Spark Plasma Sintering of Intermetallics and Metal Matrix Composites

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Abstract
Spark Plasma Sintering (SPS) or Field Assisted Sintering (FAST) is a new and innovative sintering technology with increasing importance for the preparation of several materials including composites or functionally graded materials. The process is based on hot pressing with an application of a pulsed electrical current instead of using an external heating source. Due to the pulsed electrical current and the so called "spark plasma effect" very high heating rates and short processing times can be realized. Therefore grain growth can be inhibited and materials with submicron or nanosized microstructures or composites with unique compositions can be prepared leading to improved properties. This presentation will describe examples of spark plasma sintered intermetallics and metal matrix composites. Microstructure and properties will be compared with those of conventionally sintered specimens.

1. Introduction

Spark Plasma Sintering (SPS) or Field Assisted Sintering Technology (FAST) is an innovative powder densification technology, which has been developed in recent years. The technique can be used for synthesis and processing of ceramics, metals and intermetallics [1].

SPS/FAST can be roughly compared with the conventional hot pressing technology. Additionally, high density current pulses at low voltage are applied directly to the powder and the pressing tool. The exact mechanism of densification – especially for insulating materials - is still unclear. It is suggested that the On-Off-DC pulse application in the early stage of this process generates a spark discharge and rapid Joule heating between the particles of the powder. The fast local increase of temperature and pressure promotes the elimination of adsorbed gas and breaks the oxide layer on the surface of metal particles.
SPS/FAST offers advantages such as rapid heating rate (e.g. up to 600°C/min) and short holding time compared to conventional HP or HIP. In combination with the surface activation effect, sintered bodies with meta-stable microstructures e.g. nanosized or nanostructured grains or non-equilibrium compositions can be obtained.

The aim of this study is to investigate the characteristics of spark plasma sintering for fabrication of intermetallic compound systems and metal matrix composites. $MoSi_2$, Ti_3SiC_2 and Ti6Al4V/15 SiC were fabricated by spark plasma sintering. The properties of these samples were compared with those of specimens made by conventional technique.

$MoSi_2$ and composites based thereof are promising candidates for high temperature applications because of their excellent oxidation resistance and mechanical stability up to high temperatures.
Ti_3SiC_2 is a carbide with a layered crystal structure and a remarkable combination of metallic and ceramic properties. Ti_3SiC_2 shows metallic properties like good electrical and thermal conductivity, low hardness, easy machinability and excellent thermo shock resistance. Like

ceramics, it is oxidation resistant and has low density. These properties lead to an increasing interest for the synthesis of Ti_3SiC_2-composites for possible applications.
Particulate reinforced titanium matrix composites like Ti6Al4V/15SiC exhibit some improved specific mechanical properties in comparison with those of unreinforced titanium alloys as a result of the combination of the high strength and stiffness of ceramic particles with the toughness and damage tolerance provided by the metal matrix [2]. But the preparation by conventional methods (e.g. HP, HIP) needs long cost-intensive process times at low temperatures to remove porosity and prevent reactions which form brittle intermetallic phases between SiC-particle and Ti-matrix.

2. Experimental

For the preparation of Ti_3SiC_2 and $MoSi_2$, commercial Ti, Si, C powders and Mo, Si powders respectively were used in the present study. These powders were mixed in a weight ratio corresponding to the formal composition of the target compound. After mixing, the powders were mechanically alloyed using a laboratory planetary ball mill (Fritsch Pulverisette P6) with hardened steel milling sets. The complete handling was carried out in an argon atmosphere. Details of the preparation are given elsewhere [3, 4]. The iron content, originated by abrasion from the milling tools, was less than 0.5 % for high-energy milled Ti_3SiC_2 and $MoSi_2$.
For Ti6Al4V/ 15 vol.% SiC composites, Ti6Al4V and SiC (F400) powders were mixed in a tubular shaker.
The sinter-ready powder mixtures were consolidated in an SPS/FAST apparatus (Dr. Sinter SPS 515-S (Sumitomo Coal Mining Co., Ltd., Japan) or HPD 200/180 (FCT Systeme GmbH, Germany)), using graphite dies with cavity diameters between 10 and 40 mm.
The same powder mixtures were also consolidated by a conventional HP technique.
The density of the compacted specimens was measured using Archimedes' technique. Hardness measurements were performed by Vickers diamond indentation method at room temperature on specimens polished by standard diamond polishing techniques down to 3 μm. Micrographs were additionally polished with oxide solution.

3. Results and Discussion

3.1. Molybdenum-disilicide $MoSi_2$

The powders were densified by SPS and hot pressing. For the spark plasma sintering temperatures between 1300°C and 1400°C in vacuum were used (Fig. 1).

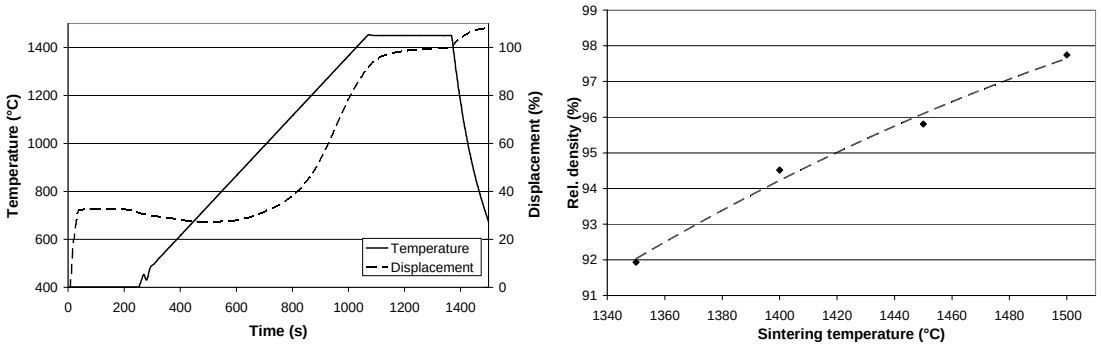

Fig. 1: Temperature and displacement profile for high energy milled $MoSi_2$ powder mixtures during spark plasma sintering (left). Bulk density of SPS samples as a function of sintering temperature (right).

Fig. 2 shows the optical micrographs of the sintered samples. The microstructure of the sintered sample exhibits a homogeneous distribution of small grains with a size of less than 5 μm. The average grain size is lower for the spark plasma sintered samples, than for the hot

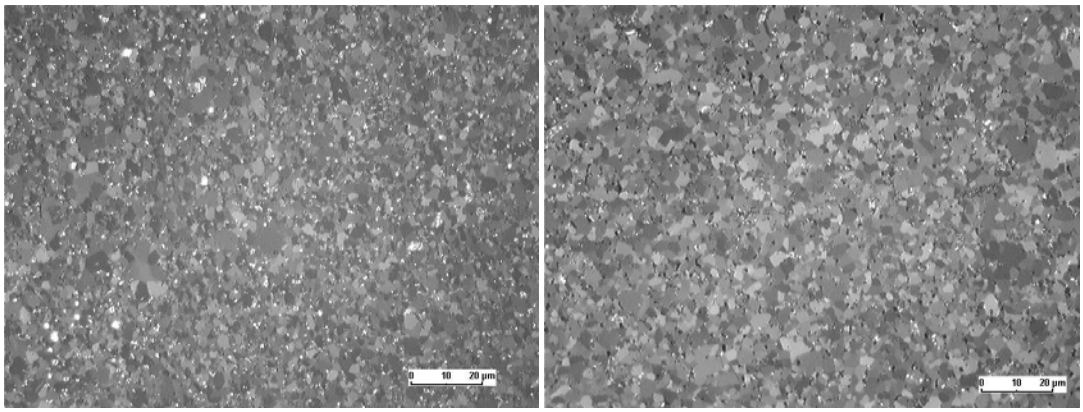

Fig. 2: Optical micrographs of $MoSi_2$ samples sintered at 1400°C (right: SPS, left: Hot pressing) (polarized light).

pressed ones. The reason for this is the much shorter heat treatment during the spark plasma sintering. The whole SPS process needs about 35 min (incl. cooling time), the hot pressing needs several hours.

3.2. Titanium-silicon-carbideTi_3SiC_2

According to the SPS technique [5], the powder mixtures were heated stepwise from room temperature to 1300°C during 25 min (heating rate ~50 K/min) and then sintered at this temperature for 5 min. Because of the high heating rates used by the SPS technique, the milled powders tend to spontaneous reactions to form Ti_3SiC_2, probably by solid-liquid reaction. To outflank this reaction, which leads to microstructure inhomogeneities with a size of less than 1 mm in diameter, the powder was annealed at 900°C for 30 min in vacuum. At die temperatures higher than 900°C, the sample starts to shrink (Fig. 3). Previous investigations showed that the shrinkage of the sample is finished under these conditions at about 1300°C.

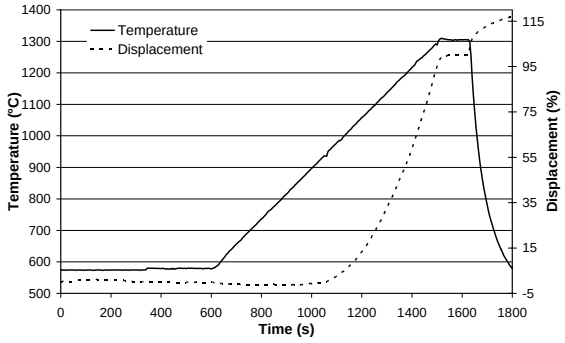

Fig. 3: Displacement and temperature profile for the Spark Plasma Sintering of a 3Ti/Si/2C powder mixture milled for 1 h.

For this reason, the maximum sintering temperature is set to this value. Heating to higher temperatures or longer isothermal sintering at this temperature leads to a higher content of TiC_x in the sample.

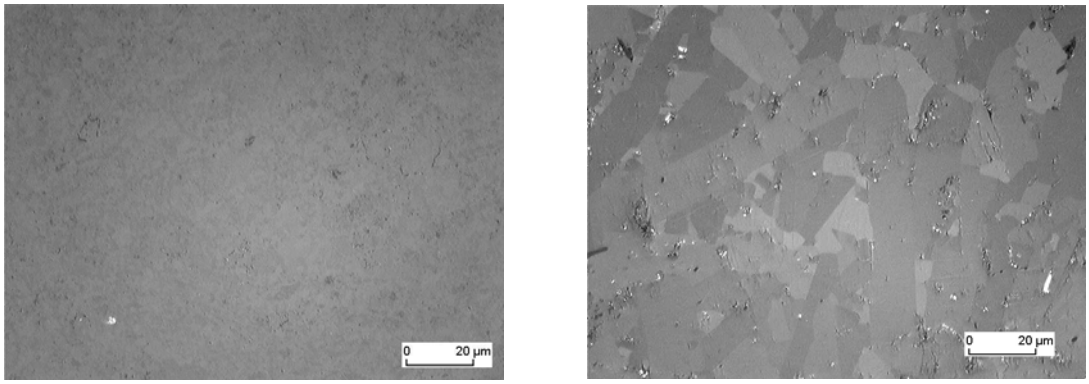

Fig. 4: Optical micrographs (polarized light) of sintered 3Ti/Si/2C powder mixtures (left: spark plasma sintered 1300°C/5 min; right: HP 1550°C/60 min).

The microstructure of the SPS samples shows a homogeneous distribution of small pores with a maximum diameter of 3 µm (Fig. 4). TiC_x as a secondary phase also exists in the microstructure. The grain size of the Ti_3SiC_2 is less then 3 µm and the grains have a nonuniform irregular shape. Packages of slab-like grains with parallel boundaries cannot be observed.

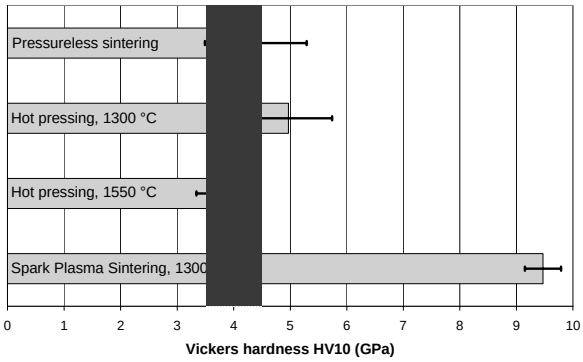

Fig. 5: The Vickers hardness of Ti_3SiC_2 samples sintered by different methods compared with the literature value (gray area between 3.4 and 4.5 GPa) [6].

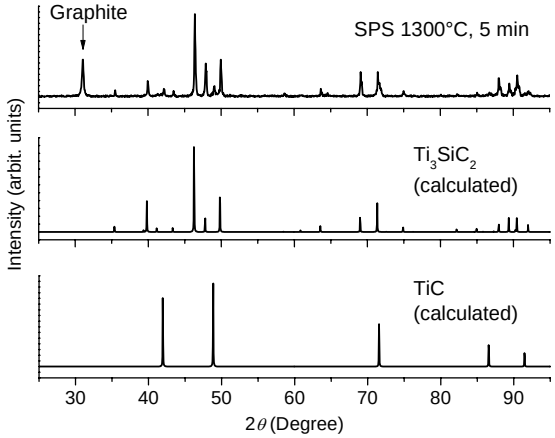

Fig. 6: XRPD patterns of the samples obtained by spark plasma sintering 3Ti/Si/2C mixtures (left). The graphite originates from residual traces of graphite foil used to protect the pressing tool.

The finer microstructure of the spark plasma sintered samples influences their mechanical properties. The Vickers hardness of Ti_3SiC_2 given in literature is about 4 GPa [6]. The

hardness for the pressureless sintered or hot pressed samples is in good agreement with these values (Fig. 5). The Vickers hardness of the SPS samples is much higher, even though the TiC_x amount is nearly the same (Fig. 6).

3.3. Titanium-alloy MMC Ti6Al4V/15 SiC

For the spark plasma sintering, the powder was heated stepwise up to temperatures between 800°C and 1100°C. The heating rate was about 50 K/min. The sintering was done with holding times between 0 and 5 min.

The density of the SP-sintered samples increases with increasing sintering temperature. Without holding time, a sintering temperature of more than 1000°C is necessary for complete densification (Fig. 7). A holding time of 5 min or higher pressure applied to the specimen (80 MPa instead of 30 MPa) leads to complete densification. The grain size hasn't changed while the heat treatment. No formation of an intermetallic (e.g. $Ti_5Si_3C_x$) phase at the boundary between Ti6Al4V matrix and SiC particles can be observed. With increasing density the Vickers hardness HV10 of the samples increases, too. Completely densified samples show hardness values of 500 GPa (Fig. 7).

To compare the SP-sintering with conventional hot pressing, the same powder mixture was pressed with 30 MPa and sintered for 15 min at temperatures between 850°C and 1000°C. Due to the slow heating rate, the exposition of the sample in the "high temperature region" was much longer than for the SP-sintered ones. Because of this, samples sintered with more than 870°C / 15 min show interfacial reaction layers.

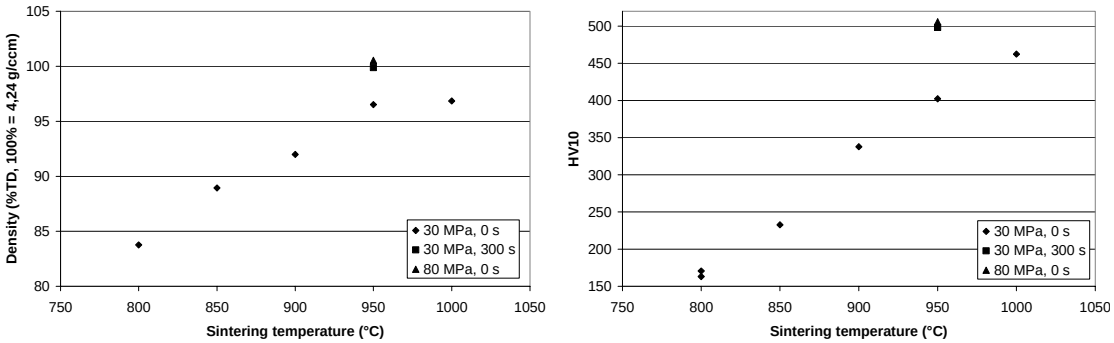

Fig. 7: Density (left) and Vickers hardness HV10 (right) of Ti6Al4V/15 SiC samples densified by SPS/FAST.

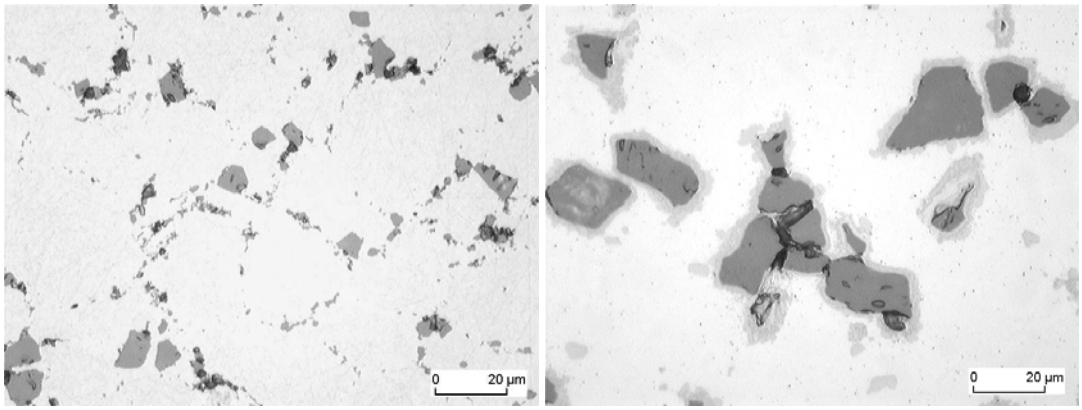

Fig. 8: Optical micrograph (bright field) of spark plasma sintered (left) and hot pressed (right; the sample contains SiC with a different grain size.) Ti6Al4V/15 SiC powder mixtures. Bright phase: Ti6Al4V, dark gray phase: SiC, light gray phase: Ti-Si intermetallics.

4. Conclusion

Dense intermetallic compounds ($MoSi_2$ and Ti_3SiC_2) and particulate reinforced titanium alloy matrix composites (Ti6Al4V/15 SiC) were successfully fabricated by spark plasma sintering / field assisted sintering technology. The rapid heating leads to homogeneous microstructures. Due to the short time sintering of the powder mixtures, significant grain growth can be suppressed and the final grain size of the sintered samples is smaller compared with them, made by hot pressing. By the same reason, chemical reactions between different phases (e. g. reinforcement phase and matrix in case for Ti6Al4V/SiC MMCs) can be prevented. The results showed SPS technique was an attractive way to fabricate intermetallics with fine grained microstructures and MMCs with non-equilibrium compositions.

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6. Literature

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