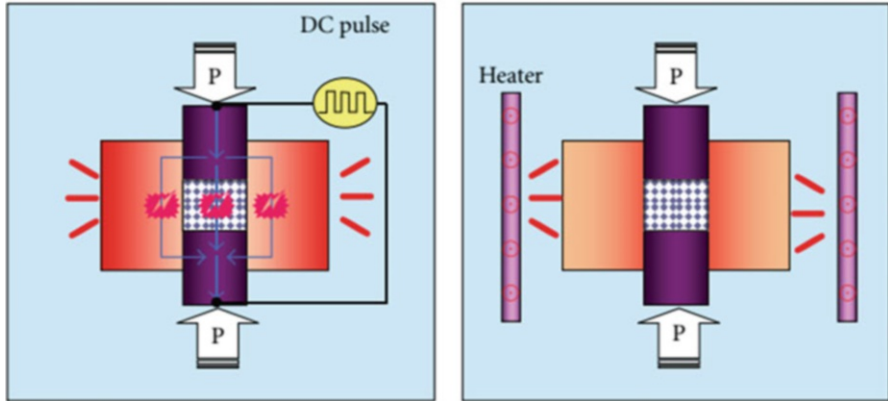


Fig. 2 Comparison between SPS and conventional sintering

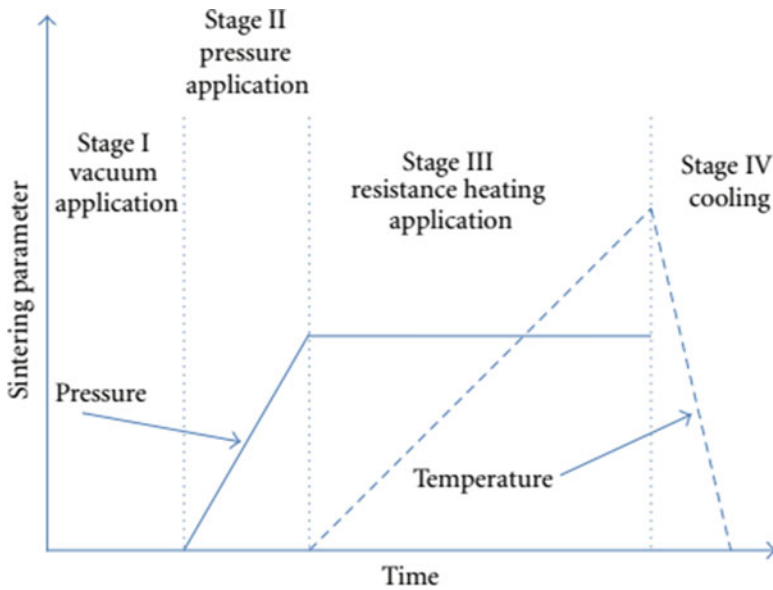
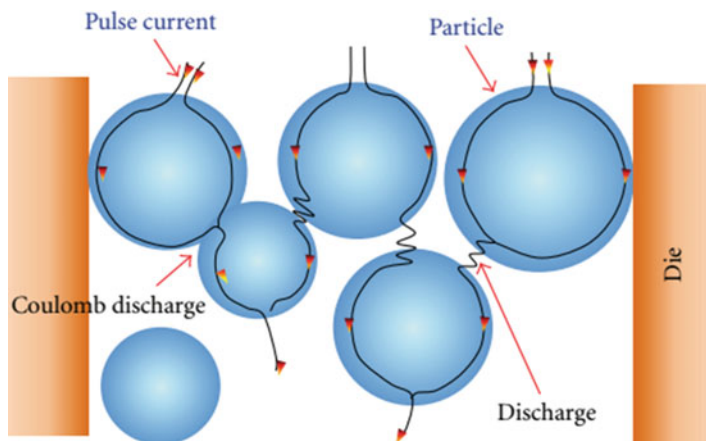


Fig. 3 SPS stages (Saheb et al. 2012)

enhancement of temperature to more than 1000 °C. This high temperature leads to evaporation of impurities and also evaporation and melting on the surface of powder particles. These melted regions are absorbed toward each other via electron current (ON time) and generation vacuum (OFF time), finally forming the necks between the powder particles.

It is known that metal powder particles show an oxide layer on the surface. The thickness of oxide layer and the applied pressure and particle size affect the



**Fig. 4** Pulsed current that flows through powder particles

electrical conductivity of the powder volume and thus will be impressed at the initial stage of sintering. The compressive stress applied in SPS results in better contact between powder particles, and it changes the amount of those contacts and promotes the existing densification mechanisms or activates new mechanisms such as plastic deformation and grain boundary sliding (Guillon et al. 2014). Decreasing contact area at particle-to-particle contacts increases the local pressure there by a factor of 100, which results in theoretical local pressures of 1000–10,000 MPa. However, increasing the pressure in SPS powder agglomerates may break them, facilitating particle rearrangement at low temperatures and consequently increasing packing. Removing pores, especially large ones, allows for homogeneous grains and thus more densification and limited grain growth. In contrast, at high temperatures, although additional densification mechanisms such as plastic deformation or power law creep may be active, grain growth nevertheless increases. Consequently, sintering at low temperatures is more effective than at high temperatures due to significant limitation of grain growth.

During the SPS process, applied electrical potential causes a flow of electrons through conductive materials. In the case of non-conductive ceramics and conductive aluminum, a potential difference across aluminum particles separated by the ceramic phases may develop. The high pressure and electrical potential can easily break up the oxide layers and create direct metal-to-metal contact. This phenomenon can facilitate atom diffusion at the contacts. Mass transport mechanisms to the necks, or mechanisms involved in sintering for neck formation, are evaporation, surface diffusion, grain boundary and volume diffusion. During the initial stage, packing and necking of particles is 2–3% of total densification. During the intermediate stage, most of the porosity is still open, and the compact shrinks until 92% of the total densification is achieved. It should be noted that the active mechanisms during this stage are volume densification, grain boundary diffusion and probably dislocation climb. Isolation of pores from one another takes place during the last stage. In most cases, isolated pores are placed among three or more particles. Figure 4

shows the basic mechanism of neck formation by spark plasma. The formed pores achieve a spherical shape, and, as shown in Fig. 4 (V), the final densification takes place with the removal of the isolated pores by diffusion. The last densification stage duration is generally slow because it is governed by the diffusion phenomenon. However, by applying pressure, some additional mechanisms such as plastic deformation, dislocation and diffusional creep based on grain sliding accelerate the densification process thanks to the elimination of isolated pores. Figure 5 shows the different mechanisms involved during SPS.

On the other hand, when a spark discharge appears in a gap or at the contact point between the particles of a material, a local high-temperature state (discharge column) of several to tens of thousands of degrees centigrade is generated momentarily. This causes evaporation and melting on the surface of powder particles in the SPS process, and “necks” are formed around the area of contact between particles.

Figures 6 show a typical conventional material transfer path mechanism of evaporation, solidification, volume diffusion, surface diffusion and grain boundary diffusion on neck formation. It has been found that the ON-OFF DC pulse facilitates some phenomena such as formation of spark plasma, spark impact pressure, joule heating and electrical field diffusion effect (Suárez et al. 2013). More detail is shown in Fig. 7.

Moreover, with regard to the effect of cleaning the surface of powders during the SPS process, particle surfaces are more activated than in conventional electrical

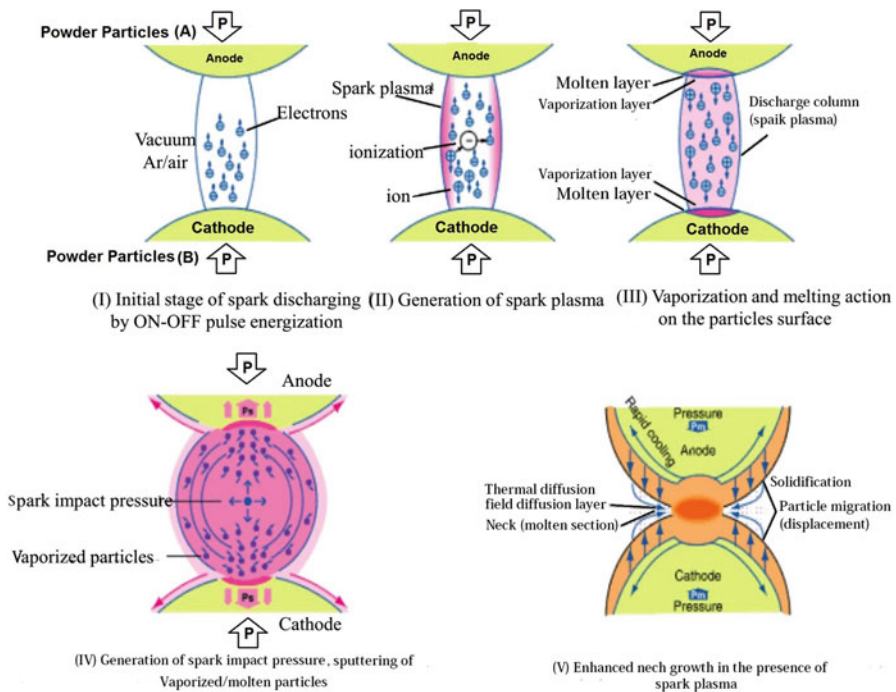


Fig. 5 Basic mechanism of neck formation by spark plasma

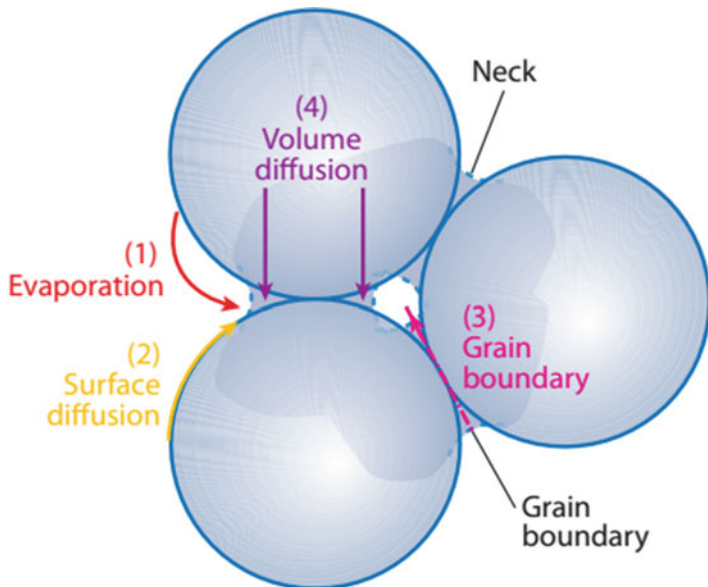


Fig. 6 Mass transport mechanisms that are involved in sintering

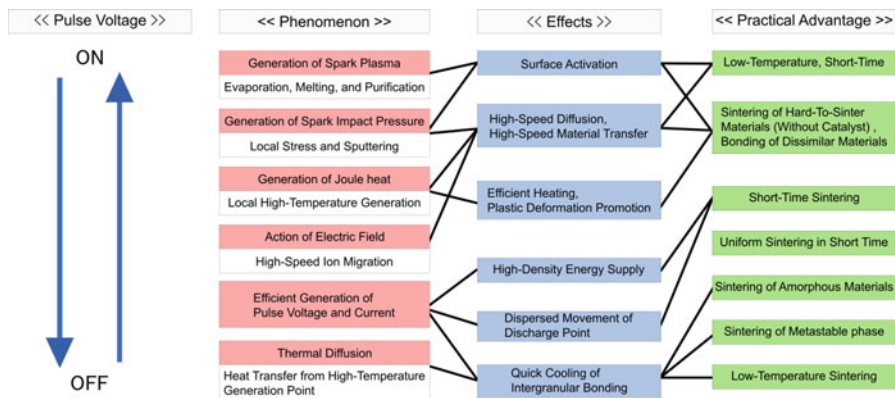


Fig. 7 Effects of ON-OFF DC

sintering processes, and, thus, diffusion is much more effective in comparison with the others (Tokita 1999; Tiwari et al. 2009).

The possibility of obtaining high heating rates during sintering is another advantage of SPS, and sintering of the powder mixture can occur within a short processing time. Heating rates during SPS are typically between 100 °C/min and 600 °C/min.

Figure 8 shows SEM micrographs belonging to SPS experiments performed at normal atmospheric pressure with graphite punches by consolidating spherical



Fig. 8 Particle deformation

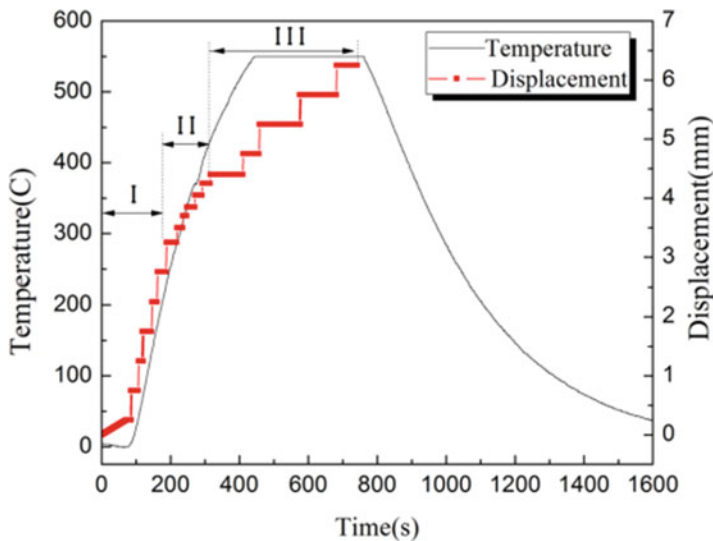


Fig. 9 Recorded shrinkage curve for Al

bronze alloy powder. The rearrangement of powder particles due to the initial press with localized deformation, bulk deformation and extensive sintering by mass transport phenomenon takes place at stages I, II and III, respectively (Fig. 9).

Rearrangement of aluminum particles is achieved by application of pressure through relative motion between powder particles. Then, with increasing temperature and time (region II), densification increases with densification rate compared with the previous stage. This is due to the localized deformation at particles contact points. At this stage, many necks between the surfaces of aluminum particles are formed by mass transport phenomena like grain boundary and volume diffusion. In fact, the localized deformation and consequent formation of necking results in slight densification. Neck formation, grain sliding and diffusion take place at the initial and intermediate stages.

Maximum displacement takes place at the end of region II, which could be due to the high displacement rate of region I. Finally, the main shrinkage (region III) starts. In this stage, the incipient propagation of deformation within the core of the

aluminum particles begins. Bulk deformation and extensive sintering by the mass transport phenomenon cause more coalescence between aluminum particles, especially in necked areas. Diffusion is one of the main reasons for the lowest densification rate in region III. By holding the pressure at the maximum temperature, no distinct change in displacement and displacement rate occurs. This means in turn that the sintering process has been completed. The final stage occurs when isolated pores are removed by diffusion. It is worth noting that densification and formation of the necking depends on many factors, e.g. materials, shape and size of particles, particle size distribution, pressure, temperature and time. It should be noted that if particle size distribution is too narrow, packing becomes inefficient and thus densification rate decreases. In fact, proper particle size distribution enables more contact area between particles, which in turn increases neck formation and densification. It can be particularly important that small particles increase total contact area in the compact, and thus the driving force for densification is increased. It is worth noting that external pressure strongly affects diffusion processes in the sintering stages. As mentioned above, in the late stage of sintering, when shrinkage has practically come to an end, the remaining porosity consists of round, isolated pores. These pores are initially connected to grain boundaries. It is known that total elimination of the residual porosity is also assisted by external pressure.

Figure 7a shows the behaviour in the initial stage of neck formation due to sparks in the plasma. Heat is transferred immediately from the centre of the spark discharge column to the sphere surface and diffused so the intergranular bonding portion is quickly cooled. As seen in Fig. 7b, which shows several necks, the pulse energizing method causes spark discharges one after another between particles. Even with a single particle, the number of positions where necks are formed between adjacent particles increases as discharges are repeated.

Figure 7c shows the condition of an SPS-sintered grain boundary after sintering has progressed, making it plastic-deformed. This state is the result of the processing conditions in which applied pressure was 29 MPa, sintering temperature 500 °C, holding time 120 s, SPS current 850 A and voltage 3.9 V. Therefore, we note the applied pressure lends a positive effect to densification by increasing contact area and introducing additional densification mechanisms for SPS sintering.

Sintering dies and punches made of graphite are subject to joule heating according to the progress of the sintering of the internal powder material; the dies and punches function as heating elements to assume the role of maintaining the homogeneity of the sintering temperature for the densification.

## 4 Influence of Direct Current

The main difference between SPS and other sintering methods is that in SPS both die and powder are directly heated by the joule effect of DC. Such techniques make it possible to raise the temperature to 2000 °C at heating rates of up to 1000 °C/min or

even higher. The role of the current and the sintering mechanism remain the subject of much debate between plasma formation (Zhang et al. 2014) and electro-migration supporters (Olevsky and Froyen 2009; Wang et al. 2011); proof of either phenomena is difficult to find. Olevsky and Froyen (2009) have studied possible mechanisms involved during SPS and categorized these effects into thermal and non-thermal phenomena. It is known that the ON and OFF DC pulse is energized to generate following effects: (1) spark plasma; (2) spark impact pressure; (3) joule heating; and (4) an electrical field, promoting material transfer and diffusion.

The plasma problem is complex. Makino has shown that only a very small part of the current (roughly 100 mA) crosses through the  $\text{Al}_2\text{O}_3$  sample, while the machine injects some 1000 A (Tomino et al. 1997). In a similar study, Tomino et al. concluded that no current passes through the sample, and they eliminated the presence of a discharge in a dense insulator. According to Munir et al. (2011), the existence of such plasma or a discharge should be evaluated with different hypotheses, including applied pressure and development of sintering, since both parameters are linked with the formation of large contact surfaces between particles (Tokita 1999). In the case of conductive powders, there is a good probability discharges will occur between the particles at the beginning of the sintering; therefore, as sintering progresses, the probability of discharge decreases. In spite of the high current, 2000 A, the current density in a sample of conductive powder 20 mm in diameter should be around  $400 \text{ A cm}^{-2}$ , a level too low to explain the observed mass transport enhancement. It has, then, been proposed that due to the extremely small interfacial contact between particles, very high local current densities are present. It is worth noting that for each experiment all parameters—temperature, pressure, heating rate, holding time, etc.—will be extremely dependent on the nature of the sample and the size of its particles (Anselmi-Tamburini et al. 2005).

## 5 Advantages and Disadvantages of SPS

- Since the temperature used in SPS is usually 200–1000 °C lower than in conventional sintering techniques, it is categorized as a low temperature sintering technique. The process steps of SPS—applied pressure, increasing temperature and holding time—occur in a short time period (5–25 min) and thus provide a possibility of microstructure control as well grain growth, especially in nano-structured materials (Kubota 2007).
- As mentioned above, the existence of high-amperage current besides local pressures as high as 300 tons leads to formation of connections—and consequently necks—between powder particles. By increasing the pressure, plastic deformation of the particles leads to high densities. However, in low pressures and temperatures and also low holding time, materials can be fabricated which possess high porosities (Fig. 10).

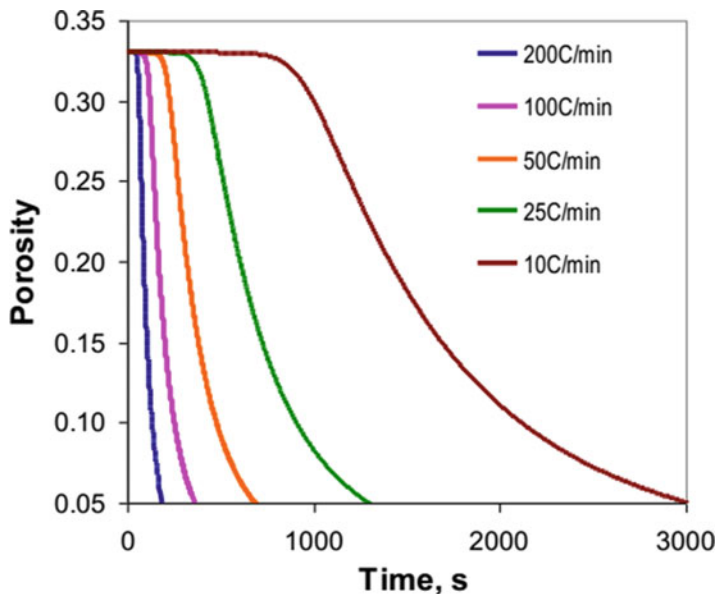
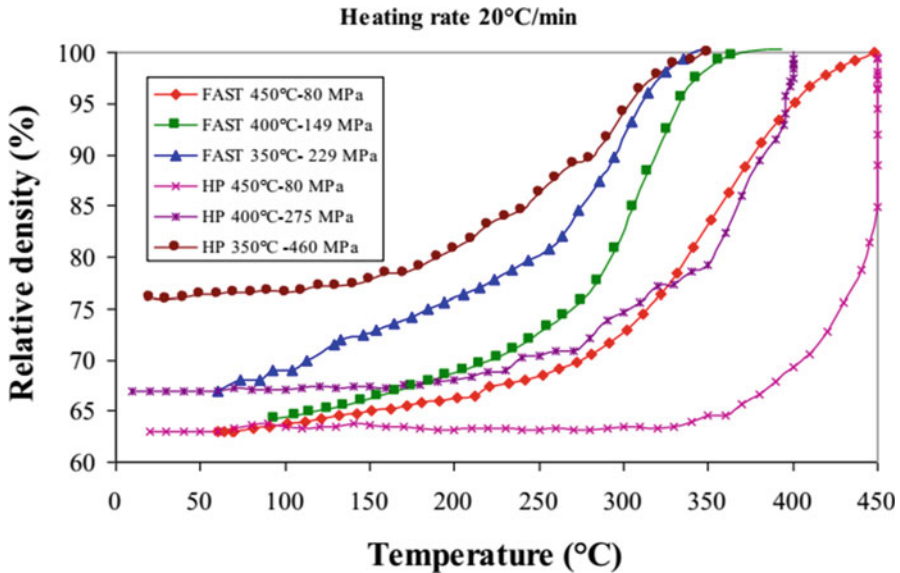


Fig. 10 Influence of high heating rates on porosity (Olevsky 1998)

- SPS is able to sinter the dissimilar materials without any melting. This technique is quite useful for the generation of composite materials with homogeneous microstructure, even though the density they experience will be low. Also, layered materials or FGMs can be produced with this technique.
- In fast sintering techniques such as microwave or SPS, enhancing of system temperature is caused by self-heating in the powder mixture.
- With regard to self-heating in SPS technique, the heating rate is high and thus the period of time for completing the SPS process is several minutes, whereas for conventional sintering techniques such as HP, the time extends from about several hours to some days. In addition, the dwelling time for SPS is typically about 5–15 min, while in conventional sintering techniques it is around several hours.
- Economically, the cost of SPS is around 50–80% lower than conventional sintering techniques. Such cost reductions have been attributed to high production rate, high heating rate and low sintering time.
- The concurrent use of temperature and pressure in SPS leads to high densification, and, consequently, the sintering temperature for attaining a high compact material is about 200–250 °C lower than that of conventional sintering techniques. In SPS, grain growth and coarsening is retarded due to the high heating rate, high relative densities are reached. Therefore, nanostructure ceramics and nanocomposites can be fabricated using SPS, materials which possess low porosity and high densities. These nanocomposites show excellent and unique mechanical properties such as strength and hardness.



**Fig. 11** Comparative study of relative density of SPS and HP (Olevsky 1998)

- Due to the high heating rate in SPS, unwanted reactions are restricted, and thus the formation of the undesirable phases and products is eliminated.
- One of the fundamental differences of SPS with other sintering techniques is apparent in the physical activation of the surface of powder particles. This surface activation, along with fast densification at lower temperatures, greatly restricts grain growth, compared to other techniques, and thus the microstructure possesses finer grains and improves mechanical and physical properties.
- Four main factors that aid increasing densification during SPS are: high heating and cooling rate; heat transfer from the die; mechanical pressure which causes the removal of porosities and pores and increases in the diffusion. Moreover, the use of DC current pulses results in increased diffusion rate.
- In SPS higher pressure can be used than in conventional sintering techniques, allowing them to reach high densities in a little time and at low temperatures (Fig. 11).
- Consolidation time of SPS is greatly decreased to a few minutes compared to the hours needed for conventional sintering, while the process' sintering temperature can be decreased by a few hundred degrees as shown in Fig. 12.
- SPS can be used to sinter a versatile and wide range of conductive and non-conductive materials.
- Fast densification by SPS reduces the time for the interaction between the sintering material and graphite die and consequently reduces the possibility of formation of undesired products. Figure 13 illustrates the impact of heating rate on shrinkage rate at the same holding time for all samples. It is clearly determined

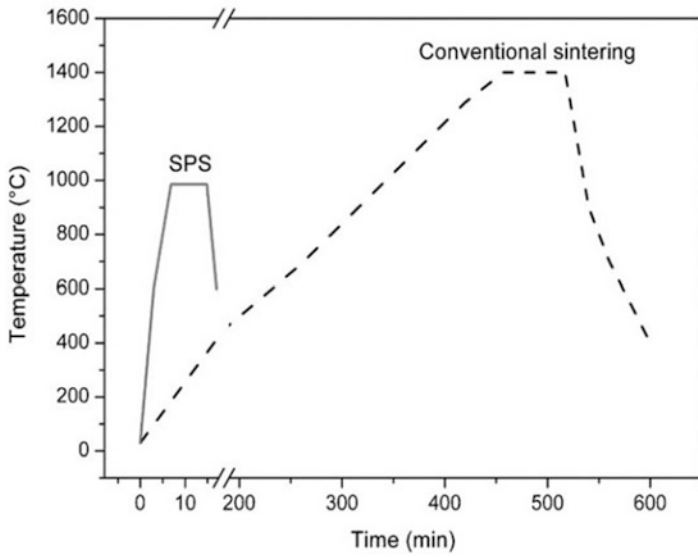


Fig. 12 Comparing time and temperature of SPS technique and conventional sintering

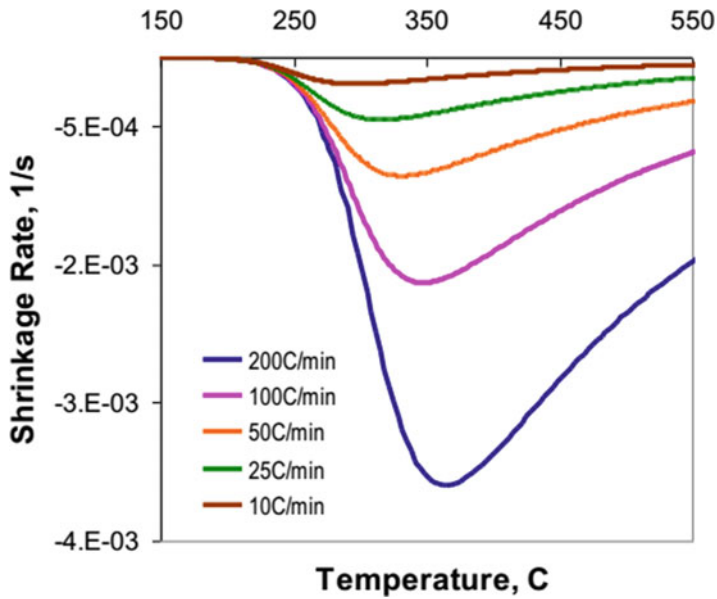


Fig. 13 Influence of heating rate versus shrinkage rate

that at high heating rates the duration of densification via surface diffusion becomes very low and subsequently intensifies the formation of necking and densification by grain boundary diffusion.

- Direction of current and pulse pattern have no effect on interaction between primary materials and growth rate, respectively.
- Other advantages of spark plasma sintering:

Reliable control of sintering process parameters and consequently control of its microstructure.

SPS can be considered a solid-phase sintering, hence, no melting occurs during the process.

Based on the die used, it is expected that temperature gradients will exist during sintering and subsequently fabrication of FGMs.

Possibility exists of combining sintering methods such as SPS-HP, SPS- microwave sintering, etc.

Low-temperature sintering via SPS due to use of temperatures below Curie temperature.

Fast sintering process.

Uniform sintering.

Low grain growth (nanograin materials may be prepared).

Compaction and sintering stages are combined in one operation.

Binders are not necessary.

Better purification and activation of powder particles surfaces.

Different materials (metals, ceramics, composites) may be processed.

High energy efficiency.

Easy operation.

- Disadvantages of spark plasma sintering:

Only simple symmetrical shapes may be prepared.

Expensive pulsed DC generator is required.

For materials powder with diameter smaller than 100 nm, it is possible to make a significant temperature gradient inside the sintered materials resulting in non-uniform densification.

## 6 Conclusions

SPS as a new technique for consolidation and sintering deserves serious attention from researchers. The SPS process' exclusive features have been recognized in many industrial sectors such as aerospace, automotive and military in comparison with other sintering techniques. Since duration of consolidation in SPS takes a maximum of 20 min, it brings time, cost and energy savings. Sintering of refractory materials, dense nanostructure materials and composite materials besides nanocomposites are a

few examples of specimens fabricated by SPS. Specimens produced via SPS possess high strength, high wear resistance and strong magnetic properties. The main advantages of SPS in comparison with other sintering techniques can be summarized as: faster cooling rates, higher heating rates, generation of products with finer or nanostructure grains and higher densification efficiency.

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# Fundamentals of Spark Plasma Sintering (SPS): An Ideal Processing Technique for Fabrication of Metal Matrix Nanocomposites



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## 1 Introduction

Spark plasma sintering (SPS), also known as pulsed electric current sintering (PECS), is a sintering technology developed in recent years. It is a novel processing technique for material development which utilizes a direct electrical current (DEC) to perform high-speed consolidation of powders in a very short period of time, using relatively high sintering pressures. During SPS the gap between the powder particles is charged with electrical energy, and a high-temperature spark plasma is applied momentarily which enables sintering at relatively low temperatures as compared to the conventional sintering and yet achieves almost full densification. Sintering assisted by plasma is expected to achieve very high levels of densification. The large current pulse energizing method generates spark plasma, spark impact pressure, Joule heating and an electrical field diffusion effect. The SPS process enjoys certain inherent advantages, such as (a) high thermo-efficiency, determined by the way and rate of heating; (b) spontaneous heating, mainly due to the high pulse power source; (c) better self-purification of the particle surface, as a strong enough electrical field is produced in the small gaps of the particles to make the electrons, cations and anions to strike the surface of the opposite particle and purify its surface; and lastly (d) fast sintering under low temperatures (Munir et al. 2006; Tokita 1993). The movement of these particles fulfils the material transportation, and a local high-temperature zone is created at the contacting areas of the particles, resulting in the quick formation of the neck, while the temperature still remains comparatively low. However, the temperature at the neck is much higher than inside the particles, as the electrical density of the current flowing through the neck is much higher than that of

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the inside of the particles. The neck region grows quickly, and faster sintering is achieved. The reason why the SPS technique is so effective is because the heating power is not only distributed homogeneously over the entire volume of the sample in a macroscopic scale but at a microscopic scale, and also the heating power is dissipated exactly at the points of contact of the powder particles in the sample. The specimen is heated by the Joule heat due to the heat transferred from the pressing die. The SPS process is capable of introducing very high rates and high pressure due to the sintering at a relatively lower temperature and in much shorter time could be achieved (Mamedov 2002). SPS is an ideal technique for the development of nanocomposites reinforced with carbonaceous nanofillers like carbon fibres, graphite, diamond, carbon foams, carbon nanotubes (CNTs) and graphene as it is possible to achieve a high level of densification without damaging the structural integrity of the nanofillers. Achieving near full density, without damaging the nanofiller structure and morphology, is one of the major challenges during the processing of the metal matrix nanocomposites (MMNCs). This is why SPS is preferred as sintering can be done at lower temperatures and in a substantially short period of holding time. In these binary nanocomposites, CNTs/graphene are added to metal matrices, to noticeably modify and enhance their properties.

The idea to compact metallic materials by an electro-discharge process was originally proposed in the 1960s. Based on this concept, three sintering processes have been developed and commercialized during the recent years and named as “spark plasma sintering” (SPS), “plasma-activated sintering” (PAS) and “electroconsolidation” (Azarniya et al. 2017). These processes are similar to conventional hot pressing, in that the precursors are loaded in a die and a uniaxial pressure is applied during the sintering. However, instead of using an external heat source, a current (DC, pulsed DC or AC) is allowed to pass through the electrically conducting pressure die and, in appropriate cases, also through the sample. This implies that the die itself acts as a heat source and that the sample is heated from both outside and inside. The characteristics of the three processes are as follows:

- (i) In the SPS process, a pulsed DC is applied from the beginning to the end of the sintering cycle.
- (ii) In the PAS process, a pulsed DC is normally applied at room temperature for a short period of time and then a continuous DC during the remainder of the sintering process. This procedure is often referred to in the literature as a “single pulse cycle process. In a few cases the pulsed DC procedure is repeated during the sintering process, and is referred to as a “multiple pulse cycle process”.
- (iii) In the electroconsolidation process, various types of currents (DC, pulsed DC or AC) can be used, i.e. the system is designed to be flexible in terms of power supply.

These processes have now been developed beyond the production of small objects with simple shapes, as the continuous production of compacts of complex geometry and of pieces with diameters larger than 150 mm has been achieved.