

Spark Plasma Preparation of Mg_2Si and Mg_2Si-Mg Composite

N. Reinfried¹, J. Schmidt², B. Kieback², Yu. Grin¹

¹*Max-Planck-Institut for Chemical Physics of Solids, Nöthnitzer Str. 40, 01187 Dresden, Germany*

²*Fraunhofer Institut Fertigungstechnik Materialforschung, Winterbergstraße 28, 01277 Dresden, Germany*

Abstract

Spark plasma sintering is generally known for the design of binder-less ceramics, refractory materials, FGM and nano-crystalline powders. We use the advantages of SPS for the preparation of intermetallic compounds. With the SPS technique and powder metallurgy it is possible to synthesise Mg_2Si (low melting Mg and high melting Si). In case of the SPS route, chemical reaction and consolidation take place in one step. The reaction mechanism and the influence of preparation conditions and some mechanical properties of Mg_2Si and a Mg_2Si-Mg composite will be discussed.

1. Introduction

Light weight materials with high specific modulus at elevated temperatures are rare. Mg_2Si is a material showing these properties, which are indicated by an elastic modulus of 120 GPa, a high melting point (1085 °C), high hardness (450 HV0.3) and a low density (1.99 g/cm³) [1, 2]. A disadvantage is the brittle behaviour of this intermetallic compound [3], which is mainly used for thermoelectric applications [4-11] and as a precursor for the production of silanes [12, 13]. The synthesis of Mg_2Si by melting techniques is difficult, due to strong affinity of the melt to oxygen and the high vapour pressure of Mg (44.3 kPa at 1077 °C) [14]. Mechanical alloying of Mg and Si to form Mg_2Si was recently investigated in detail [15-24]. The oxidation and contamination from milling balls and containers are the key preparative problems. Sintering of Mg_2Si by usual sintering techniques like Hot Pressing or Hot Isostatic Pressing is complicated by the high vapour pressure of Mg causing a decomposition of Mg_2Si . By application of the SPS technique to a powder mixture of MgH_2 and Si most of these problems can be avoided [25, 26].

SPS is a pressure sintering method based on high temperature plasma (spark plasma) generated in the gaps between powder particles by electrical discharge at the beginning of ON-OFF DC pulse energising. The large current pulse generates: (1) spark plasma, whereat impurities, such as oxide and adsorptive gas existing on the surface of the particles, are dispersed, (2) spark impact pressure, which gives strain to the particle and assists to increase the diffusion speed, (3) Joule heating, and (4) an electrical field diffusion effect [27].

Mechanical properties of melted Mg_2Si materials were already investigated [28, 29], but data for Mg_2Si and Mg_2Si-Mg composites prepared by sintering techniques could not be obtained. The aim of this work is the investigation of sintering conditions and the measurement of the bending strength and the elastic modulus of SPS made specimens of Mg_2Si and Mg_2Si-Mg .

2. Experimental

The samples were prepared from mixtures of magnesium hydride powder (95 %) and silicon powder (99.9999 %). Both brittle powders were ball milled in argon atmosphere in a FRITSCH P7 planetary ball mill. To avoid contamination, wear resistant ceramic (SiAlON) milling containers and balls were used. A ball to powder weight ratio of 1:25 was chosen. With 800 rpm and a total milling time of 1 h (sequences 5 min of milling time followed by 5 min to allow cooling) homogeneous powder mixtures could be achieved.

SPS synthesis was done under dynamic vacuum in order to observe decomposition of MgH_2 . The powder mixture was filled into a graphite tool. For optimisation of the sintering conditions cylindrical samples (diameter 10 mm, height 3 mm) were used. The temperature was controlled by a K1 thermocouple mounted in the die wall at a distance of approx. 2 mm from the sample. Samples for the three point bending tests (18 mm length, 3.5 mm width and 3.1 mm height) were obtained with modified tools. The sample surface was ground with 1000 SiC paper, prior to the test with a ZWICK Z005 at room temperature. The distance between the support bearings was 13.5 mm. Ultrasonic measurements were performed on cylindrical samples (diameter 15 mm, height 5 mm), using 5 MHz frequency for longitudinal and transversal waves.

3. Results and Discussion

3.1 Reaction Mechanism of Mg_2Si Formation

During powder milling a homogeneous distribution of Si and MgH_2 can be achieved in addition to particle size reduction. The formation of Mg_2Si during the SPS process can be divided into two steps. The first step is determined by the decomposition of MgH_2 . The decomposition temperature of MgH_2 at different heating rates during the SPS process was compared with DTA measurements. The results of both methods are in good agreement (e.g. at 20 K/min; SPS: 429 °C, DTA: 437 °C). The second step starts with the occurrence of elemental Mg (ca. 340 °C) which reacts exothermally with Si to form Mg_2Si . This reaction is complete at 600°C [25, 30]. The reaction mechanism of the Mg_2Si formation as described above is independent from the heating rate (10, 20, 30, 60, 100 K/min, $T_{\text{sinter}} = 600$ °C).

3.2 Influence of the Milling Conditions

The decomposition temperature of MgH_2 decreases by ball milling, which is caused by the breaking of oxide layers of MgH_2 , particle size reduction and lattice distortion [31]. In Fig. 1 the punch displacement and the chamber pressure dependencies on temperature on three different powder mixtures are shown. The displacement curve of the an untreated mixture of Si and MgH_2 shows one step in the densification of the sample at about 400 °C followed by a slight increase up to 600 °C. The peak in the chamber pressure curve indicates the decomposition of MgH_2 at about 440 °C. Thus, the densification is caused by two processes, decomposition of MgH_2 and formation of Mg_2Si .

The powder mixture which was ball milled at 600 rpm for 30 min represents the two-step densification over a larger temperature range. This can be explained by different

particle types of MgH_2 , because two steps of decomposition of MgH_2 are recorded. The first step is due to particles with clean surface and the second step can be ascribed particles with an oxide layer.

When the milling energy is increased (800 rpm, 60 min) only one peak in the vacuum curve is recorded. That leads to the assumption that most of the powder particles have a small particle size and crashed oxide layers on the surface, resulting in enhanced diffusion and a decreased decomposition temperature.

In Fig. 2 the microstructure of samples made from different ball-milled powders are shown. Low-energy milling results in a more inhomogeneous microstructure. EDX analyses reveal remaining Si and traces of MgO in the material (Fig. 2, left). After high-energy milling (Fig. 2, right) the microstructure is remarkably homogenous, although MgO and traces of remaining Si could be detected with EDX analyses at high magnification (5000x).

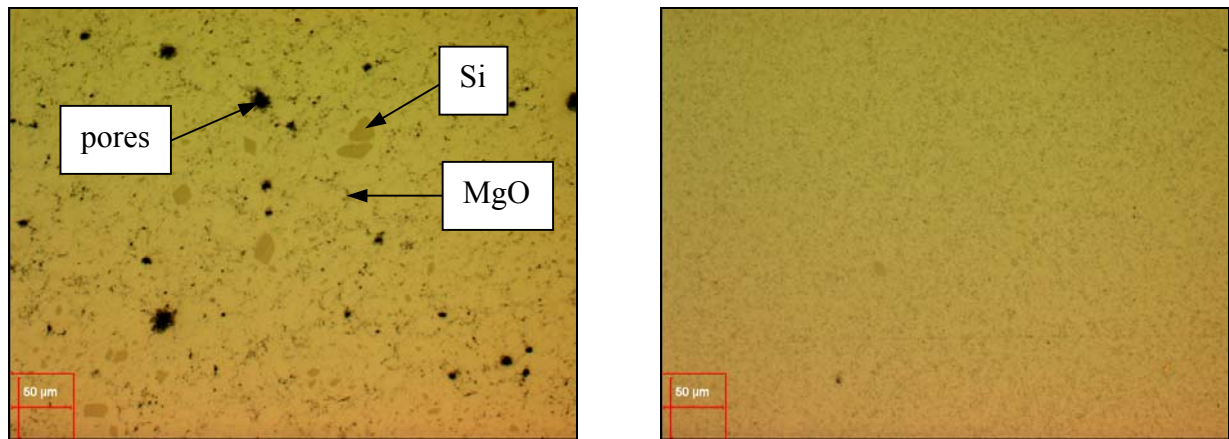


Fig. 2: Microstructure of Mg_2Si samples after SPS preparation (600 °C, 20 K/min, 30 min): (left) ball-milled mixture with 600 rpm for 30 min; (right) ball-milled mixture with 800 rpm for 60 min

3.3 SPS Sintering Conditions

The advantage of the SPS technique is a suppression of grain growth by short sintering times and low temperatures, in comparison to conventional sintering techniques. To optimise the microstructure of the samples, different heating rates, temperatures and pressures were tested. As the starting mixture the sieved powders of Si (<100 μm) and MgH_2 (<100 μm) were used. With increasing heating rate the formation of Mg_2Si becomes incomplete, the annihilation of pores is reduced and the density decreases. Increasing soaking time at 600 °C has no influence at low heating rates (20 K/min). At high heating rates (100 K/min), the formation of Mg_2Si is complete and the samples become more dense. When the temperature is increased to about 800 °C, evaporation of Mg can be observed as an increase of the chamber pressure curve. Further heating results in melting of the sample at 1040 °C. The temperature difference to the melting point of Mg_2Si (1085 °C) is caused by temperature measurement set-up. Samples prepared at different pressures (30, 60, 100 MPa) show increased density. The best conditions for a production of dense samples were found to correspond to a heating rate of 20 K/min up to 600 °C with a pressure of 100 MPa and a soaking time of 30 min.

3.4 Three Point Bending Test

The samples for the three point bending test and the ultrasonic measurements were prepared at optimised conditions (see chapter 3.3). The composite Mg_2Si -Mg was tested with four different compositions (Tab. 1) and compared to pure Mg and Mg_2Si . The microstructure of the samples (Fig. 4) can be described as a framework of Mg_2Si interpenetrated by Mg. In Fig.

Fig. 3: The stress – strain – diagram of Mg, Mg₂Si and Mg₂Si-Mg composite

3 the stress – strain – diagram clearly shows the difference between Mg and the Mg₂Si-Mg composite. The elastic modulus is increased in comparison to Mg, but the plastic deformation properties are insufficient. The bending stress decreases with decreasing Mg content from 300 to 200 MPa, while an increase of the elastic modulus from 36 to 47 GPa can be observed (Tab. 1). The characteristics given in literature (Mg: 29 GPa (pure Mg) - 44 GPa (hot-rolled and annealed) [33], Mg₂Si: 78-114 GPa [27], 120 GPa [2]) were not met, which might be due to the difficulties of elastic modulus determinations from three point bending tests because sample shape and geometry strongly influence the results.

Sample Composition	number of samples tested	max. stress	max. strain	elastic modulus (bending)	elastic modulus (ultrasonic)	elastic modulus (literature)
		in MPa	in %	in GPa	in GPa	in GPa
Mg	5	360	8.2	12.565.8	29.260.8	29 ¹ -44 ² [33]
Mg ₂ Si + 40 at.% Mg	4	280	0.5	36.467.3	84.964.4	-
Mg ₂ Si + 30 at.% Mg	5	300	0.6	40.265.6	84.864.0	-
Mg ₂ Si + 20 at.% Mg	3	220	0.4	43.968.7	85.564.2	-
Mg ₂ Si + 10 at.% Mg	1	200	0.3	46.968.1	87.964.3	-
Mg ₂ Si	4	140	0.2	52.367.8	85.564.2	120[2] 7666 ³ [28] 78-114 ⁴ [28]

Tab. 1: Bending test sample composition and results of bending tests and ultrasonic measurements (values are averages of the given number of samples); ¹ pure Mg

(distilled and remelted); ² Mg hot-rolled and annealed; ³ measured by a compression test; ⁴ calculated on the basis of data given in [32]

3.5 Ultrasonic Measurements

In comparison to the three point bending test the elastic modulus was also determined by ultrasonic measurements using the impulse echo method. A slight increase of the elastic modulus with decreased Mg content was measured. The elastic modulus obtained from ultrasonic measurements meets the literature data at the lower limit (Tab. 1).

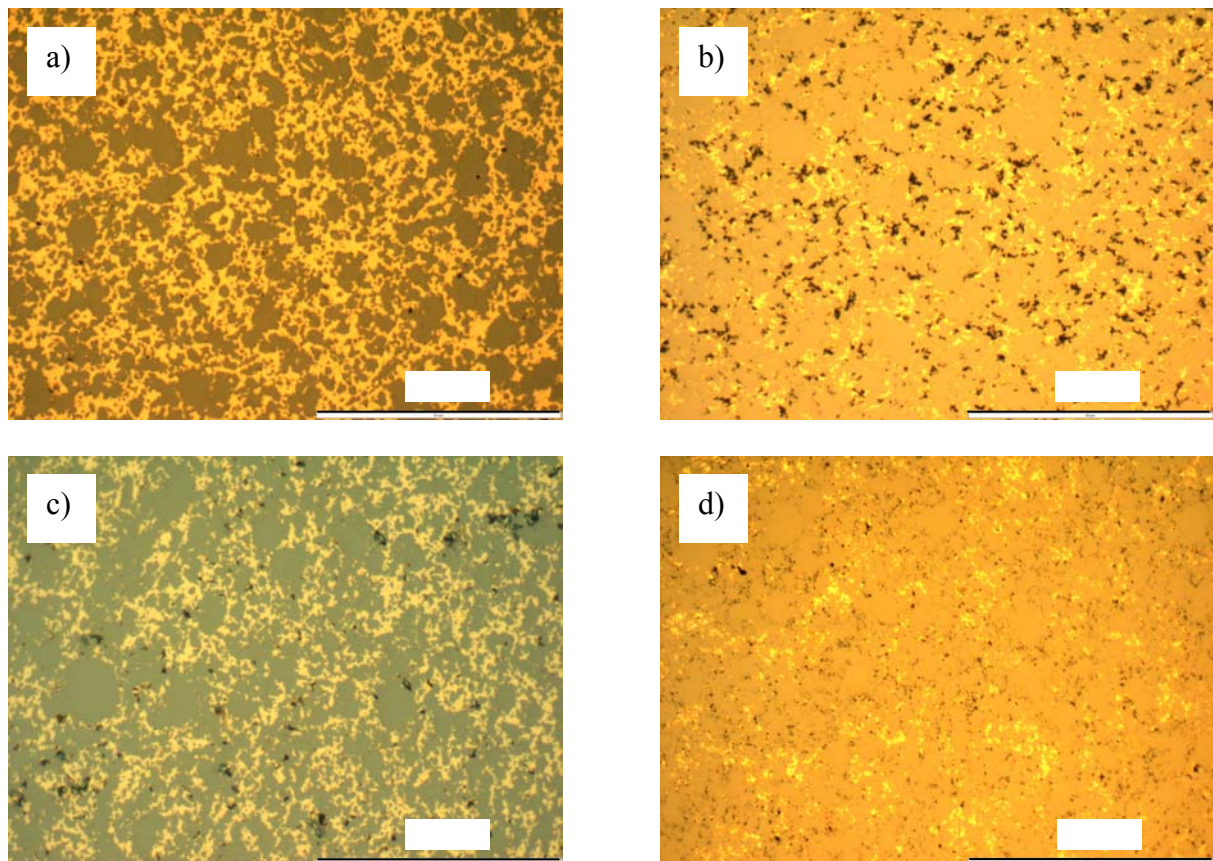


Fig. 4: Microstructures of Mg_2Si – Mg composites. Bright areas are assigned to Mg, dark ones to Mg_2Si and black spots are pores: (a) 60 at.% Mg_2Si + 40 at.% Mg; (b) 80 at.% Mg_2Si + 20 at.% Mg; (c) 70 at.% Mg_2Si + 30 at.% Mg; (d) 90 at.% Mg_2Si + 10 at.% Mg.

According to the results of bending tests and ultrasonic measurements the properties of the Mg_2Si -Mg composite are determined by the properties of Mg_2Si . Even if there is some plastic deformation in Mg, the framework of Mg_2Si will fracture and therefore the whole sample. The bending strength varies smoothly with the Mg content in the Mg_2Si -Mg composite, but an increase in elasticity can be seen for increased Mg contents.

The ideal microstructure of a Mg_2Si -Mg composite would be a Mg_2Si grain surrounded by a thin layer of Mg. Than a combination of a hard material (Mg_2Si) with some plastic deformation (Mg) could be expected. A promising way to achieve this is ball milling of Mg_2Si with Mg to get a Mg coating around Mg_2Si . Sintering of a powder mixture of Mg_2Si and MgH_2 may also lead to this result. Further investigation of milling conditions are in progress.

4. Conclusions

The SPS technique allows efficient preparation of bulk Mg_2Si as well as Mg_2Si -Mg composites. The density of the samples can be improved by powder milling, heating rate, soaking time and pressure during SPS. The elastic modulus of spark plasma sintered Mg_2Si and Mg as determined by the three point bending test is lower than data given in literature. Using the ultrasonic impulse echo method, the literature data are met at the lower limit. The Mg_2Si -Mg composite shows increased elastic deformation with increased Mg content, e.g., by adding 30 at.% of Mg.

References

- [1] Varin, R. A., Li, G., and Gill, J. S.; *The Minerals, Metals & Materials Society* (1993) 127-140
- [2] Frommeyer, G., Beer, S., and von Oldenburg, K.; *Zeitschrift für Metallkunde* 85 (1994) 372-377
- [3] Takeuchi, S., Hashimoto, T., and Suzuki, K.; *Intermetallics* 4 (1996) S147-S150
- [4] Hosono, T., Matsuzawa, Y. et al.; *Solid State Phenomena* 93 (2003) 447-452
- [5] Jiang, H. Y., Shen, Q., and Zhan, L. M.; *Journal of Wuhan University of Technology* 17 (2002) 36-38
- [6] Kajikawa, T., Shida, K., Sugihara, S., Ohmori, M., and Hirai, T. XVI ICT '97. Proceedings ICT'97. 16th International Conference on Thermoelectrics (Cat. No.97TH8291). IEEE. (1997) 275-278
- [7] Noda, Y., Kon, H., et al.; *Materials Transactions* 33 (1992) 845-850
- [8] Riffel, M. and Schilz, J.; *Fifteenth International Conference on Thermoelectrics.* (1996) 133-136
- [9] Sugiyama, A., Kobayashi, K. et al.; *J.Japan Inst.Metals* 63 (1999) 1145-1148
- [10] Zhang, L. M., Leng, Y. G. et al.; *Materials Science and Engineering B B86 (7-3-2001)* 195-199
- [11] Busch, G., and Winkler, U.; *Physica* 20 (1954) 1067-1072
- [12] Feher, F., Schinkitz, D., and Schaaf, J.; *Zeitschrift für anorg. allgemeine Chemie* 383 (1971) 303-313
- [13] Mulla, I. S., Choube, A. C. et al.; *Indian Journal of Chemistry* 27A (1988) 756-758
- [14] Caulfield, H.J.; Hudson, D.E.; *Solid State Communications*, 4 (1966) 299-301
- [15] Riffel, M., and Schilz, J.; *Scripta Metallurgica et Materialia* 32 (1995) 1951-1956
- [16] Riffel, M., and Schilz, J.; *Journal of Materials Science* 33 (1998) 3427-3431
- [17] Muñoz-Palos, J. M., Adeva, P., and Cristina, C.; *Materials Transactions* 37 (1996) 1606
- [18] Kondoh, K., Oginuma, H., Yuasa, E., and Aizawa, T.; *Materials Transactions* 42 (2001) 1293-1300
- [19] Kondoh, K., Oginuma, H. et al.; *Materials Transactions* 44 (2003) 981-985
- [20] Füglein, E., and Schubert, U.; *Chemical Materials* 11 (1999) 865-866
- [21] Fehér, F., and Ocklenburg, F. J.; *Zeitschrift für anorganische allgemeine Chemie* 530 (1985) 187-190
- [22] Clark, C. R., Wright, C. et al.; *Materials Letters* 33 (1997) 71-75
- [23] Aizawa, T. and Ichige, K-I.; *Materials Science Forum* 350-351 (2000) 333-338
- [24] Lu, L., Thong, K. K., and Gupta, M.; *Composites Science and Technology* 63 (2003) 627-632
- [25] Schmidt, J.; PhD-Thesis, (2003) TU-Dresden
- [26] Schmidt, M., Schmidt, J., Grin, Yu., Kieback, B. et al.; *Patentanmeldung DE 101 17 929.3 (10.04.2001)*
- [27] Tokita, M.; *Nyn-seramikasu (engl. New Ceramics)* 10 (1997) 43-53
- [28] Milekhine, V., Onsoien, M. I., Solberg, J. K., and Skaland, T.; *Intermetallics* 10 (2002) 743-750
- [29] Milekhine, V., Solberg, J. K., and Onsoien, M. I.; *Zeitschrift für Metallkunde* 94 (2003) 1331-1335
- [30] Schmidt, J., Niewa, R., Schmidt, M., Grin, Yu.; *J.Am.Chem.Soc.* (2004) accepted
- [31] Zaluska, A.; *Journal of Alloys and Compounds* 289 (1999) 197-206
- [32] Whitten, W. B., Chung, P. L. et al.; *Journal of Physics and Chemistry of Solids* 26 (1965) 49-56
- [33] *Gmelin handbook of inorganic chemistry* (1952), Verlag Chemie GmbH, Weinheim/Bergstrasse