Formation of Mg-silicates by reaction of perhydropolysilazane with MgO during pyrolysis in air

Martin SEIFERT, Mateus Lenz LEITE and Günter MOTZ[†]

Ceramic Materials Engineering (CME), University of Bayreuth, Ludwig-Thoma-Straße 36B, 95447 Bayreuth, Germany

The present study deals with the synthesis of Mg_2SiO_4 (Forsterite) applying the route of polymer derived ceramics (PDCs). The liquid, inorganic perhydropolysilazane (PHPS) was used because it is very reactive during pyrolysis in air and forms amorphous SiNO ceramic containing a tremendous amount of SiO_2 . Both facts are crucial for the reaction with MgO in order to synthesize Mg-silicates. The results of this study demonstrate, that the Mg-orthosilicate phase is formed at the MgO/SiNO interface via solid state reaction at comparably low temperatures of 1100°C during pyrolysis in air for 2 h. Furthermore the high reactivity of the polysilazane leads to an almost full conversion of the MgO to Mg_2SiO_4 under the used conditions.

©2016 The Ceramic Society of Japan. All rights reserved.

Key-words : Solid state reaction, Polymer derived ceramics, Forsterite, MgO, PHPS

[Received January 26, 2016; Accepted May 22, 2016]

1. Introduction

In general, materials in the magnesia-silica system are known to be suitable as machinable biomaterials for dental or orthopedic applications.^{1)–3)}

Moreover, the compound Mg_2SiO_4 (Forsterite) seems to be an attractive candidate for electronic implementations like millimeter wave dielectric devices, such as on ultra-high speed LAN, car anti-collision system on intelligent transport system, dielectric resonators and filters, revealing a low dielectric constant and an extremely low dielectric loss, associated to ultra-high quality factor and high-frequency electromagnetic waves.^{4)–7)}

In general, the synthesis of Mg_2SiO_4 or related composite ceramics involves multi-stage processes based on powders as starting materials, sol-gel routes or liquid phase deposition at sintering temperatures ranging from 1100 to 1500°C .^{1)–10)} Forsterite synthesis has also been described by the pyrolysis in air of a mixture of a siloxane resin and MgO nano-powder, based on polymer derived ceramics (PDCs) route.^{11),12)} The authors explain in short the mechanism of silicate formation, however disregard the influence of the remaining carbon in the polysilsesquioxane resin backbone upon pyrolysis. To the best of our knowledge, there is no literature dealing with the use of a polysilazane precursor, in order to synthesize Mg_2SiO_4 in a one-step reaction.

Preliminary results on active filler loaded organopolysilazanes demonstrated the potential for manufacturing of composite ceramics employing the PDC technology.^{13),14)} Thereby, the high reactivity of the precursor system during pyrolysis is used to generate tailored phase compositions in inert or reactive atmospheres.

The approach to synthesize Mg_2SiO_4 described in this work is different to the conventional methods. The formation of the Mg-orthosilicate phase results from the reaction of a commercially available inorganic perhydropolysilazane and small MgO cuboids. The present work focuses on the investigation of the phase

formation and reaction mechanisms leading to Mg_2SiO_4 during pyrolysis of the polysilazane in air and simultaneous reaction with MgO through an alternative and easy route.

2. Experimental procedure

For this work the liquid perhydropolysilazane PHPS-NN 120-20 (Merck KGaA, Germany) was used, which is commercially available as a solution of 20 wt % of PHPS in di-n-butyl ether.

Thus, in order to investigate the interface formation during the reaction of both components in detail, transparent MgO cuboids (Alfa Aesar, USA, Fig. 1) were used as received for this work. Thereby, the MgO cuboids were coated by using a 10 wt % solution of PHPS, which was added dropwise to the MgO cuboids, in order to fully wet the cuboid surface with the precursor. Subsequent removing of the solvent at 110°C in air, results in the crosslinking of the polymer and the formation of a dense and homogeneous coating, which is a precondition for the solid-state reaction between the components during pyrolysis.

The pyrolysis of the MgO/PHPS samples was performed in a furnace (HT 04/18, Nabertherm, Germany) at temperatures of up to 1100°C in air, applying a heating rate of 5 K/min and an annealing time of 2 h at the maximum temperature. To follow the weight change during pyrolysis, pure PHPS powder with a particle size smaller than $63\ \mu\text{m}$ and the MgO/PHPS samples were pyrolyzed in a TGA device (L81 A1550, Linseis, Germany) up to 1100°C applying a heating rate of 5 K/min.

Fig. 1. MgO cuboids used for this work.

[†] Corresponding author: G. Motz; E-mail: guenter.motz@uni-bayreuth.de

[‡] Preface for this article: DOI <http://dx.doi.org/10.2109/jcersj2.124.P10-1>

The microstructure of the coated and pyrolyzed cuboids was analyzed using a Zeiss 1540ESB SEM equipped with a field emission cathode. EDS analysis (Noran System Six, Thermo Fisher Scientific, USA) revealed information about the elemental distribution within the reaction zone of the MgO/PHPS samples. Crystalline phases were detected by X-ray powder diffraction analysis (D8 ADVANCE, Bruker AXS, Karlsruhe, Germany) using monochromatic CuK α radiation. Therefore, the MgO cuboids were first milled in a vario-planetary mill (Pulverisette, Fritsch, Germany) and coated by the PHPS solution in order to increase the surface for an almost quantitative solid state reaction of both compounds during pyrolysis. For crystallographic information the PDF-4+ 2014 structural database was used.

3. Results and discussion

The X-ray diffraction pattern of the the MgO/PHPS samples pyrolyzed at 900 and 1100°C for 2 h in air are shown in **Fig. 2**. The results demonstrate, that the pyrolysis at 1100°C in air is sufficient to form mainly Mg₂SiO₄ besides a minor amount of MgSiO₃ and residual MgO, while the sample pyrolyzed at 900°C in air shows no apparent reaction between the components to form magnesium silicates, thus only depicting the signal for crystalline MgO.

According to the synthesis route via solid state reactions between MgO and SiO₂ powder mixtures,¹⁰ the orthosilicate phase (Forsterite) is formed at the silica side of the MgO/SiO₂ interface. Thereby, MgO diffuses into the silica phase generating a layer of MgSiO₃ which is amorphous at first and crystallizes subsequently [s. Eq. (8)]. Sustained MgO diffusion through this layer leads to the formation of the Mg₂SiO₄ orthosilicate phase.

The structure of the inorganic PHPS polymer is composed of a Si–N backbone with highly reactive Si–H groups, thus excluding any influence that carbon may yield upon pyrolysis. The pyrolysis behaviour of pure PHPS in air is already well investigated.^{15)–18)} Under these conditions, PHPS can react with both oxygen and moisture. As it can be seen in **Fig. 3**, the TG-curve exhibits a remarkable weight gain in the temperature range from 100 to 400°C. This behaviour is attributed to the oxidation of the Si–H groups forming silanol groups in a first step [s. Eqs. (1)–(3)].

Fig. 2. XRD analysis of the MgO/PHPS samples after pyrolysis at 900 and 1100°C for 2 h in air. [◆: Mg₂SiO₄ (04-007-7321), ◇: MgSiO₃ (00-035-0610), ○: MgO (04-010-4039)]

As it is reported in the literature,^{15)–18)} these reactive silanol groups lead to the formation of Si–O–Si bridges and gaseous species in form of hydrogen, water or ammonia [Eqs. (4)–(7)] at higher temperatures, in a second step.

During these reactions, the nitrogen atoms are increasingly replaced by the oxygen atoms resulting in an amorphous silicon oxynitride ceramic with an elemental composition after pyrolysis in air at 1000°C for 1 h of SiN_{0.47}O_{1.08}.¹⁵⁾

Preliminary results¹³⁾ on active filler loaded organopolysilazanes demonstrated, that metal particles act as an active filler and react with the amorphous SiCN network formed during pyrolysis above temperatures of 1000°C in inert atmosphere. For the MgO/PHPS samples we expect a comparable pyrolysis behaviour where the reaction of magnesia and the formed silicon oxynitride should lead to the formation of Mg₂SiO₄. Based on these facts, we propose a similar, diffusion controlled reaction mechanism for the magnesia silicate phase formation at the MgO/SiNO interface. Due to the vast amount of SiO₂ formed within the amorphous SiNO ceramic, Mg₂SiO₄ results from the reaction of MgO and SiO₂ described in Eq. (9).

Furthermore it should be mentioned, that the temperature reported in the literature for synthesizing the Mg-orthosilicate via solid state reactions of mixed powders through conventional methods are in the range of 1100 to 1400°C.¹⁰⁾ Due to the high reactivity of the PHPS precursor in combination with the grinded MgO, an almost full conversion to forsterite was achieved at a maximum temperature of 1100°C, whereas no reaction was observed at 900°C (see Fig. 2). This result is an evidence for the assumption that the solid state reaction between both components only starts after the formation of the SiO₂ phase during the chosen conditions.

Figure 3 shows the weight change of the MgO/PHPS samples in comparison with pure PHPS powder. The detected mass gain for both samples is attributed to the oxidation reactions [s. Eqs. (1)–(7)] of the precursor.

In comparison to the pure PHPS precursor, where no further

Fig. 3. TGA of the MgO/PHPS samples and pure PHPS powder after pyrolysis at 1100°C in air applying a heating rate of 5 K/min.

Fig. 4. Microstructure of the interface after pyrolysis at 1100°C for 2 h in air and the elemental distribution.

mass gain was detected at temperatures exceeding 1000°C, we assume that the small weight gain of 0.7% of the MgO/PHPS sample can be attributed to further oxidation reactions of the amorphous SiNO ceramic during Mg-silicate phase formation.

Figure 4 shows the SEM image of the microstructure of the MgO/PHPS samples pyrolyzed at 1100°C for 2 h in air, which is an evidence for the expected interface formation during pyrolysis. In order to correlate the detected crystalline phases with the microstructure, EDS analysis of different spots within the interface area was performed (see Fig. 4). The results revealed an elemental composition of 11 at. % Mg, 35 at. % Si and 54 at. % O in average leading to a theoretical phase composition of $\text{MgSi}_{3.2}\text{O}_{4.9}$. Therefore we conclude, that the interphase is composed of a mixture of MgSiO_3 and SiO_2 . The fine grained structure is composed of 30 at. % Mg, 15 at. % Si and 55 at. % O. The resulting normalized composition of $\text{Mg}_2\text{SiO}_{3.7}$ is in a good agreement with Forsterite. Additionally, it cannot be excluded that a small amount of nitrogen is still present in the sample.¹⁵⁾

4. Summary

The results of the present study demonstrate the feasibility to synthesize Mg_2SiO_4 via solid state reaction of a polysilazane and

MgO during pyrolysis in air. The high reactivity of the PHPS precursor enables an almost full conversion of the used MgO cuboids into the desired phase at relatively low temperatures of 1100°C. The aim of further work will be the manufacturing of dense Mg_2SiO_4 composite ceramics based on MgO/PHPS powder mixtures.

Acknowledgements The authors acknowledge the DFG and CAPES for financial support and the framework program BRAGECRIM (Brazilian German Collaborative Research Initiative on Manufacturing Technology).

References

- 1) J. C. Dubois, P. Exbrayat, M. L. Couble, D. Goueriot and M. Lissac, *Biomaterials*, **20**, 1841–1849 (1999).
- 2) D. Goueriot, J. C. Dubois, D. Merle, F. Thevenot and P. Exbrayat, *J. Eur. Ceram. Soc.*, **18**, 2045–2056 (1998).
- 3) S. Ni, L. Chou and J. Chang, *Ceram. Int.*, **33**, 83–88 (2007).
- 4) S. Meng, Z. Yue, H. Zhuang, F. Zhao and L. Li, *J. Am. Ceram. Soc.*, **93**, 359–361 (2010).
- 5) H. Ohsato, T. Tsunooka, T. Sugiyama, K. Kakimoto and H. Ogawa, *J. Electroceram.*, **17**, 445–450 (2006).
- 6) K. X. Song, X. M. Chen and X. C. Fan, *J. Am. Ceram. Soc.*, **90**, 1808–1811 (2007).
- 7) S. Sano, N. Saito, S. Matsuda, N. Ohashi and H. Haneda, *J. Am. Ceram. Soc.*, **89**, 568–574 (2006).
- 8) I. Kagomiya, J. Sugihara, K. Kakimoto and H. Ohsato, *J. Electroceram.*, **22**, 327–333 (2009).
- 9) N. T. Andrianov, S. S. Strelnikova and S. M. Dyagilets, *Glass Ceram.*, **61**, 16–18 (2004).
- 10) G. W. Brindley and R. Hayami, *Philos. Mag.*, **12**, 505–514 (1965).
- 11) P. Colombo, E. Bernardo and G. Parciannello, *J. Eur. Ceram. Soc.*, **33**, 453–469 (2013).
- 12) E. Bernardo, L. Fiocco, G. A. Giffin, V. D. Noto and P. Colombo, *Adv. Eng. Mater.*, **16**, 806–813 (2014).
- 13) M. Seifert, N. Travitzky, W. Krenkel and G. Motz, *J. Eur. Ceram. Soc.*, **34**, 1913–1921 (2014).
- 14) M. Seifert, P. Concalves, T. Justus, N. Martins, A. N. Klein and G. Motz, *Mater. Des.*, **89**, 893–900 (2016).
- 15) M. Günthner, T. Kraus, A. Dierdorf, D. Decker, W. Krenkel and G. Motz, *J. Eur. Ceram. Soc.*, **29**, 2061–2068 (2009).
- 16) K. Wang, X. Zheng, F. S. Ohuchi and R. K. Bordia, *J. Am. Ceram. Soc.*, **95**, 3722–3725 (2012).
- 17) F. Bauer, U. Decker, A. Dierdorf, H. Ernst, R. Heller, H. Liebe and R. Mehnert, *Prog. Org. Coat.*, **53**, 183–190 (2005).
- 18) G. Motz, T. Schmalz, S. Trassl, R. Kempe, *Design, Processing and Properties of Ceramic Materials from Preceramic Precursors*, **[1]**, 15–36 (2011).