Germany

Sintering Ceramic Materials with FAST/SPS Machines

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FAST-SPS sintering (Field-Assisted Sintering Technique/Spark Plasma Sintering) of metallic materials has long been state of the art. One major application is the diamond tool industry. Recently, there have been a number of attempts to sinter ceramic materials with this technology in order to utilise the many benefits of FAST-SPS. However, sintering ceramics is much more challenging. The lack of electrical conductivity, the brittleness of the material and its reaction with the mould material make it more difficult to get fast results. This paper covers several materials such as B_4C, Al_2O_3, ZrO_2 TiB_2 as well as others. It also looks at different applications such as defence, sputtering targets, jewellery and in the electronics industry. Another focus of the paper is graded materials and heterogeneous materials, e.g. bonding of ceramic powders to metallic surfaces.

Introduction

For the production of solid parts from powder, FAST-SPS-sintering has become an established manufacturing process. The process itself is closely associated with the name "Dr Fritsch" – one of the pioneers of FAST-SPS-sintering. Founded in 1953, Dr. Fritsch Sondermaschinenbau (Dr Fritsch) has been manufacturing sintering equipment for 70 years. We believe that the first commercially available machine was developed by Dr Otto Fritsch in the late 1950s.

Initially, the FAST-SPS process was used to solidify metal powder around a large piece of natural diamond. This diamond had a small hole and was used as a drawing die – a device to reduce a given metal wire to a smaller diameter in a drawing process. As diamond is sensitive to high temperature, the powder technology was used to bond the diamond to a metal ring so that it could be held in place.

The next step was to use diamond grit and metal powder to make diamond saw blades, diamond grinding wheels and other diamond tools. All these tools are mainly produced with FAST-SPS technology.

Dr. Fritsch has now supplied more than 1000 machines to the industry. In addition to sintering machines, Dr. Fritsch now offers other equipment, powder materials, joint product development, training in sintering technology and pilot production. The company's customers are able to test new materials, as well as produce small-scale product samples to get into new markets.

Difficulties hindering a scientific approach

Although the FAST-SPS process (naturally) follows scientific rules, the technology is not yet fully understood. Process parameters such as heating rate, specific pressure at a given time, process atmosphere, mould design, cooling parameters, insulation, material composition of the part and heating current application are only some of the parameters that need to be taken into account. There are so many factors influencing material behaviour, and therefore process control, that a strictly scientific approach does not yet seem possible. Therefore, this paper describes the possibilities for processing different materials with FAST-SPS-technology, rather than an in-depth case study of a single material.

A lot of the insights in FAST-SPS has been gained by the company in specific customer projects. Therefore, many process parameters are classified information covered by NDAs (Non-Disclosure Agreements).

In most cases, the first priority was to obtain a solid workpiece free of defects and cracks. The second objective was to maximise density to further improve the finished component's strength. The first objective, in particular, is sometimes very difficult to achieve, requiring many tests and modification of process parameters. This is a key qualification, especially for large components.

FAST-SPS-sintering of metal materials

Sintering metal materials with FAST-SPS is now a fairly standard process. As the material and the mould are conductive, current flows between the graphite electrodes of the machine, through the mould and through the workpiece (Fig. 1).

A typical FAST/SPS sintering cycle is shown in Fig. 2. The red line shows the actual sintering temperature. The material in a mould is first heated to a debinding temperature. At this temperature, residual binder such as oil, wax or organic binder can evaporate. Depending on the sensitivity of

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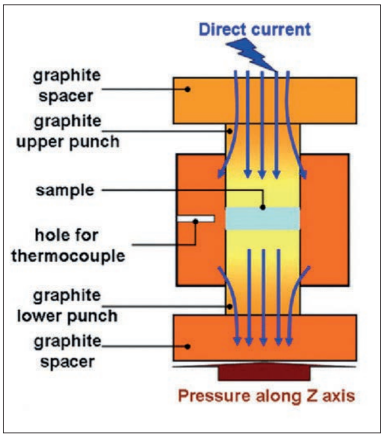


Fig. 1 Schematic showing a FAST-SPS system in the sintering zone [1]

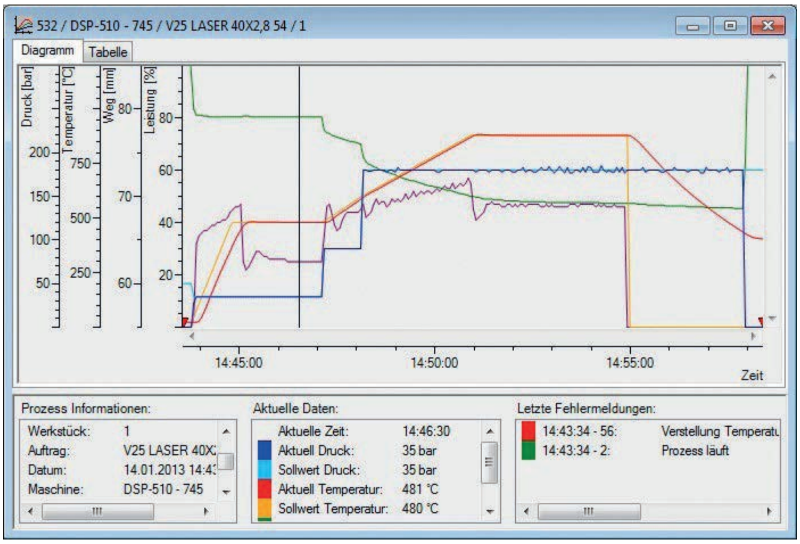


Fig. 2 A typical sintering cycle for metallic materials [2]

the material, debinding is often performed in a normal atmosphere and the fumes are extracted by an exhaust system. At the end of the debinding cycle, sintering is performed under vacuum. Once the vacuum pump is in operation, a small amount of inert gas can be used in addition or alternatively.

After the debinding stage, the temperature is raised at a defined rate to the final target temperature. The temperature is then held at this level for a dwell time. After this dwell time, sintering has taken place, the current is switched off and the mould cools down (cooling cycle).

The green line shows the distance between the graphite electrodes. At the beginning of the cycle, the distance between the electrodes is large and the electrodes are moved towards each other to make electrical contact.

During the debinding cycle, pressure is maintained at a minimum contact pressure. This low pressure allows dust to leave the mould without premature solidification. This avoids contamination from residual pelletizing or granulating agents.

After the debinding stage, the pressure is increased, the electrodes move further together and solidification of the material begins. The green line is almost parallel to the x-axis during the dwell time as the material reaches its final density. When the heating is switched off, some movement can be observed as the mould and material begin to shrink.

New challenges with FAST-SPS sintering of ceramic materials – selected materials and results

Unlike for metals, FAST SPS sintering of ceramics is the exception rather than the industry standard. In the past, the high temperatures, difficult tooling and very high electrical resistance of ceramics have been major challenges. These have prevented the technology from being more widely used in the ceramics sector.

But some key advantages have made the technology attractive, such as short cycle times and the use of mechanical pressure to bond the material. Now that more experience has been gained in this field, more ceramics are being processed by means of FAST SPS sintering.

However, many issues still require investigation: The risk of cracks in the workpiece, contamination of the target material by the mould material and the difficulty of temperature measurement in the mould are just a few of the main problems.

Various ceramic materials have been successfully sintered for many different applications at Dr. Fritsch. Here are a few examples from different application areas. It should be noted that the majority of the successful tests and experiments are covered by NDAs and therefore cannot be disclosed to the public.

Sintering MgB_2

During Daniel Wilkinson's work for his undergraduate degree (Bachelor thesis) at Oxford University, many samples of MgB_2 were sintered. This is a material that is widely known for its use in traditional superconducting devices.

The measured success of the production is appropriate to the level of "superconductivity". The results were very good in comparison with the conventional production of the components.

The complexity of the task was increased by the fact that not only tablets but also rings were manufactured. This is difficult because different thermal expansion coefficients cause the ring to shrink onto the central pin of the dies. Sintering was performed at around 1400 °C.

Fig. 3 Sintering of MgB_2 sintered with FAST-SPS [3, 4], courtesy of Daniel Wilkinson

Sintering B_4C plates for defence applications

In the defence industry, B_4C is a widely used material. It is very attractive as an armour material for bullet proofing and automotive applications thanks to its low density (2,52 g/cm³) and very high hardness. The raw material is supplied as a more or less coarse powder. The ability to apply pressure and temperature at the same time makes FAST-SPS technology attractive for production. B_4C changes its resistance at higher temperatures and becomes much more conductive, compounding the complexity of production. This increases the risk of partial overheating and the risk of inhomogeneous temperature distribution in a sintering mould. The result of inhomogeneous temperature in the mould can be seen in Fig. 4 (round pattern in a 100 mm × 100 mm plate). Cooling needs to be adapted to the mould design and can cause the product to crack.

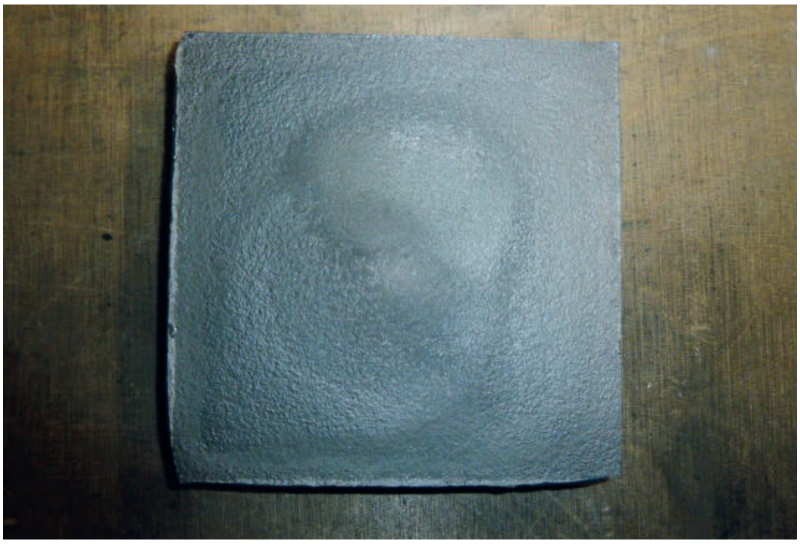


Fig. 4 B_4C plate 100 x 100 x 10 mm [2]

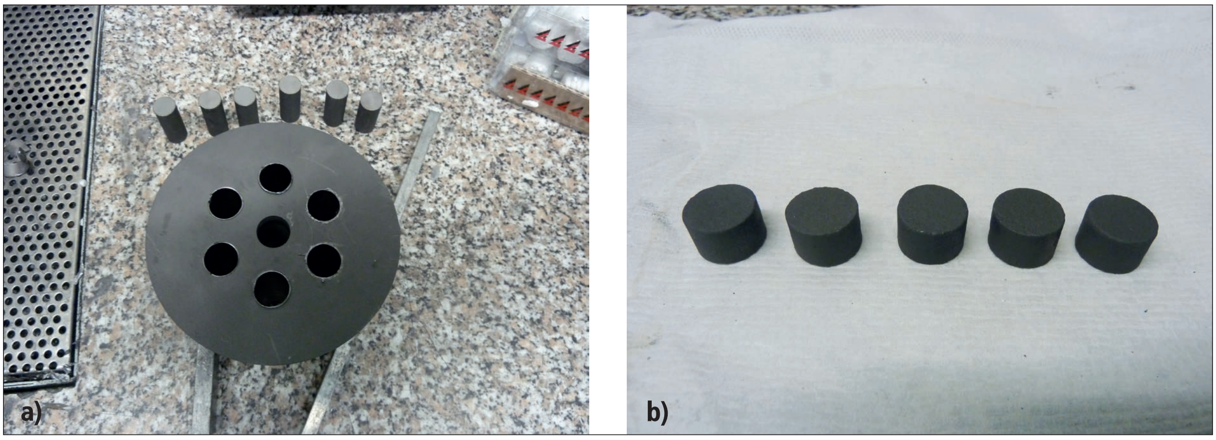


Fig. 5 a–b Graphite mould a) for B_4C parts and b) B_4C pellets [2]

Sintering B_4C pellets for nuclear power plants

B_4C is a form of boron that is very stable at high temperatures. Boron is an excellent neutron shielding material. In some nuclear power plants, these B_4C pellets are used as control rods. In order to reduce the nuclear chain reaction, they are moved between the uranium rods as required.

B_4C plates as components of a fusion reactor

In some of the more recent designs of fusion reactors, a first-level heat shield made of B_4C is used. Recently, there has been a switch from homogeneous B_4C to graded or bonded material combinations in some of these designs.

ZrO_2 for medical applications

ZrO_2 is a material that is widely used in medical applications. It is well known for its toughness. It can be therefore used for dental prostheses. In this application, a matrix mould was used to increase production capacity. The material of the mould and the release agent were the tricky issues in this application. In the past the customer

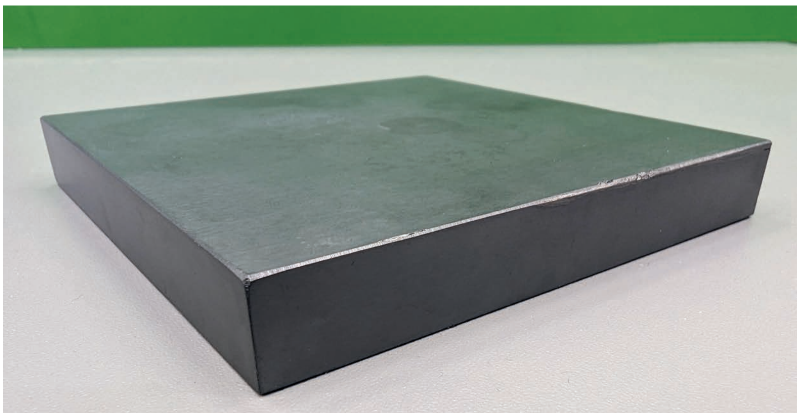
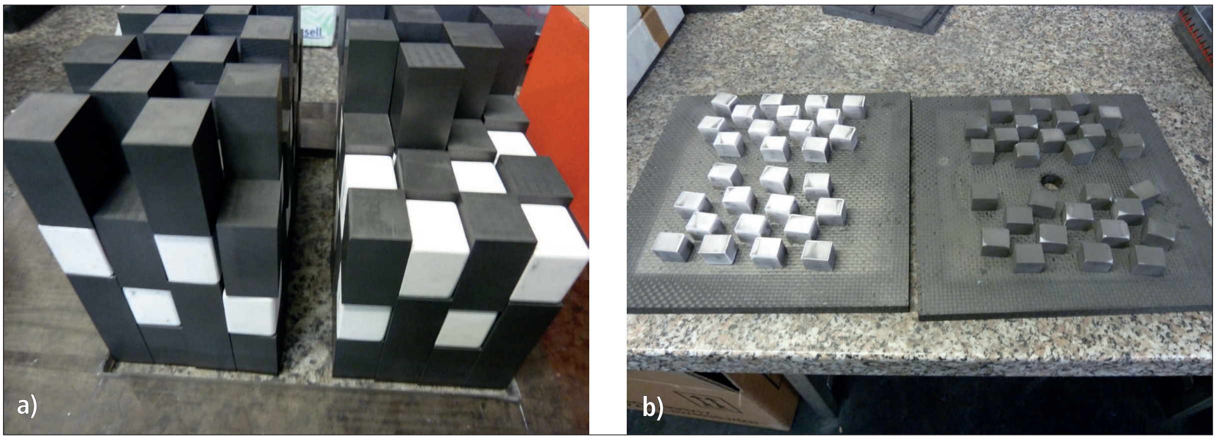


Fig. 6 Homogeneous B_4C plate 100 mm × 100 mm × 25 mm [2]



Figs. 7 a–b ZrO_2 parts with graphite multi mould [2]

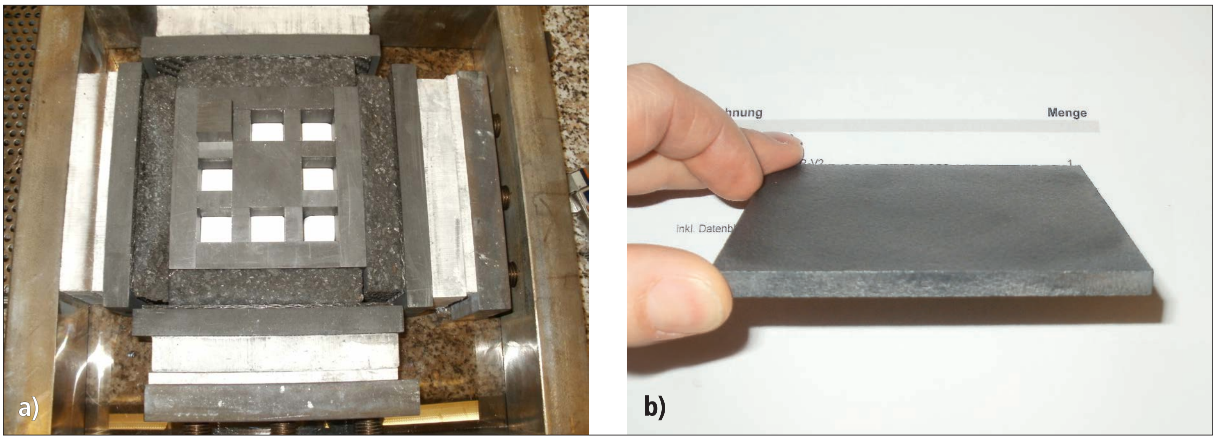


Fig. 8 a–b a) Al_2O_3 parts in a mould and b) sintered Al_2O_3 plate [2]

used to make large plates and then cut out the parts after sintering. With FAST-SPS, it proved better to produce the smaller parts first by means of cold pressing and then to sinter them in this multi-cavity mould using the near-net-shape approach.

Al_2O_3 for automotive applications

A number of smaller parts and larger sheets were produced for the automotive industry. The labour involved in assembling the moulds and the productivity of the batch process were difficult for the customer to justify and the project was discontinued.

SiC plates for armour and brake discs

Another good material for armour is SiC. It is a very hard and tough material. For testing purposes, some plates have been sintered. The use of SiC in brake discs is another application. A maximum level of brake dust that must not be exceeded is defined in the new Euro 7 standard. New brake concepts are therefore required.

In addition, ceramic brake discs are much lighter than the traditional cast iron material. In addition to the concept of using pure SiC for the brake discs, other concepts are working with an Al-SiC composite material.

Other ceramic materials

Other ceramic materials such as WC and TiB_2 have been successfully sintered by Dr. Fritsch.

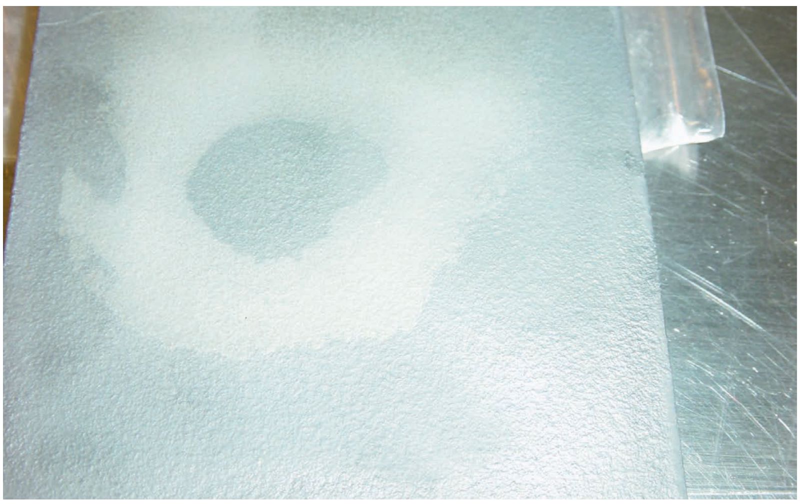


Fig. 9 SiC plate for armour [2]

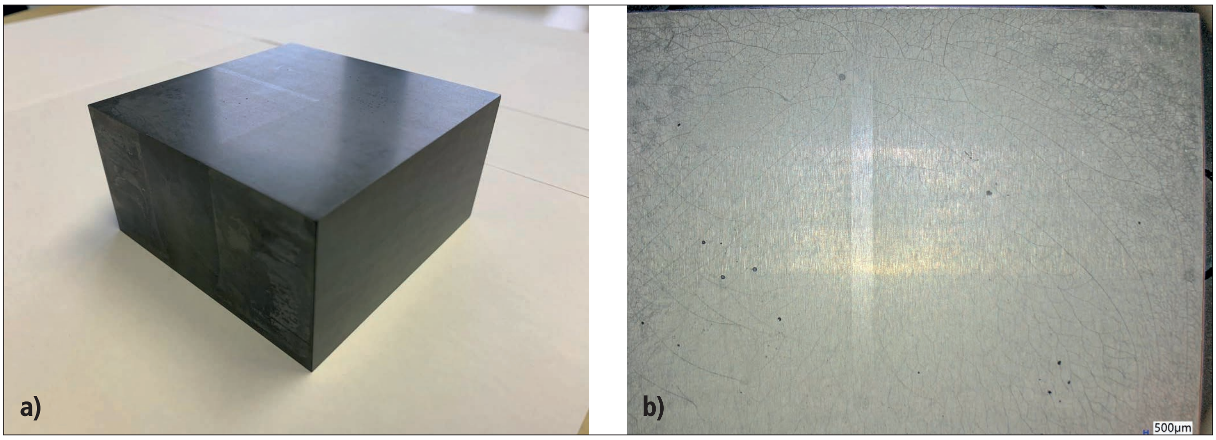


Fig. 10 a–b Composite material of B_4C and W [2, 3]

WC is hard and heavy. It is used for armour and shields in nuclear power plants.

TiB_2 is also used in armour and nuclear shields. In addition, it plays an important role in aluminium coating technology in evaporation boats. TiB_2 is one of the few ceramics with relatively high electrical conductivity. This makes it much easier to sinter in FAST-SPS-equipment.

The next level – graded material and bonded material

Dr. Fritsch has also been able to bond B_4C blocks with thin W (tungsten) coatings using FAST-SPS. Despite the fact that these materials have very different properties, a very strong bond was achieved. These tests were also carried out in combination with other tests related to fusion power plant research.

A number of tests have been carried out on a graded material, also with B_4C and W as material partners.

Fig. 12 shows a composite in which several layers of B_4C have been combined with layers of W. We therefore call it a laminated workpiece.

Ongoing research

All the figures above show pieces which were mostly intact. Most of the broken parts have been broken on purpose to reveal the inner structure of the parts. These parts are the result of very many tests, trials, revisions of process parameters and possibly more breakage. Typically, each new ceramic material requires its own set of process parameters, a different mould set-up and, in some cases, a completely new approach to achieved the desired success.

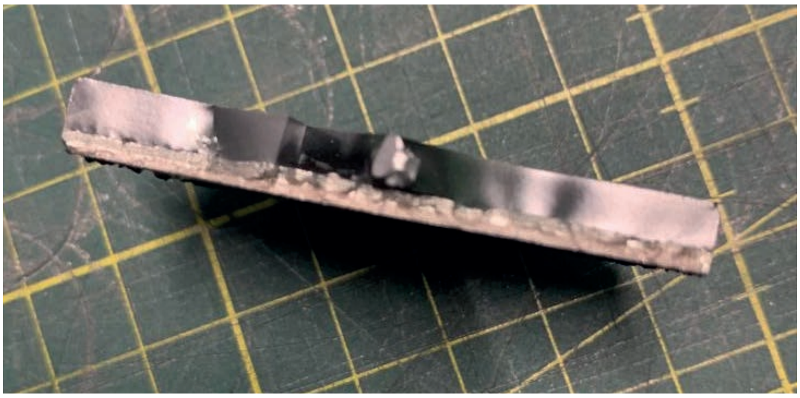


Fig. 11 Graded material – W/B_4C – B_4C [2, 3]. A layer of B_4C (dark layer on top) was combined with a layer of mixed B4C/W and a layer of pure W (copper colour at the bottom). This resulted in a good bond

This shows that many challenges must be overcome for sintering new materials. In addition, sound technical expertise and analytical thinking are required. The road to success requires a lot of experience, a stock of different sintering moulds and CFC plates, and patience. We at Dr. Fritsch are striving to follow this path to new materials by developing new FAST/SPS equipment, developing new raw materials and investing in new people.

Summary & conclusion

- FAST-SPS sintering of ceramics is much more difficult than sintering metals.
  - The heating process is different as ceramics are not normally electrically conductive.
  - Ceramic materials have a lower thermal conductivity than metals. There is a tendency for greater temperature variation within the sintering mould.
  - Ceramic materials are more brittle and therefore tend to crack more easily.
- Compared to metal sintering, some process details are now more important.
- Most ceramics are electrically non-conductive materials. Heating is through

Fig. 12 Laminated composite design with B_4C and W [2, 3]

the mould and not through the workpiece.

- The mould material is a key aspect. The release agent and e.g. graphite foil are important.
- The design of the mould is now more important
- Mould tolerances are now more significant.
- More attention needs to be paid to temperature measurement. Getting a good and reliable value by measuring close to the part.
- Cooling down after the process takes a long time – production machines with a cooling station are a good option.
- It can take longer to achieve success (as compared to metallic materials). However, excellent results can be obtained.
- In particular, graded materials and bonded materials are now possible with FAST-SPS technology.

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