

# Spark Plasma Sintering Effect on the Decomposition of MgH<sub>2</sub>

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Spark plasma sintering (SPS) is one of the advanced consolidation techniques developed in the last few decades. We have studied the decomposition behavior of  $MgH_2$  and  $MgH_2/graph$ ite 1:1 mixtures in the SPS process. The standard SPS setup chosen was modified by including the temperature measurement inside the sample, so that the data can be compared with findings from thermal analysis. The results show clearly the reduction of the decomposition temperature measured in the SPS process if the necessary conditions (sufficient current density by applying the insulation) are realized.

### I. Introduction

**S**<sup>PARK</sup> plasma sintering (SPS) system is a combination of hot pressing and pulse current generation.<sup>1</sup> This technique has been developed for compaction of various metals, composites, and, especially, ceramics.<sup>2,3</sup> In the SPS method, current pulses with a length of about 3 ms pass through the die and the sample while mechanical pressure is applied. This procedure is suggested to generate sparks between powder particles due to the pulsed current.<sup>1</sup> However, the mechanism of the spark formation in insulating materials is unknown.

The effects caused by SPS are summarized as follows:

(1) Destruction of the surface oxidation layers on metal particles.<sup>4</sup>

- (2) Promotion of neck growth between particles.<sup>1</sup>
- (3) Cleaning of powder surfaces from adsorbed materials.
- (4) Intensification of diffusion.
- (5) Increase of sintering efficiency.

While effects (1) and (2) were confirmed for metal sintering, they have not been sufficiently investigated for sintering of ceramics, although several investigations were carried out in order to explore the effect of pulse current on rapid sintering of insulating materials in SPS, e.g., there are indications for an enhanced sintering of AlN.<sup>5</sup> On the other hand, Tomino et al.<sup>6</sup> measured the electric current passing through an alumina compact in the SPS process and reported that the current was very weak compared with the operating current applied on the sintering tool with alumina powder. These results are in agreement with microstructure investigations on Al2O3 bodies formed during the similar plasma-activated sintering technique.<sup>7,8</sup> The densification of the compact was shown to be driven by Joule heat transferred from the graphite die without any indication for a plasma. The findings of  $^9$  indicate a difference between the measured temperature of the die and the temperature inside the sample, which depends on the material properties, especially the electrical resistivity and the thickness of the sample.<sup>10</sup> This temperature difference complicates a straight comparison of the SPS with other sintering techniques.

The present paper describes the influence of the pulsed electric current on the decomposition of magnesium hydride during the SPS process. This particular reaction was investigated in detail, because it was subsequently used for preparation of magnesium compounds, i.e. magnesium diboride  $Mg_{0.96}B_2^{-11,12}$  or magnesium silicide  $Mg_2Si$ .<sup>13</sup> A thermocouple measuring the temperatures inside the sample allowed comparison with results obtained by differential thermal analysis (DTA). The decomposition of pure  $MgH_2$  and  $MgH_2$  in a 1:1 mixture with graphite was studied in electrically conducting graphite dies as well as in insulating alumina dies.

### **II. Experimental Procedure**

Commercial powders of magnesium hydride (95 wt%, 5 wt% excess Mg, Th. Goldschmidt AG, Essen, Germany) and graphite (99.9+ wt%, particle size—100  $\mu$ m, Chempur GmbH, Karlsruhe, Germany) were used as starting materials. Chemical analysis of the magnesium hydride gave the following results (in wt%): Mg—91.61±0.15, H—6.96±0.07, O—0.27±0.010, N—0.92±0.08. Magnesium hydride and graphite powder (50 wt% each) were blended using a vibrating mill with a polyethylene capsule and SiAlON balls for 24 h. To avoid contamination with oxygen during milling or mixing, the complete handling was carried out in a dry argon atmosphere (argon 99.999%, Messer Griesheim, Kirchen, Germany, H<sub>2</sub>O and O<sub>2</sub> content <0.1 ppm).

The experiments were performed using an SPS system (Dr. Sinter<sup>\*\*</sup> SPS 515-S, Sumitomo Coal Mining Co., Ltd., Tokyo, Japan). The standard SPS setup was modified, and a second thermocouple was placed inside the sample to analyze the temperature difference between the wall of the die and the reaction mixture. This thermocouple (type S,  $\emptyset$  1.5 mm, Inconel<sup>\*\*</sup>-sheeted) was plunged through the upper punch and fixed with a zirconia-based cement with the measuring tip 4 mm inside the sample space (Fig. 1). The temperature was controlled by a digital programmable controller CHIO KP 1000 (Chino Corp., Tokyo, Japan). Temperature calibration in the range from 300° to 950°C was carried out with three melting points of pure elements (Pb, Al, Ge). All experiments were performed in dynamic vacuum (*P*<sub>Vacuum</sub> <3 Pa), and a uniaxial pressure of 14 MPa on the die was applied during the entire process.

For reacting, magnesium hydride powder or powder mixture was SPS heated stepwise from ambient temperature to 500°C at different heating rates (varying from 2 to 20 K/min) and subsequently annealed at this temperature for 10 min. For process control, the temperature within the die ( $T_D$ ) was used. The relevant parameters—die temperature  $T_D$ , sample temperature  $T_S$ , gas pressure *P* inside the vacuum chamber, and displacement *D* along the pressing direction—were recorded with the time increment of 2 s. Graphite and alumina dies were used in order to investigate the influence of the resistivity of the die material on the decomposition process.

In order to determine the decomposition temperature of  $MgH_2$ , all SPS experiments were carried out at at least four different heating rates. Two different variables indicating the decomposition (*D* and *P*) can be used for further analysis. The displacement reflects the shrinkage of the sample and the thermal expansion of the graphite punches, the spacers, and the plungers. In combination with the experimental noise, this pre-

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Fig. 1. Schematic representation of the experimental setup.

vents a reasonable extraction of exact onset temperatures. Exact monitoring of the gas pressure P is difficult due to the large amount of hydrogen (up to 2–3 dm<sup>3</sup>) formed during the relatively short time of the reaction. This results in an overflow of the pressure-measuring unit and makes a definition of the onset impossible. Therefore, the starting point of the reaction is defined as the first deviation in the P(t) curve from the corresponding baseline. The obtained decomposition temperature values ( $T_{\rm S}$  scale) are heating rate dependent and therefore were linearly extrapolated to a heating rate of 0 K/min (extrapolated decomposition temperature).

DTA/TG measurements (STA 449, NETZSCH, Selb, Germany, completely integrated into an argon-filled dry box; argon purified with Oxisorb<sup>\*</sup>; alumina crucibles with lid; thermocouple type S) were performed to analyze the decomposition behavior of pure MgH<sub>2</sub> and its mixture with graphite in the absence of SPS conditions. Temperature calibration was carried out with melting points of five pure elements (Bi, Sn, Al, Ag, Au). The obtained decomposition temperature values ( $T_S$  scale) were extrapolated to a heating rate of 0 K/min to account for the heating rate dependence.

After the reaction, the samples were analyzed by X-ray powder diffraction (HUBER Guinier Image-Plate camera G670, Huber Diffraktions technik, Rimsting, Germany; CuK $\alpha$  radiation,  $\lambda = 1.54060$  Å; germanium monochromator).

Chemical analysis of the commercial MgH<sub>2</sub> was performed with an ICP-OES system (VARIAN Vista RL, Middelburg, The Netherlands) and specific elemental analyzers (for hydrogen— LECO RH 402; for oxygen and nitrogen—LECO TC-436 DR, Mönchengiadbach, Germany) by the carrier-gas hot-extraction method.

For electrical resistivity measurements (four-probe van-der-Pauw method, 23°C, argon atmosphere), the powder mixture was cold compacted in a sapphire cell with four platinum wires pressed into the powder.

### III. Results and Discussion

# (1) Decomposition of Magnesium Hydride in the Graphite Die

The displacement D in the direction of pressing, the temperatures of the die  $(T_D)$  and the sample  $(T_S)$ , as well as the gas pressure inside (P) the reaction chamber versus time t are presented in Fig. 2. While the sample is heated up to  $300^{\circ}$ - $400^{\circ}$ C,



**Fig. 2.** Time dependences of displacement (*D*), temperature of the die  $(T_D)$ , temperature of the sample  $(T_S)$ , and gas pressure inside the reaction chamber (*P*) for the SPS decomposition of MgH<sub>2</sub> (heating rate 6 K/min).

both the displacement and the gas pressure display an abrupt increase as the decomposition starts. After the reaction, the evolution of gas stops, the displacement rate decreases, and the pressure inside the chamber reverts to the initial value due to the dynamic vacuum conditions.

During the entire heating period before the decomposition reaction,  $T_{\rm S}$  is lower than  $T_{\rm D}$ . From this fact it can be inferred that the heat is transferred from the graphite die and the punches to the reaction mixture. Because of the insulating nature of magnesium hydride, no generation of Joule heat in the powder takes place. As the decomposition starts, the electrical conductivity of the sample increases with magnesium content. Consequently, the temperature of the sample rises faster than the temperature of the die, even though the decomposition reaction is endothermic ( $\Delta H_{\rm R, 600 \ K} = 79 \ \text{kJ/mol}^{14}$ ). During the decomposition, the PID controller of the SPS setup does not work exactly, because the changes of the electrical and thermal conductivity in the reaction mixture are faster than the on/off time of the control system. Thus, some deviations from a linear heating rate were observed. With increasing heating rate, the decomposition reaction shifts to higher temperatures. The extrapolated decomposition temperature for MgH<sub>2</sub> in the SPS process was found to be 379(8)°C (Table I). The XRD pattern of the reaction product showed only Mg and a small amount of MgO (originating from the oxide impurities in the starting powder; see analytical results above).

On heating of magnesium hydride, the DTA measurement showed only one endothermal peak in the temperature range between  $370^{\circ}$  and  $600^{\circ}$ C depending on the heating rate (Fig. 3). As in the SPS process, the peak onset shifts to higher temperatures with increasing heating rate. The endothermal reaction is accompanied by a weight loss of about 6.9 wt%, which is in good agreement with the analytically determined amount of 6.96 wt% hydrogen in the commercial magnesium hydride powder (see above). XRD patterns of the product revealed the presence of only Mg and a small amount of MgO, similar to the SPS process. The onset of the decomposition of MgH<sub>2</sub> in the DTA process, extrapolated to the heating rate of 0 K/min, was found to be  $394(7)^{\circ}$ C (Table I).

Table I. Extrapolated Decomposition Temperatures  $(T_{\text{Decomp}})$ for MgH<sub>2</sub> Based on the Measurements of the Temperature of the Sample  $(T_{c})$ 

the Sample (18)		
	$T_{\text{Decomp.}}$ (°C) for SPS	T <sub>Decomp.</sub> (°C) for DTA
MgH <sub>2</sub>	379 (8)	394 (7)
MgH <sub>2</sub> +graphite	386 (6) (graphite die) 314 (7) (alumina die)	397 (7)

SPS, spark plasma sintering; DTA, differential thermal analysis.



**Fig. 3.** DTA results for  $MgH_2$  (top) and a 1:1 mixture of  $MgH_2$  with graphite (bottom).

# (2) Decomposition of Magnesium Hydride in the Mixture with Graphite

In order to study the influence of the electrical conductivity of the initial powder mixture on the reaction course in the SPS process, the decomposition of a 1:1 MgH<sub>2</sub>/graphite mixture was investigated. We did not observe any indication for a reaction between carbon and magnesium under the applied conditions.

Before the decomposition reaction starts, the reaction mixture shows a conductor-like behavior. The temperature of the sample increases faster than the temperature measured in the graphite die (Fig. 4). This finding is in good agreement with the observed value of about 230  $\mu\Omega \cdot m$  for the electrical resistivity of the cold-compacted powder mixture (own measurements) in comparison with the resistivity of about 14  $\mu\Omega \cdot m$  for the graphite, used for the production of the pressing tool (value



**Fig. 4.** Time dependences of displacement, temperature of the die and the sample, and gas pressure inside the reaction chamber for the SPS decomposition of  $MgH_2$  in the 1:1 mixture with graphite in the graphite die (heating rate 6 K/min).



Fig. 5. Time dependences of displacement, temperature of the die and the sample, and gas pressure inside the reaction chamber for the SPS decomposition of  $MgH_2$  in the 1:1 mixture with graphite in the alumina die (heating rate 6 K/min).

given by manufacturer). The decomposition reaction starts at higher temperatures with increasing heating rate. The extrapolated decomposition temperature for MgH<sub>2</sub> in the mixture with graphite in the SPS process is  $386(6)^{\circ}$ C (Table I). XRD patterns showed only Mg, graphite, and a small amount of MgO in the reaction product. Both the DTA and the TG curves for the decomposition of MgH<sub>2</sub> in the 1:1 mixture with graphite reflect only one event. The heat flow per mass is only half of that found for pure MgH<sub>2</sub>, because of the graphite amount in the mixture (Fig. 3). The extrapolated onset of the decomposition for MgH<sub>2</sub> in the mixture with graphite in the DTA is  $397(7)^{\circ}$ C (Table I). This value is very close to the value assumed for pure MgH<sub>2</sub> (see above).

Because of the sufficiently high electrical conductivity for the MgH<sub>2</sub>/graphite mixture, it was possible to replace the graphite die by one made of dense sintered alumina (density =  $3.9 \text{ g/cm}^3$ ; BCE Special Ceramics, Mannheim, Germany) with the same dimensions, and applying the graphite punches. By this, the electric current is constrained to pass through the reaction mixture. An indirect heating of the sample caused by the generation of Joule heat in the die walls is impossible in this setup. Before the decomposition of the hydride, the temperatures in the sample and the die are nearly equal (Fig. 5). With the beginning of the evolution of hydrogen, the temperature inside the sample and the displacement increase faster. The temperature difference between the sample and the die, in combination with the low thermal conductivity of the alumina die causes a strong oscillation tendency in the control circuit of the SPS process (see below). These circumstances resulted in fluctuation of the temperatures in the sample and the die, combined with fluctuation of the gas pressure inside the vacuum chamber. To avoid damages, the PID controller setup was manually regulated when the decomposition started. For this, the PID setup was changed to conditions with a higher P ratio.

With the increasing amount of magnesium formed by the decomposition of the hydride, the temperature difference between the sample and the die increases. The extrapolated decomposition temperature for MgH<sub>2</sub> in the 1:1 mixture with graphite in the SPS process is found to be  $314(4)^{\circ}$ C if the alumina die was used (Table I). This value is remarkably lower (by 72°C) compared to the graphite die data.

Points measured with more than 20 K/min have no corresponding points in the DTA analysis. For this, the points are shown in Figs. 7 and 8, but were neglected in all calculations.

The SPS system allows the measurement of the electrical current and voltage during the process (Fig. 6, top, middle). From these data, the average resistivity of the experimental setup can be calculated. Before the reaction, the resistivity of the system with an alumina die was higher than those with a graphite die. After the reaction, the resistivity is practically independent of the



**Fig. 6.** Voltage (top), current (middle), and total resistivity of the system (bottom) during the SPS process for the decomposition of  $MgH_2$  in the 1:1 mixture of  $MgH_2$  and graphite.

die material. This behavior becomes transparent when the different paths of the electrical current are considered. In case of the graphite die, the current flows simultaneously through the die and the reaction mixture, while it only passes through the powder if an alumina die is used. After the decomposition reaction, the conductivity of the sample was much higher than the conductivity of graphite (due to the formation of metallic magnesium); thus, the current flows predominantly through the sample. This leads to nearly the same overall resistivity for conducting or insulating die after decomposition of MgH<sub>2</sub> to Mg and H<sub>2</sub> (Fig. 6, bottom).

## (3) Determination of Activation Energies

Determination of the apparent activation energy for the decomposition of MgH<sub>2</sub> has given useful information concerning the possible changes in the nature of the reaction. The onset temperature for the decomposition increases with increasing heating rate for both processes, SPS and DTA (Fig. 7). The temperature dependence of the onset of the reaction is shown in an Arrhenius plot in Fig. 8. In this representation, a straight line can be well fitted to the data. The slope of the fitted line, which represents the activation energy for different experimental conditions, has values between 106 and 195 kJ/mol (Table II). This is in the same range with the published data for pure  $MgH_2$  (91–142 kJ/ mol).<sup>15-17</sup> On the one hand, the fluctuations may be explained by the oxide content in the used MgH<sub>2</sub>, because there is a strong influence of surface oxide films on the decomposition reaction. In addition, the activation energy values for SPS processing fall in the middle of the range of the literature data (obtained, e.g., by DTA). On the other hand, the activation energy in the SPS process (114–116 kJ/mol) seems to be significantly lower than for the DTA experiments (191-195 kJ/mol) independent of the



**Fig. 7.** Determination of the decomposition temperature for pure  $MgH_2$  (top) and  $MgH_2$  in a 1:1 mixture with graphite (bottom) in the DTA and SPS processes. The point at very high heating rate (SPS, alumina die) was not accounted.

different starting powders, which suggests a different decomposition mechanism at least for our experiments.

Independent of this, the SPS process in the alumina die clearly shows a different behavior. Despite the activation energy is in the range of the other SPS experiments, the interaction occurs at a significantly lower temperature of the reaction mixture and shows different dynamics of the hydrogen evolution in comparison with the graphite die.



**Fig.8.** Arrhenius plots for the decomposition of  $MgH_2$  in DTA and SPS processes.

Table II. Activation Energies for the Decomposition of MgH<sub>2</sub>

Sample	Process	Activation energy (kJ/mol)
MgH <sub>2</sub>	DTA	195
$MgH_2 + C_{Graphite}$	DTA	191
MgH <sub>2</sub>	SPS (graphite die)	114
$MgH_2 + C_{Graphite}$	SPS (graphite die)	116
$MgH_2 + C_{Graphite}$	SPS (alumina die)	106

DTA, differential thermal analysis; SPS, spark plasma sintering.

## IV. Conclusions

Our results show that there is no significant difference in the extrapolated decomposition temperature for pure MgH<sub>2</sub> and for its 1:1 mixture with graphite in SPS (graphite die) and DTA processes. For the chosen experimental setup, the SPS processing is comparable with a conventional heating technique. By replacing the graphite die with the corundum one, the extrapolated decomposition temperature of MgH<sub>2</sub> is significantly lower than that observed by DTA or by SPS using a graphite die.

It is obvious that a high current density inside the sample is necessary to cause this SPS effect. Up to now, it is impossible to finally conclude on the exact mechanism of this influence. A generation of plasma, according to the mechanism proposed by Tokita,<sup>1</sup> cannot be excluded. An alternative explanation can also be suggested: the electrical current produces local overheating at the graphite particles in the powder mixture; close to these hot spots, the decomposition of the MgH<sub>2</sub> starts earlier than in more distant regions. Plasma does not necessarily appear in this case.

The presented results clearly show that the SPS processing for materials with an electrical conductivity differs considerably from conventional heating if the necessary current density is achieved. The reduction of the temperature of the reaction mixture at the start of a decomposition reaction (e.g., of MgH<sub>2</sub>) by pulsed electric current is documented for the first time.

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#### References

<sup>1</sup>M. Tokita, "Trends in Advanced SPS Spark Plasma Sintering System and Technology," *J. Soc. Powder Technol. Jpn.*, **30**, 790–804 (1993).

<sup>2</sup>L. Gao, Z. Shen, H. Miyamoto, and M. Nygren, "Superfast Densification of Oxide/Oxide Ceramic Composites," *J. Am. Ceram. Soc.*, **82** [4] 1061–3 (1999).
<sup>3</sup>Z. Shen, Z. Zhe, H. Peng, and M. Nygren, "Formation of Though Interlocking

Microstructures in Silicon Nitride Ceramics by Dynamic Ripening," *Nature*, **417**, 266–9 (2002).

<sup>4</sup>K. Matsugi, T. Hatayama, and O. Yanagisawa, "Effect of Direct Current Pulse Discharge on Specific Resistivity of Copper and Iron Powder Compacts," *J. Japan Inst. Metals*, **59** [7] 740–5 (1995).

<sup>5</sup>S. H. Risebud and J. R. Groza, "Clean Grain Boundaries in Aluminium Nitride Ceramics Densified Without Additives by a Plasma-activated Sintering Process," *Phil. Mag.*, **B69** [3] 525–33 (1994).

<sup>6</sup>H. Tomino, H. Wantanabe, and Y. Kondo, "Electric Current Path and Temperature Distribution for Spark Sintering," *J. Japan Soc. Powder Powder Metall.*, 44, 974–9 (1997).

<sup>7</sup>S. W. Wang, L. D. Chen, T. Hirai, and Y. S. Kang, "Microstructure Inhomogeneity in Al<sub>2</sub>O<sub>3</sub> Sintered Bodies Formed During the Plasma-activated Sintering Process," *J. Mater. Sci. Lett.*, **18** [14] 1119–21 (1999).

<sup>8</sup>M. Ishiyama, "Plasma Activated Sintering (PAS) System;" pp. 931–4 in Proceedings of 1993 Powder Metallurgy World Congress, Edited by Y. Bando, and K. Kosuge. Japan Society of Powder and Powder Metallurgy, Kyoto, Japan, 1993.

<sup>9</sup>M. Nanko, T. Maruyama, and H. Tomino, "Neck Growth on Initial Stage of Pulse Current Pressure Sintering for Coarse Atomized Powder Made of Cast-Iron," *J. Japan Inst. Metals*, **63** [7] 917–23 (1999).

<sup>10</sup>J. Schmidt "Anwendung des Spark Plasma Sinterverfahrens für Präparationszwecke in der Festkörperchemie," Ph.D. Thesis, Technische Universität Dresden, Dresden, 2003.

<sup>11</sup>J. Schmidt, W. Schnelle, Yu. Grin, and R. Kniep, "Pulse Plasma Synthesis and Chemical Bonding in Magnesium Diboride," *Solid State Sci.*, **5** [1] 535–9 (2003).
<sup>12</sup>J. Schmidt and Yu. Grin, "Method for Producing Magnesium Diboride and

<sup>12</sup>J. Schmidt and Yu. Grin, "Method for Producing Magnesium Diboride and Magnesium Diboride Moulded Bodies Made from Magnesium Hydride and Elementary Boron by Pulse-plasma Synthesis Int. Patent PCT/EP02/03952, 09.04.2002.

 $^{13}M.$  Schmidt, J. Schmidt, Yu. Grin, A. Böhm, B. Kieback, R. Scholl, Th. Schubert, Th. Weissgärber, and M. Zumdick, "Production of Mg<sub>2</sub>Si and Ternary Compounds Mg<sub>2</sub>(Si,E); E = Ge,Sn,Pb and Transition Metals; <10wt. %) Made of MgH<sub>2</sub> and Silicon and Production of Magnesium Silicide Moulded Bodies by Pulse-Plasma Synthesis. Int. Patent PCT/EP02/03953, 09.04.2002.

<sup>14</sup>I. Barin, "Thermochemical Data of Pure Substances 3rd edition, VCH, Weinheim, 1995.

<sup>15</sup>H. Kawano, Y. Zhu, A. Tanaka, and S. Sugimoto, "Activation Energies for the Desorption of H<sub>2</sub>, H<sup>-</sup> and Electron from Saline Hydrides Heated in Vacuum," *Thermochim Acta*, **371** [1–2] 155–61 (2001).

<sup>16</sup>J. Huot, G. Liang, S. Boily, A. van Neste, and R. Schulz, "Structural Study and Hydrogen Sorption Kinetics of Ball-milled Magnesium Hydride," *J. Alloys Compds.*, **293–295**, 495–500 (1999).

<sup>17</sup>J. S. Han, M. Pezzt, and J.-Y. Lee, "A Study of the Decomposition of Magnesium Hydride by Thermal Analysis," *J. Less-Common Met.*, **130**, 395–6 (1987).

<sup>18</sup>A. Zaluska, L. Zaluski, and J. O. Ström-Olsen, "Synergy of Hydrogen Sorption in Ball-milled Hydrides of Mg and Mg<sub>2</sub>Ni," *J. Alloys Compds.*, **289** [1–2] 197–206 (1999). □