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# POWDER METALLURGY REVIEW

POWDER METALLURGY IN INDIA

AUTOMOTIVE APPLICATIONS FOR PM

SPARK PLASMA SINTERING

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INOVAR COMMUNICATIONS

POWDER METALLURGY REVIEW

## India's growing Powder Metallurgy market

Having attended the APMA Conference this year in Pune, India, it was evident that the Indian Powder Metallurgy market is thriving, reporting continued growth that is mirroring the state of the country's expanding automotive sector.

The country's PM structural part makers are not just subsidiaries of leading global PM companies, but also include many locally established enterprises. As the market grows, investment in these companies is continuing, with many reporting facility expansions.

Not content with meeting the needs of the growing local market, a number of the larger PM part manufacturers are also seeking to attract new overseas customers. Reporting from within the industry, Kadambari Gopinath, offers a unique insight into the region, considers the state of its automotive market and identifies the key players in the country's PM structural parts industry.

There are, of course, many applications in the automotive sector for the use of Powder Metallurgy. The process offers numerous advantages over alternative manufacturing routes, from cost savings to novel designs and unique material properties. Much of this innovation has been recognised through industry awards over the years and in this issue, we present award winning PM structural parts from the automotive sector.

Paul Whittaker
Editor, Powder Metallurgy Review

**Cover image**
*ABS sensor rings are just one of the many automotive components suited to Powder Metallurgy (Courtesy Sintercom India)*

POWDER METALLURGY REVIEW


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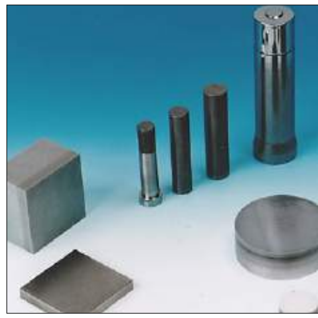
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# in this issue



## regular features






# Spark Plasma Sintering: Method, systems, applications and industrialisation

For around thirty years, Spark Plasma Sintering (SPS) has been of great interest to the Powder Metallurgy industry and academia alike, for both product manufacturing and advanced material research and development. Today in Japan, a number of components made using SPS are already in production, with the process moving from the R&D stage to practical industrial use. In this article, Dr Masao Tokita, of NJS Co., Ltd., introduces the latest in SPS technology, discusses the development of SPS systems and highlights a number of industrial applications.

It is widely recognised that the Spark Plasma Sintering (SPS) method is an advanced processing technology, used to produce a homogeneous, highly-dense, nanostructural sintered compact, as well as in Functionally Graded Materials (FGMs), fine ceramics, composite materials, wear-resistant materials, thermo-electric semiconductors and biomaterials. Originating in Japan, the technology, also referred to as a pressure-assisted pulse energising process, Field-Assisted Sintering Technology (FAST), Electric Current Activated/assisted Sintering (ECAS) or Pulsed Electric Current Sintering (PECS), is today finding new applications in many global regions.

As of January 2019, over five hundred SPS systems are installed in Japan alone, located in universities, technical colleges, national institutes and private companies for use in both the R&D and manufacturing sectors. It is estimated that around one thousand SPS systems are currently installed globally, including those found in Europe, the USA, Russia, China, Korea and others.

SPS technology is seen as a promising technology for innovative processing in the field of advanced new materials fabrication in the 21st century [1-3]. Today's fifth generation SPS systems are capable of producing parts of increasing size, offering improved functionality, reproducibility, productivity and cost effectiveness.

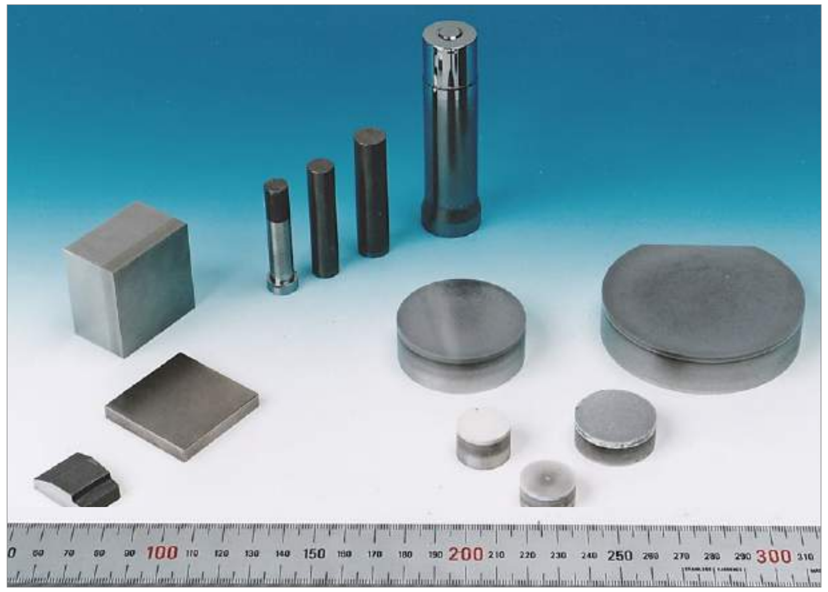


*Fig. 1 Spark Plasma Sintering (SPS) can be used to produce a variety of components, from FGMs to porous filters*

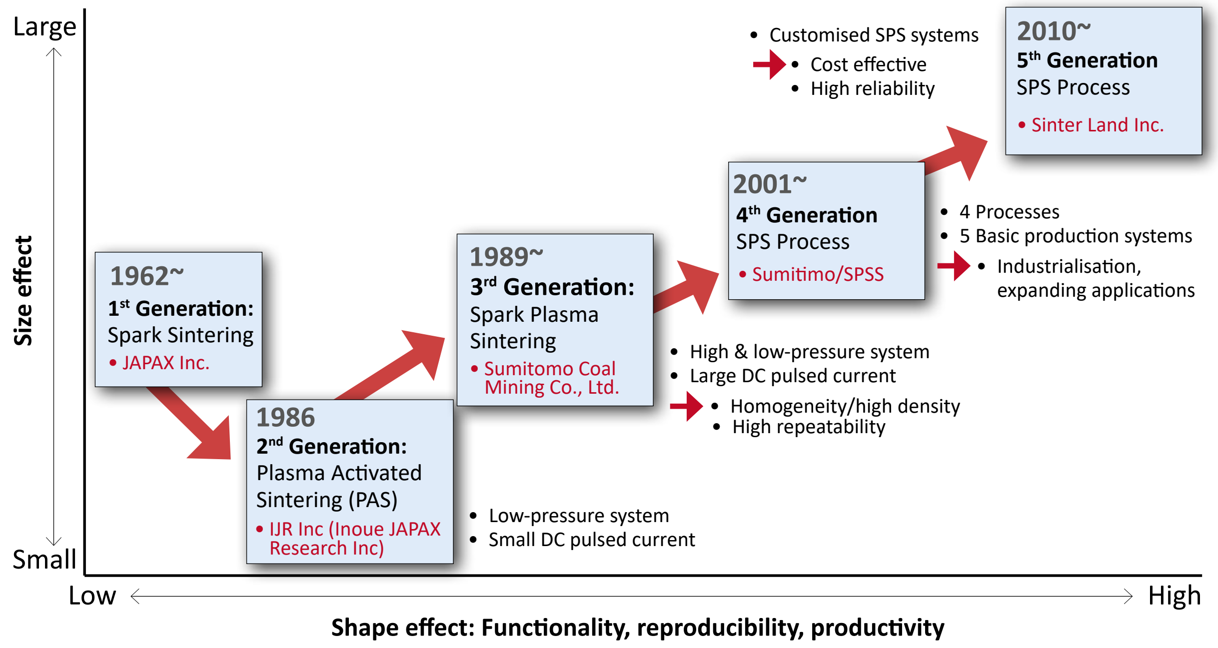



*Fig. 2 Historical progress of the Spark Plasma Sintering method and technology*

## A story of continual innovation

Initial studies, dating back to around 1910 in Germany, report a process where an electric energising technique was applied to consolidate a powder material. In the USA, a few years later in 1933, G F Tayler patented the first resistance sintering method for sheet metals [4]. These processes are considered as the origin of the Hot Pressing (HP) technique, where a high-frequency induction heating method is applied.

It was in the 1960s that a method of Spark Sintering (SS) was developed by Dr Kiyoshi Inoue of JAPAX Inc., Japan [5, 6]. As shown in Fig. 2, this is now referred to as a first generation SPS system. The process was further developed by Inoue, resulting in a second generation technique known as Plasma-Activated Sintering (PAS) released in 1986. Thereafter, in 1989, the Spark Plasma Sintering method was introduced by Sumitomo Coal Mining Co., Ltd, Japan [7], being recognised as the third generation of large DC pulse applied sintering techniques.

Ongoing R&D for the implementation of SPS methods and systems was initiated to design practical hardware and software for industrial applications. The development of small- to medium-sized box-type experimental use SPS systems for new materials preparation, and single-head open-type limited production systems, followed. From 2001 to 2009, as the fourth-generation technology developed to accommodate for product manufacturing, five basic styles of SPS production systems emerged to suit medium- to mass-production scales [8]. In addition to sintering, SPS technology also found application in solid phase diffusion bonding and joining [9], surface modification (treatment) [10] and a synthesis technique, for example, of a single-crystal fabrication.

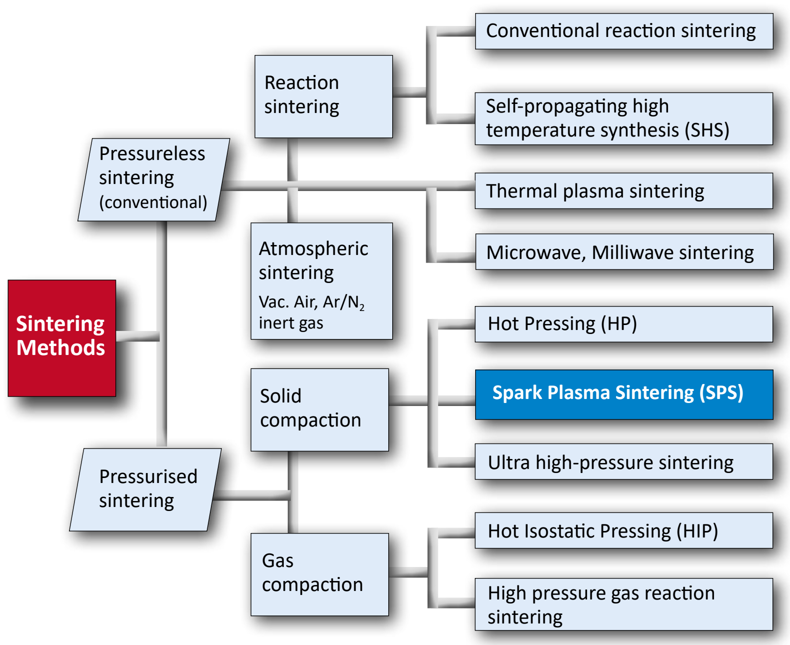



*Fig. 3 Typical classification of sintering methods*






After 2010, the progress of SPS technology was such that new, advanced SPS systems are now seen as being fifth-generation machines. Customised SPS apparatus, along with more practical manufacturing applications, offer high reliability and reduced production costs.

A further interesting technology, derived from the ongoing development of SPS, is the emergence of Flash Sintering and Flash-SPS, a category of Electric Current Activated/assisted Sintering [3,11]. Still under research, Flash Sintering could prove an innovative future technology.

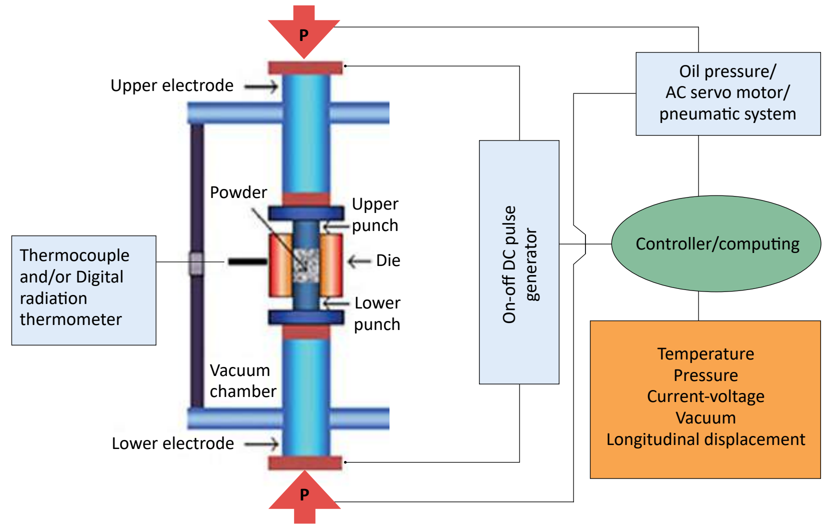



*Fig. 4 Basic theory of the SPS process*

## The Spark Plasma Sintering process

The Spark Plasma Sintering process enables sintering and sinter-bonding, at low temperatures and at high speed. The technique, a form of pressurised sintering as seen in Fig. 3, involves the application of a high-energy, low-voltage electrical current, believed to result in a 'spark plasma' phenomenon in the powder. Although the precise mechanism of the spark plasma remains unclear, many years of research by many different material researchers has resulted in a number of theories [12-16].

One of the most accepted explanations is based around the illustration in Fig. 4 where, once compacted and still under pressure, an on-off DC pulse voltage, at high current, is applied to the powder using a special pulse generator. It is understood that the electrical discharge results in a high-temperature spark plasma, up to several thousand degrees centigrade, generated momentarily at the initial stage of energising. This forms uniformly throughout the compact and the generated heat fuses, purifies and activates the surface of the powder particles (Fig. 5).

The initial stage of the pulse energising results in a discharge between the powder particles and between the powder and the graphite die wall surface (Fig. 6). When sparking occurs, a high-temperature sput-

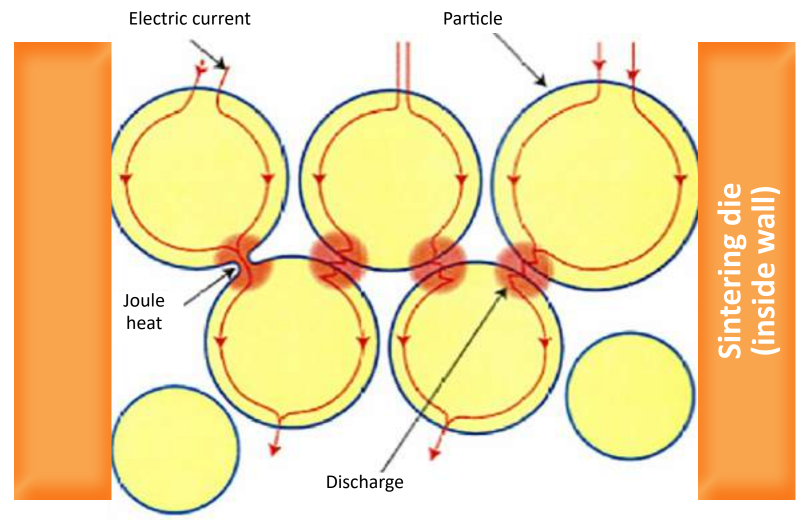



*Fig. 5 ON-OFF DC pulsed current path and pulsed current flow through powder particles*

*Fig. 6 The sintering stage in a graphite mould and vacuum chamber*

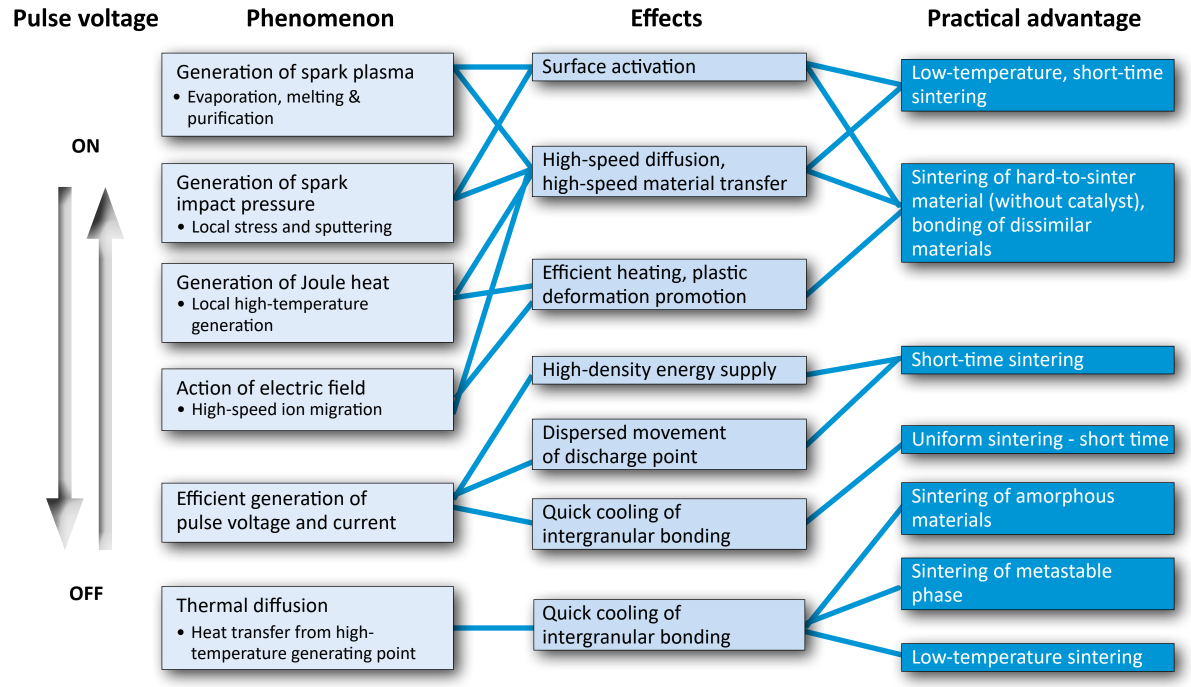



*Fig. 7 Effects of ON-OFF DC pulse energising*


*Fig. 8 This medium-sized 5th Generation SPS system produced by Sinter Land Inc, Japan, offers high-precision process control and short cycle times. Systems such as this can be used with multiple materials and offer wide temperature ranges (Courtesy Sinter Land)*

tering effect is generated by spark plasma and spark impact pressure. This works to eliminate adsorptive gases and oxide films and impurities existing on the surface of the powder particles. The action of the electro-magnetic field enhances high-speed diffusion due to the electro-migration effects of ions.

A Joule heating stage, caused by the passage of electric current through the powder whilst under mechanical pressure, further assists in the SPS process. The intense joule heating effect can often result in localised high-temperature generation, and therefore leads to localised vaporisation or cleaning of powder surfaces. Such a phenomenon ensures a favourable path for current flow. Further effects of the on-off pulse DC voltage are shown in more detail in Fig. 7.

## Configuration of an SPS system

The configuration of a typical SPS system consists of a compacting press with a vertical, single-axis pressurisation mechanism, incorporating specially designed punch electrodes made from graphite. The system can







*Fig. 9 World's largest semi-tunnel type automatic SPS production system has three vacuum chambers, 6 MN press with a pallet-type special conveyer, and inverter-type 40,000 A DC pulse generator (Courtesy Sinter Land)*

incorporate a water-cooled vacuum chamber, a vacuum/air/argon-gas atmosphere control mechanism, a special DC-pulsed power generator, Z-axis position measuring and control unit, temperature measuring and control units, an applied pressure display unit, a data analysing unit and various safety interlock devices. A typical 5th Generation medium-sized system can be seen in Fig. 8. This model is ideally suited to R&D work, as well as prototype and product manufacture.

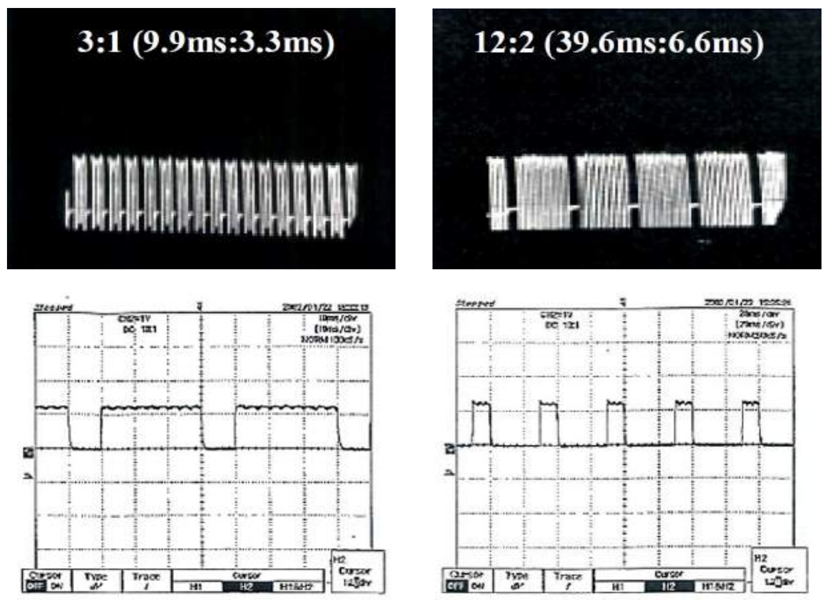
### Production-scale SPS systems

Custom built SPS systems are also available today, as well as large production-based machines such as the example seen in Fig. 9. The move to production-scale SPS systems requires consideration of many factors. The cost and development of optimum systems will depend on production strategies, including the required cycle time, technologies to support scale expansion, mass-production, automation and numerical control systems. There is also the development of process technologies for high functionality, reproducibility, uniformity and structural control. In addition, pre- and post-processes for manufacturing must be considered.

In order to meet different productivity levels, there are typically five options to consider. These include: multi-head, batch, tunnel, rotary and shuttle-type SPS systems. In addition to these, scaling-up process, automatic handling and powder stacking equipment for materials and process optimisation have also been developed [17].

### Development of pulse generators

Presently, there are two basic types of DC pulse generator for SPS apparatus, thyristor-type and invertor-type power supply. Fig. 10 shows examples of typical on-off pulse waveforms and different pulse width and ratio. The waveform, max./min. on-time/off-time pulse width, peak current, frequency, duty factor settings, control system




ON-time: 30 ms OFF-time: 10 ms

ON-time: 10 ms OFF-time: 30 ms

*Fig. 10 Typical wave form of a thyristor-type pulse generator (ON-OFF ratio in 50 Hz)*

| Classification | | Materials for SPS processing | |
|---|---|---|---|
| Metals | | Fe, Cu, Al, Au, Ag, Ni, Cr, Mo, Sn, Ti, W, Be, C | Virtually any metal possible |
| Ceramics | Oxides | $Al_2O_3$, Mulite, $ZrO_2$, $MgO$, $SiO_2$, $TiO_2$, $HfO_2$ | |
| | Carbides | SiC, $B_4C$, TaC, TiC, WC, ZrC, VC | |
| | Nitrides | $Si_3N_4$, TaN, TiN, AlN, ZrN, VN | |
| | Borides | $TiB_2$, $HfB_2$, $LaB_6$, $ZrB_2$, $VB_2$, $MgB_2$ | |
| | Fluorides | LiF, $CaF_2$, $MgF_2$ | |
| Cermets | | $Si_3N_4$+Ni, $Al_2O_3$+Ni, $ZrO_2$+Ni | |
| | | $Al_2O_3$+Ti, $ZrO_2$+stainless steel, $Al_2O_3$+stainless steel | |
| | | WC+Co, WC+Ni, TiC+TiN+Ni, BN+Fe, | |
| Intermetallic compounds | | TiAl, $MoSi_2$, $Si_3Zr_5$, NiAl | |
| | | NbCo, $Nb_3Al$, $LaBaCuSO_4$, $Sm_2Co_{17}$ | |
| Other materials | | Organic materials (polyimide, etc.), FRM, FRC, CNT composite materials | |

*Table 1 Suitable materials for SPS process*

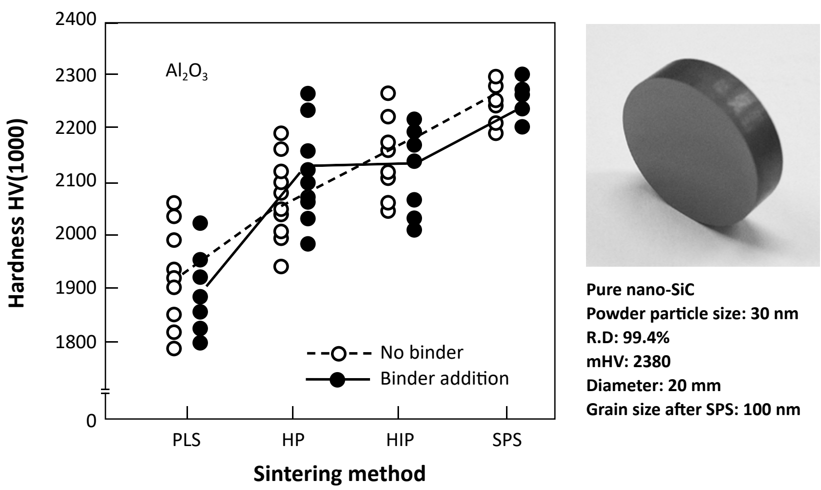



*Fig. 11 Nano-SiC compact by SPS and $Al_2O_3$ HV hardness distribution behaviour sintered by various methods*

and energy consumption vary between each system. Each pulse generator has its own advantages and should be chosen based on the desired purpose and usage of the SPS system.

The majority of SPS systems installed in universities, national institutes and private companies employ the thyristor-type pulse generator, due to a rich reference database on SPS and higher reliability of power supply hardware. The invertor type, with a Pulse Width Modulation (PWM) control, offers a lower power consumption and a more compact size, which could make it a more attractive option for economical low-cost production. The development of pulse generators is still ongoing.

## Materials

The SPS process is suited to a number of materials, including conductive and non-conductive powders. An example of suitable materials for SPS is provided in Table 1; these include metals, ceramics, cermets, intermetallic compounds and others.

When using non-conductive materials, where no sparking occurs between powder particles, it is considered that the effect of on-off DC pulse current still exists, energising particles, which results in an enhancement of the sinterability and densification rate of the material. The large pulsed energy generates an electro-magnetic field effect, such as an electro-migration, and preferential orientation of crystalline structure [18].

| | | SPS | HP Sintering |
|---|---|---|---|
| Temperature gradient sintering | | ◎ | × |
| Grain boundary controlled sintering | | ◎ | × |
| Fine crystalline structure controlled sintering | | ◎ | × |
| Temperature rise rate | | ◎ | × |
| Sintering time | Temperature rise time | Fast | Slow |
| | Holding time | Short | Long |
| Homogeneous sintering | | ○ | ○ |
| Expandability | | ◎ | △ |
| Productivity | | ◎ | △ |
| Investment in equipment | | ○ | △ |
| Running cost | | ◎ | △ |
| (◎ excellent \| ○ good \| △ fair \| × difficult) | | | |

*Table 2 Comparison of the characteristics of SPS and HP sintering*






## Comparing traditional sintering processes to Spark Plasma Sintering

The method of applying heat directly to the compact results in extremely high heating and cooling rates, and is therefore capable of reducing sintering time from hours to minutes. Compared with conventional sintering, the SPS method has demonstrated superior material properties, as it can offer a structure tailoring effect, minimise grain growth, enhance electro-migration and provide a strong preferential orientation effect.

A comparison of various sintering techniques and the resulting HV Vickers hardness is shown in Fig. 11 for an $Al_2O_3$ example. The results indicate that SPS offers hardness equal to and greater than processing by HIP or conventional hot press sintering. A comparison of specific characteristics of the SPS method, against conventional Hot Press (HP) sintering, is shown in Table 2.

As a sintering technique, SPS has drawn considerable attention as one the newest rapid sintering methods. The novel process also benefits from low power consumption of between 1/5 and 1/3 that of conventional sintering techniques, such as pressureless sintering, hot press sintering and Hot Isostatic Pressing (HIP).

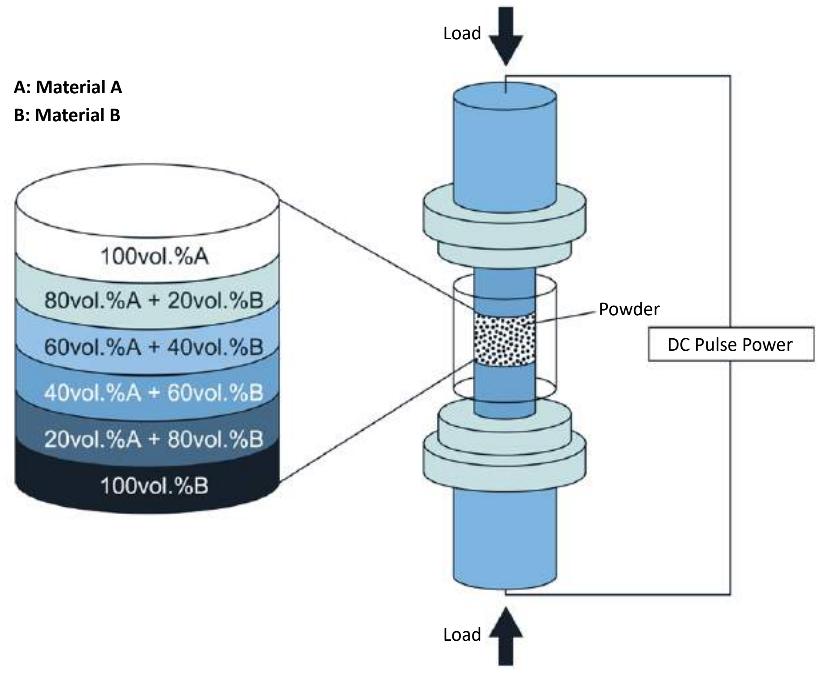



*Fig. 13 A typical fabrication process for FGMs by Spark Plasma Sintering*

## Examples of SPS process applications

### Functionally Graded Materials

Functionally Graded Materials (FGMs), often referred to as having 'dream' properties, are advanced materials characterised by a gradual variation in composition and structure, resulting in changes to the properties of the component. The original concept of FGMs was proposed in 1984 by material scientists in Japan during an aerospace research project.

Examples of bulk FGM compacts, produced by Spark Plasma Sintering, are demonstrated in Fig. 12. Seen from the left, (a) $ZrO_2$(3Y)/stainless steel compact with six interlayers, (b) $ZrO_2$(3Y)/nickel compact with seven interlayers, (c) copper/stainless steel compact with five interlayers, (d) aluminium/polyimide compact with three interlayers and, on the right, (e) $Al_2O_3$/titanium compact with three interlayers. The SPS process resulted in full-density sintered compacts, with no micro-cracks detected.

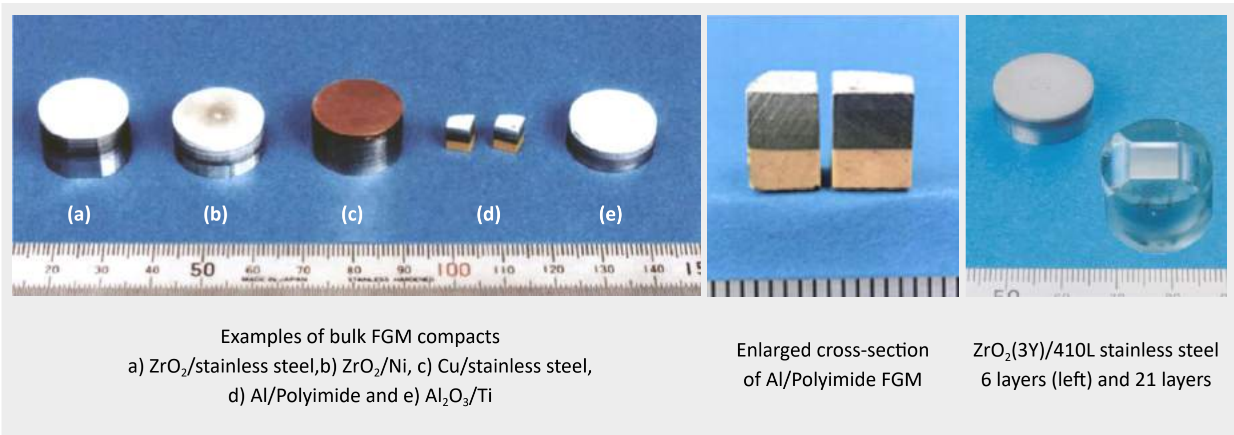



*Fig. 12 Typical examples of bulk FGMs*

Utilising a temperature gradient sintering technique of SPS, the process has successfully created a wide range of bulk FGMs with multiple layers, including various systems of $ZrO_2$/stainless steel, $ZrO_2$/TiAl, $ZrO_2$/Ni, $Al_2O_3$/stainless steel, $Al_2O_3$/Ti, $Al_2O_3$/Ti-6Al-4V, WC/stainless steel, WC/Co, WC/Ni, Cu/stainless steel, $SiO_2$glass/stainless steel, Al/polyimide resin, Cu/phenol resin and Cu/polyimide resin materials, etc. [19-22].

Fig. 13 shows a schematic illustration of an SPS temperature gradient die assembly and an example of multi-layered $ZrO_2$(3Y)/stainless steel FGMs compact, which contains a 3 mol.% yttrium partially stabilised zirconia (PSZ) powder, a 410L stainless steel powder and mixed powders of the two as intermediate layers with a different volume fraction. The FGM powders were stacked in a graphite temperature-gradient die of 20 mm internal diameter. The stainless steel powder has an average particle size of 9 µm while the PSZ powder is of granulated particles with an average particle size of 50 µm (its crystalline size is 350 Å). The sintering pressures used were 20–40 MPa, SPS temperatures of 1243–1293 K, with a temperature rise rate of 50 K/min measured near the stainless steel layer [20, 21].

**Horn-tip tool for an ultrasonic homogeniser**

Ultrasonic homogenisers act through the rapid vibration of a titanium probe, or horn, transmitting ultrasonic energy to the sample. The vibration causes homogenisation directly through the ultrasonic forces as well as through cavitation, where the rapid formation and collapse of bubbles occurs as a result of the vacuum formed when the probe retracts. Conventional titanium horn-tips, although chemically stable and mechanically easy to produce to the desired shape, result in low wear resistance, can lead to contamination and have a short life span. Alternative options, such as brazed $ZrO_2$ plates on a Ti body, can result in weakness at the brazed layer. Monolithic ceramic horn-tips have good hardness, but are brittle and can result in a short life span.

The FGM horn-tip shown in Fig. 14 is based on the optimised sintering conditions of $Al_2O_3$/Ti-Ti, with a five layered $ZrO_2$/Ti/Ti-6Al-4V alloy FGM developed for the structure. The ceramic-metal material achieved a hardness of HV 1364 and, due to the the high hardness at the surface, offered greatly improved corrosion resistance during the cavitation process. A sintering temperature of 1573 K, at a pressure of 30 MPa, resulted in the lowest 17 mg wear amount following a 50 h homogenising operation test.

The life span of the new horn-tip has proved to be around eight-to-ten times greater than conventional options, without cracking, peeling or breakage. It is expected that remarkably less contamination will present a highly reliable production process, and the available large-sized horn-tip encourages higher output power oscillation with much better productivity.

**Sputtering target fabrication**

With the SPS process, highly-dense sintered products can be fabricated at a much lower temperatures and with shorter heating up and holding times, compared with hot pressing and HIPing. Thus, sputtering target materials are another application field for SPS that can provide positive results. Indeed, several companies have developed a profitable business using SPS in this way.

Fig. 15 shows a typical example of a large-sized metallic sputtering target with a diameter of 350 mm produced by a large-size SPS system. When producing this part by SPS, productivity was approximately seven-to-eight times higher than conventional sintering of HP and HIP

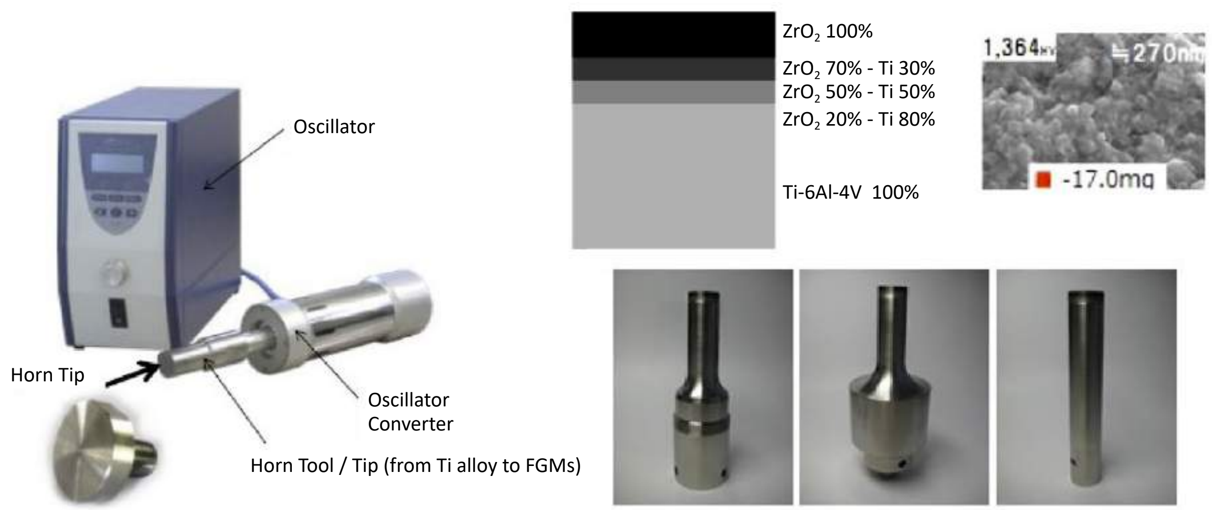



*Fig. 14 Ultrasonic homogeniser and $ZrO_2$/Ti alloy system FGM horn tip tool (manufactured by Mitsui Electric Co.,Ltd, Japan)*

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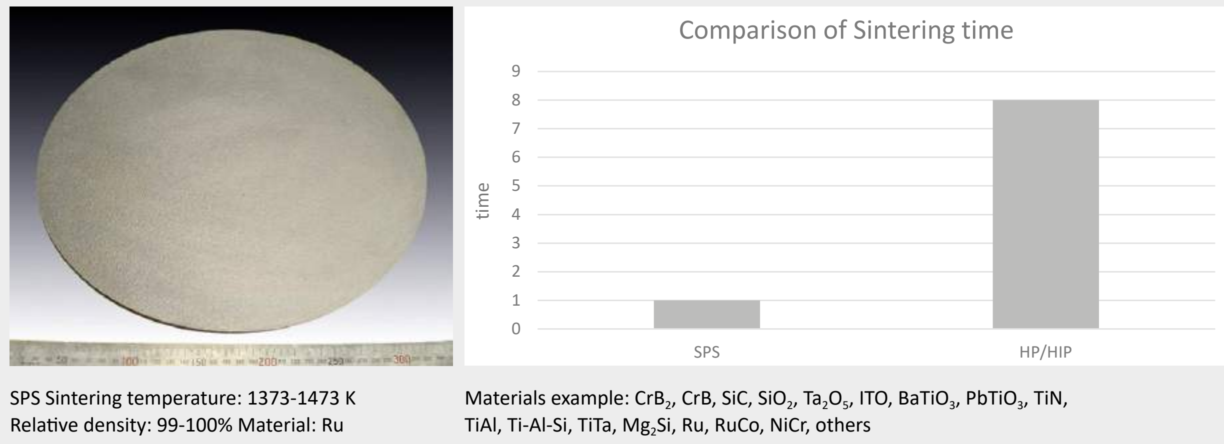



*Fig. 15 Example of Ø350 mm large-size metallic sputtering target material*

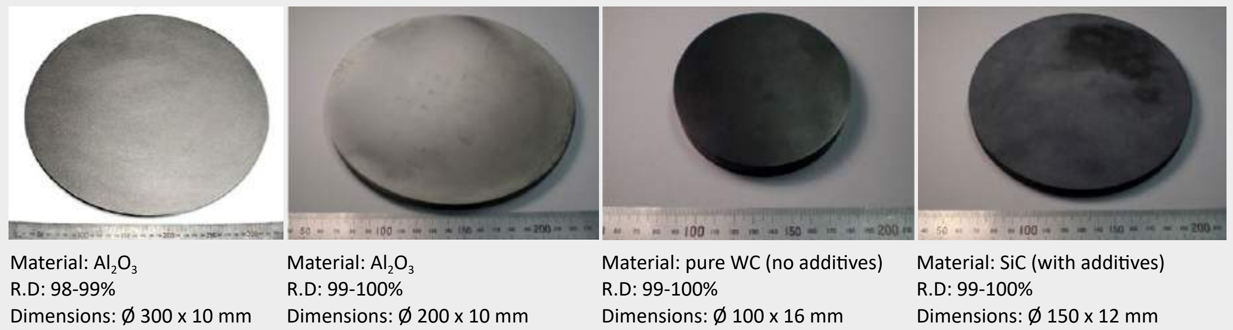



*Fig. 16 Example of large-size ceramics by SPS*

processes. Also, due to the obtained finer grain size of the SPS sputtering target materials, superior sputtering performances can result where, for example, no splashing phenomenon occurs in the coating process.

Large-sized oxide ($Al_2O_3$, $ZrO_2$, $SiO_2$), carbide (WC, SiC, $B_4C$), nitride ($Si_3N_4$) and boride ($TiB_2$) ceramic materials have also been fabricated homogenously with finer grain size and almost full density. The samples shown in Fig. 16 were investigated by SEM and it was observed that almost no residual micro pores and no cracks were present in the sintered compacts.

**Pure WC (tungsten carbide) aspheric glass lens mould**

The growing demand for in-vehicle camera systems for monitoring road conditions, as well as general surveillance and security cameras, has greatly increased the need for the cost-effective production of high performance aspherical glass lenses used in the digital cameras. To meet this need, SPS has been utilised in the production of moulds used to form the aspherical glass lenses. The mould consists of three pieces; an upper punch, lower punch and sleeve die part. Fig. 17 shows examples of such moulds used commercially in the optics industry, which are made from a binderless pure-tungsten carbide (WC single phase, HV 2600) material.

The SPS moulds were homogenously consolidated in nano-structured fine grain size material. By using an ultra-fine grinding machine, a superior mirror surface finish, with a roughness of Ra 2-6 nm, can be obtained. The advantages of SPS pure WC are that no

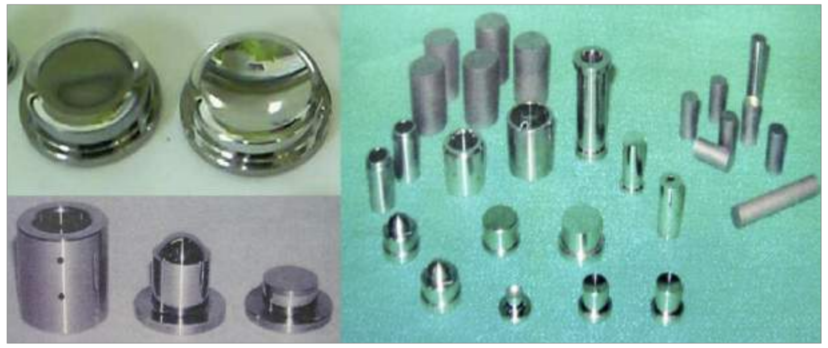
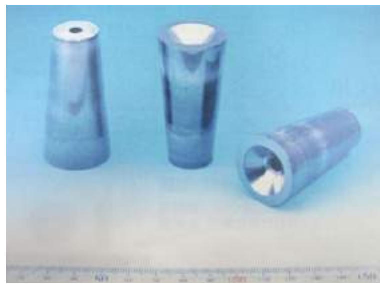


*Fig. 17 Examples of pure WC Aspheric glass lens mould materials*


Material: $Al_2O_3$ Length: 60mm
Outer dia. (Tapered):30/15mm
Inner dia. (Straight):6mm

| | General commercial products | SPS sintered nozzle | Advantage of SPS sintered nozzle |
|---|---|---|---|
| Vickers hardness (HV) | 900 - 1100 | 2100 - 2200 | High hardness |
| Relative density (%) | 91 | 100 | High density |
| Surface | Rough | Mirrored surface | Mirror finished surface by near-net shape |
| Lifetime | One day | Ten days | Ten times longer lifetime |

*Fig. 18 Comparison of SPSed nozzle and other commercial product*

additives are used in the solid-phase sintering and a finer grain size as well as higher oxidation resistance is achieved, compared to conventionally produced binderless WC materials. By running a 10 h oxidisation test in an atmospheric furnace at 973 K, a 30-60% better oxidisation rate in volume (g/cm$^3$) was demonstrated.

**Complex near-net shape forming of $Al_2O_3$ blasting nozzle**

An example of an $Al_2O_3$ ceramic nozzle, used in sand-blasting apparatus, is shown in Fig. 18. Comparative testing between a conventionally manufactured nozzle and one made using SPS process, was undertaken in real-time blast operating conditions. The SPSed $Al_2O_3$ nozzle achieved ten times longer life span than a conventionally sintered one produced in an atmospheric pressureless sintering furnace.

The SPS nozzle is produced without post processing and has Vickers hardness of HV 2100-2200, compared to a conventional nozzle with HV 900-1100. Produced to near-net shape accuracy, a Ra 0.64 µm surface roughness was obtained.

**Emerging super-plasticity and high specific strength of aluminium-Si alloy materials**

The SPS process can be used to achieve nanostructured dense high-silicon/aluminium alloys. The rapidly solidified Al-Si powder, of average particle size 120-150 µm, silicon content 12–17% or higher and nanocrystalline structure, was successfully consolidated into Ø 60–120 mm x 40–60 mm cylindrical compacts with between 600–800 nm grain size as shown in the TEM micrograph in Fig. 19. The sintered compacts, with relative density of almost 100%, were obtained at temperatures of 723–773 K, applied pressures of 100–150 MPa and heat up and holding time of 20 min. When the Ø 60 mm x 40 mm nanostructure SPSed bulk body was formed into a three dimensional shape for an automotive engine piston component, by a high-speed forging press machine, it was demonstrated to provide full forming for lengths of 75 mm within 15–20 seconds per stroke with the strain rate of $10^{-2}S^{-1}$ or higher. The results indicate the phenomenon of 'super-plasticity' occurred, improving the ductility and elongation of the sintered compact. The tensile strength was 350 MPa and it was approximately 1.5 times stronger than a conventionally forged component. This Al-Si alloy with nanostructural material is expected to find wide applications in various electric appliances, electronics and automotive components [23].

**Porous materials prepared by SPS**

The fabrication of both metallic and ceramic porous structures is another application where SPS could offer advantages over existing sintering methods. In this example, the pure titanium and $ZrO_2$(3Y) bead structures seen in Fig. 20 are formed by applying a low sintering pressure in the range of 0–5MPa, demonstrating that it is possible to obtain high porosity with higher bonding strength at the neck portion.

Potential commercial applications for this process include materials for a bio-reactor, filters, artificial bone joints, vent core materials for a plastic moulding die, electric and hybrid-electric vehicle applications, solid oxide fuel cell (SOFC) batteries, thermoelectric semi-conductors, heat spreaders for thermal conductive components and others.

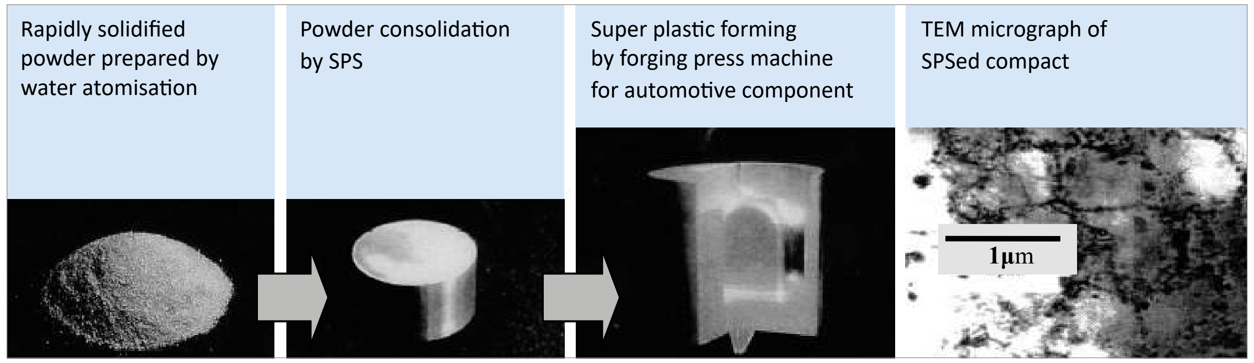



*Fig. 19 Appearance of Super-plasticity on automotive component*





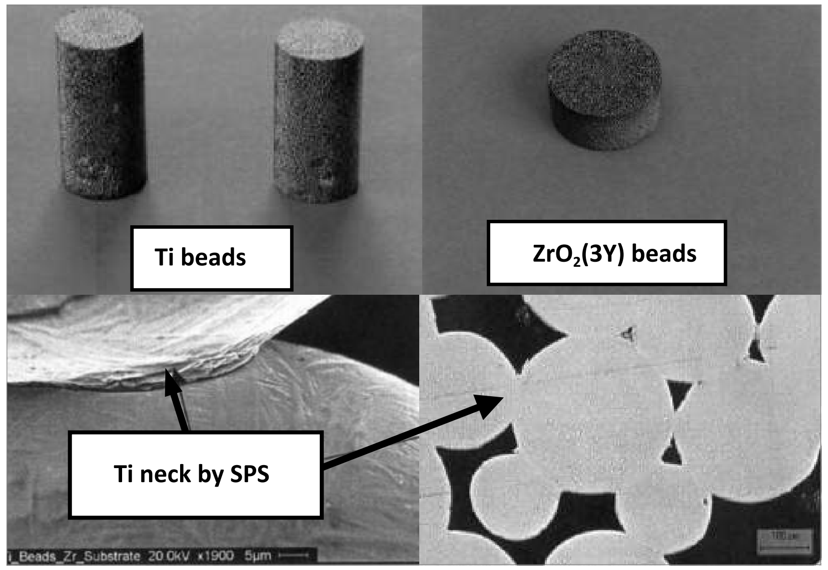




*Fig. 20 Examples of porous material*

**Fine-WC/Co hard alloy FGMs for die & mould and wear-resistant materials industries**

As a typical high-wear resistant material, WC/Co or WC/Ni system cemented carbides are now widely used in various press-stamping dies and cutting tools for industrial applications. Although the fabrication of WC/Co hard alloys usually takes many hours, with the development of new automated SPS systems, it is proving possible to sinter such materials in a significantly shorter period, taking advantage of the characteristics inherent in SPS rapid sintering technology.

Table 3 highlights the typical mechanical properties of SPS fine WC system hard alloy products. Fig. 21 shows the production machine's system configuration and an outside view of the fully-automated five-stage chamber-type continuous SPS system. Using this full tunnel automated system and optimised conditions, large square-shaped WC/Co cemented carbide hard alloys, with dimensions of 70 mm × 100 mm × 5-20 mm, were homogeneously fabricated in a shorter sintering time and with a finer grain size than conventional sintering methods. The fine-WC/Co hard alloys obtained by SPS show higher hardness, transverse rupture strength and fracture toughness, than those obtained by conventional methods.

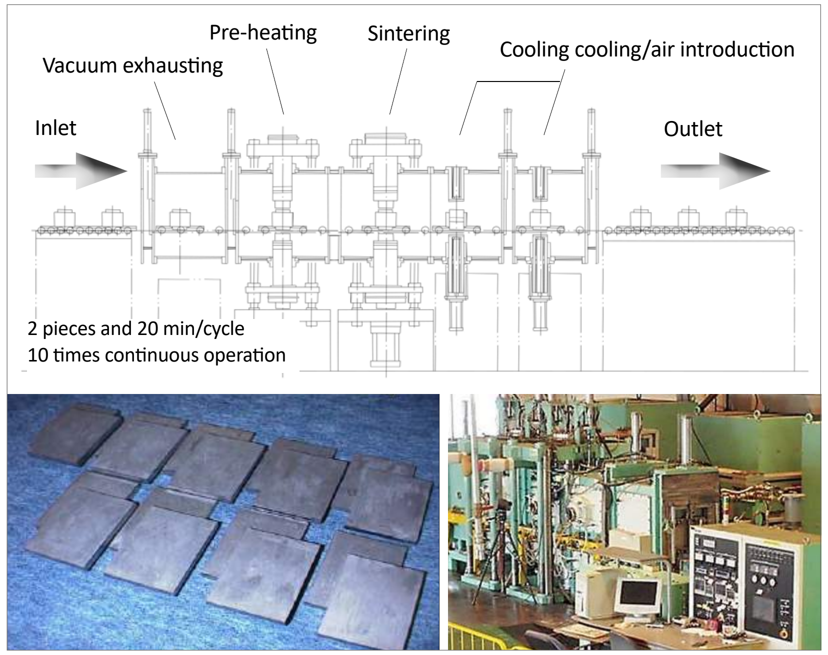



*Fig. 21 System configuration and outside view of tunnel-type SPS and large-size 100×70 mm WC/Co cemented carbide hard-alloy compacts fabricated in 10 times continuous operation*

| Product code name | Co content wt.% | WC pdr. grain size µm | Density g/cm$^3$ | Hardness mHV | Transverse rupture strength MPa | Fracture toughness K1C |
|---|---|---|---|---|---|---|
| TC-05 | <2 | <0.5 | 15.2 | 2350 | 2300 | 6.2 |
| TC-10 | <4 | <0.5 | 15.0 | 2150 | 2640 | 6.5 |
| TC-20 | <6 | <0.5 | 14.8 | 2050 | 2940 | 7.3 |
| M78 | 0 | <0.2 | 15.4 | 2600 | 1500 | 5.1 |
| WC100 | 0 | <0.08 | 15.6 | 2700 | 1470 | 5.6 |
| NC100 | 0 | <0.5 | 15.4 | 2570 | 1180 | 5.4 |

*Table 3 Typical mechanical properties of Fine WC/Co hard alloys by SPS*

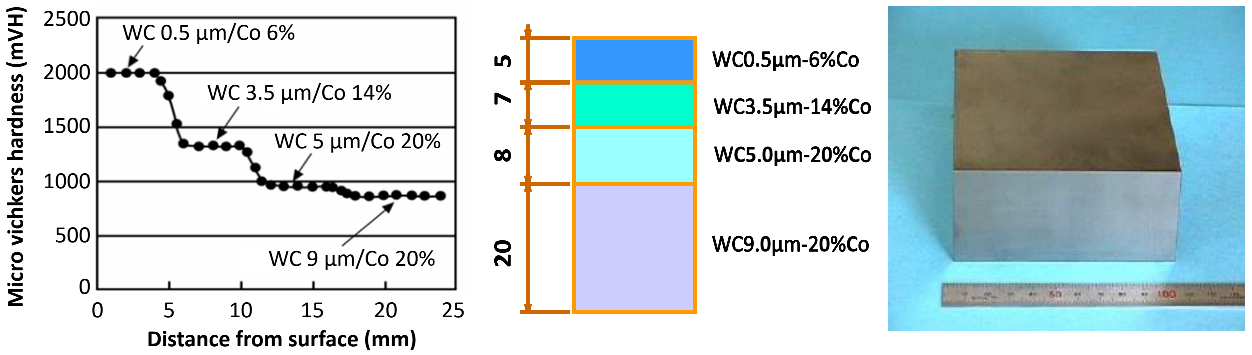



*Fig. 22 Large-size WC/Co FGM fabricated by SPS (100 mm × 100 mm × 40 mm) and profiles of micro-hardness on Co content graded cemented carbide by SPS*

**WC/Co and WC/Co/Ni FGMs for industrial applications**

In the first example, a WC/Co FGM block, compositionally graded by cobalt content and measuring 100 × 100 × 40 mm, was produced using SPS within an hour (Fig. 22) [32, 33]. The FGM was then machined by numerically-controlled wire-cut electrical discharge machine to remove smaller pieces of the material. As shown in Fig. 23, the smaller piece of WC/Co FGM was ground to form the specified profiles. The fine WC/Co FGM hard alloy demonstrated high hardness in the top layer and higher strength and fracture toughness in the bottom layer than a monolithic WC/Co hard alloy material. When assembled to form a press stamping progressive die set, the FGM sample achieved an approximately three and a half to ten times longer life time compared with conventional commercial WC/Co cemented carbides.

In a further project, a weld-able WC/Ni FGMs screw, used in an extruding machine, was also produced using the SPS process (Fig. 24). The working life proved to be over three times longer than that of the conventional screw, resulting in more than 3000 h service compared to around a typical 800 h in the conventional screw. This FGM screw has proved a successful example of SPS manufacturing and has now been in operation for a number of years at Japan's Hokkaido Electric Power company [24].

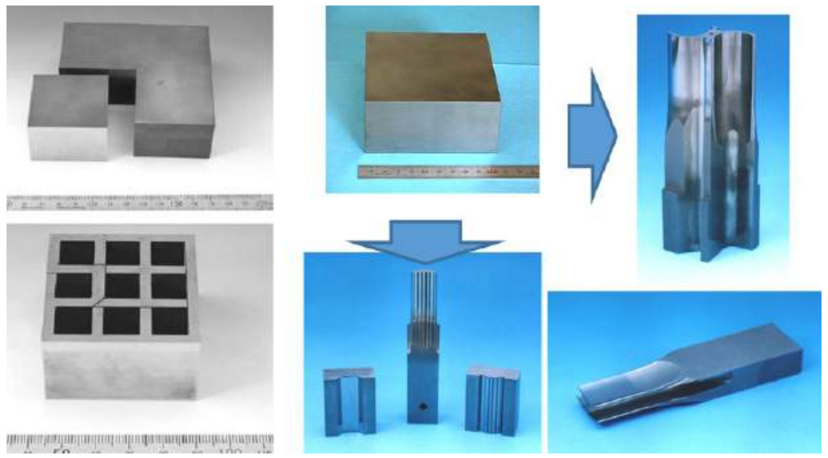
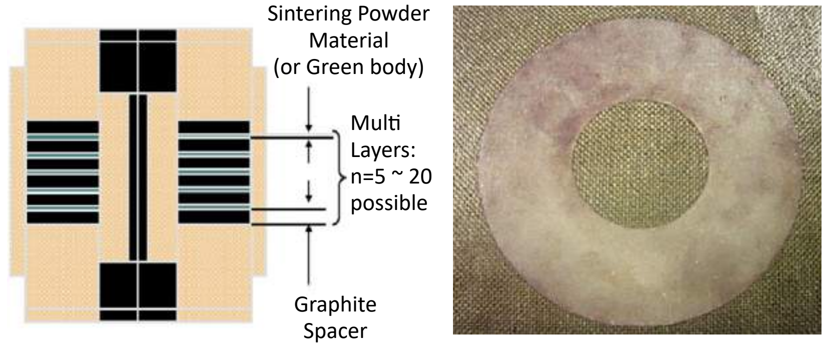


*Fig. 23 Example of press stamping die and punch made of WC/Co FGMs for electronic component*

*Fig. 24 Weldable WC/Ni FGMs tile and the FGMs screw product for the extruding machine*

**Diamond dicing blades for cutting tool industry**

The manufacture of diamond dicing blades, for use in the cutting tool and wear-resistant materials industry, is a further example of how the SPS process can offer distinct advantages. As shown in Fig. 25, metal bonded dicing blades of 100/150 mm diameter and 0.35/0.4 mm thickness can be produced with a flatness level within ± 20 µm and minimal residual stresses. Obtaining such flatness by SPS eliminates a grinding process. The sintered WC/Co plate has relative density 99-100% and a Young's modulus 500-580 GPa was attained under SPS temperature of 1473–1523 K. To achieve series production, in this example continuous SPS operation through multiple work shifts per day resulted in the simultaneous fabrication of 15–20 plates per batch.




| | |
|---|---|
| Outer Diameter | Ø 100/150 mm |
| Inner Diameter | Ø 40/60 mm |
| Thickness | 0.35/0.40 mm |
| SPS sintering temp. | 1473 ~ 1523 K |
| Sintering Pressure | 40 ~ 50 MPa |
| Relative Density | 99 ~ 100% |
| Young Modules | 500 ~ 580 GPa |
| **Flatness** | **<± 20 µm** |

*Fig. 25 WC/Co sintered very thin plate with diamond of Dicing Blade*

**Other Industrial Applications**

Although not discussed in this article, research into the use of SPS in other categories of materials includes MMC/FRC/FRM composites, thermoelectric semiconductors of SiGe, $Bi_2Te_3$, $FeSi_2$, $CoSb_3$, $MnSi_2$, $Mg_2Si$ systems for clean energy generation, Nd-Fe-B, $Sm_2Co_{17}$ and ferrite for magnetic materials, $MgB_2$ superconducting materials [25], $BaTiO_3$ [26], $PbTiO_3$ dielectric materials, shape memory alloys, solid cell materials, glassy metals, optically functional materials and nanocrystalline materials [27]. All could be promising candidates for industrial SPS applications [28].

Applications for SPS 3D forming methods and titanium/hydroxyapatite (HAP) for biomedical applications could also move from the R&D/prototype level into practical use in the near future [29,30].

## Summary & outlook

In this article, the history and fundamentals of SPS, as well as the wider availability of SPS systems and related industrial applications have been discussed. Typical advantages of SPS processing are indicated in the synthesis of FGMs, nanocrystalline materials and wear-resistant hard materials. Due to the versatility of SPS, the remarkable and rapid growth in the number of presented papers and patents in the last decade should be noted, resulting from a new, worldwide adoption of SPS technology in both the scientific community and the industrial sector.

SPS features an electrical energy concentration at areas where current flows easily. In terms of the high energy density of dynamic sintering, further study of these characteristics will lead to the successful advancement and expansion of SPS applications for commercial production. The SPS process has the potential to become a major manufacturing tool in the automotive, electronics, mould & die, tooling, clean energy and aerospace industries, to name just a few, with opportunities in both high-value added, small scale and mass-production markets.

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## References


[1] M. Tokita, "Development of Advanced Spark Plasma Sintering (SPS) Systems and Its Industrial Applications", *Ceramic Transaction* Vol.194, Am. Ceram. Soc., Wiley-Interscience, (2006) 51-60

[2] Z.A. Munir, U.Anselmi-Tamburini, M. Ohyanagi, "The effect of electric field and pressure on the synthesis and consolidation of materials: A review of the spark plasma sintering method", *J. Material Science*, 41 (2006)763-777

[3] S. Grasso, Y. Sakka and G. Maizza, "Electric current activated/assisted sintering (ECAS): a review of patents 1906-2008", *Science and Technology of Advanced Materials*, Vol. 10(2009)1-24

[4] G.F. Taylor, "Apparatus for making hard metal compositions", U.S. Patent No. 1, 896.854 (1933)

[5] K. Inoue, "Electric Discharge Sintering", U.S.Patent No 3,241,956(1966) ( Ser. No. 247,387 filed 1962)




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[6] K. Inoue, "Apparatus for electrically sintering discrete bodies", U.S.Patent No 3,250,892 (1966)

[7] M. Tokita, "Trends in Advanced SPS Spark Plasma Sintering Systems and Technology", *J. Soc. Powder Technology*, Jpn., 30[11] (1993)790-804

[8] M. Tokita, Development of Automatic FGM Manufacturing Systems by the Spark Plasma Sintering (SPS) Method", *Ceramic Transaction* Vols. 114, Am. Ceram. Soc., (2001) 283-290

[9] Y. Miyasaka, M. Tokita, H. Karasawa, F. Nishiyama, "Electric joining methods and apparatus and a joined unit of members", U.S.Patent No. 6, 515, 250(2003)

[10] K.A. Khor, X.J. Chen, S.H. Chan, L.G. Yu, "Microstructure-property modifications in plasma sprayed 20 wt% yttria stabilised zirconia electrolyte by spark plasma sintering technique", *Materials Science and Engineering* A366, (2004) 120-126

[11] M. Yu, S. Grasso, R. Mckinnon, T. Saunder, M.J. Reece, *Adv. in Applied Ceramics*, 116 (1), (2016), 24-26

[12] K. Ozaki, K. Kobayashi, T. Nishio, A. Matsumoto, A. Sugiyama, "Sintering Phenomena on Initial Stage in Pulsed Current Sintering". *J. Jpn. Soc. Powder and Powder Metallurgy*, 47(2000)293-297

[13] Z. Shen, M. Johnsson, Z. Zhao and M. Nygren, "Spark Plasma Sintering of Alumina", *J.Am.Ceram. Soc.* 85[8] (2002)1921-27

[14] X. Song, X. Liu and J. Zhang, "Neck Formation and Self-Adjusting Mechanism of Neck Growth of Conducting Powders in Spark Plasma Sintering", *J. Am. Ceram. Soc.*, 89 (2) (2006)494-500

[15] R. Chaim, "Densification mechanisms in spark plasma sintering of nanocrystalline ceramics", *Materials Science and Engineering*, A 443 (2007) 25-32

[16] T. Misawa, N. Shikatani, Y. Kawakami, et al., "Influence of Internal Pulsed Current on the Sintering Behavior of Pulsed Current Sintering Process", *Material Science Forum*Vols.638-642, (2010)2109-2114

[17] Y. Makino, "Crystallographic behaviors of nano-powder anatase consolidated by SPS method", *CeramicTransaction* Vol. 194, Am. Ceram. Soc., Wiley-Interscience, (2006) 301-312

[18] M. Tokita, "Method and system for automatic electrical sintering", US. Patent No 6,383,446 B1 (2002)

[19] F. Watari, H. Kondo, S. Matsuo, R. Miyao, A. Yokoyama, M. Omori, T. Hirai, et al., "Development of Functionally Graded Implant and Dental Post for Bio-Medical Application", *Material Science Forum* Vols.423-425(2003)321-326

[20] M. Tokita, "Development of Large-Size Ceramic/Metal Bulk FGM Fabricated by Spark Plasma Sintering", *Materials Science Forum*, Vols.308-311(1999)83-88

[21] M. Tokita, M. Kawahara, M. Sonoda, M. Omori, A. Okubo and T. Hirai, "Preparation and Triborogical Characterization of ZrO2(3Y)+20wt%Al2O3/410L Stainless Steel Composite Functionally Graded Material Fabricated by Spark Plasma Sintering Method", *J. Jpn. Soc. Powder and Powder Metallurgy*, 46 (3) (1999)269-276.

[22] M. Belmonte, J.Gonzales-Julian, P. Miranzo, M. I. Osendi, "Continuous in situ functionally graded silicon nitride materials", *Acta Materialia* Vols.57, 9(2009)2607-2612

[23] N. Kuroishi, "High-Strain-Rate Superplasticity in Sintered Pre-Forms Produced by Plasma Spark Sintering", Proc. NEDO Int. Sympo. on Functionally Graded Materials, Tokyo, Japan, (1999) 67-74

[24] M. Tokita, "Development of Square-Shaped Large-size WC/Co/Ni system FGM Fabricated by Spark Plasma Sintering (SPS) Method and Its Industrial Applications", *Materials Science Forum*, Vols.492-493 (2005)711-718

[25] J. Schmidt, W. Schnell, Y. Grin. R. Kniep, "Pulse plasma synthesis and chemical bonding in magnesium diboride", Solid State Sciences, 5(2003)535-539

[26] T. Takeuchi, M. Tabuchi, Y. Suyama and H. Kageyama, "Preparation of Dense BaTiO3 Ceramics with Submicrometer Grains by Spark Plasma Sintering", *J. Am. Ceram. Soc.*, 82 (4) (1999)939-943

[27] U.Anselmi-Tamburini, J.E. Garay, Z.A. Munir, "Fast low-temperature consolidation of bulk nanometric ceramic materials", *Scripta Materialia*, 54(2006)823-828

[28] Y. Makino, K. Mizuuchi, M. Tokita, Y. Agari, M. Kawahara and K. Inoue," Synthesis of new structural and functional materials by SPS processing", *Materials Science Forum*, Vols.638-642 (2010)2091-2096

[29] M. Tokita, "The potential of Spark Plasma Sintering (SPS) method for the fabrication on an industrial scale of Functionally Graded Materials", *Advances in Science and Technology* Vol. 63 (2010)322-331

[30] M. Tokita, "Development of ZrO2/Ti alloy FGMs Horn tip tool for Ultrasonic Homogenizer by Spark Plasma Sintering (SPS) method", proceedings of ISFGMs2018 15th International symposium on Functionally Graded Materials, Kitakyushu, Japan (Aug. 2018) O-17/1-6