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

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The present study deals with the synthesis of Mg$_2$SiO$_4$ (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$_2$SiO$_4$ under the used conditions.

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

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$_2$SiO$_4$ (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$_2$SiO$_4$ 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$_2$SiO$_4$ 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$_2$SiO$_4$ 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$_2$SiO$_4$ 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 cubic 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 μm 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.
The microstructure of the coated and pyrolyzed cuboids was analyzed using a Zeiss 1540 ESB 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 Cu Kα 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 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 MgSiO3 besides a minor amount of MgS2O3 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, 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 the interface. Thereby, MgO diffuses into the silica phase generating a layer of MgSiO3 which is amorphous at the interface 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. 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)].

\[
\begin{align*}
\text{Si–H} + \frac{1}{2} \text{O}_2 & \rightarrow \text{Si–OH} \\
\text{Si–H} + \text{H}_2\text{O} & \rightarrow \text{Si–OH} + \text{H}_2 \\
\text{Si–NH–Si} & \equiv + \text{H}_2\text{O} \rightarrow \text{Si–OH} + \equiv \text{Si–NH}_2
\end{align*}
\]

As it is reported in the literature, 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.

\[
\begin{align*}
\text{Si–OH} + \text{H}_2\text{O} & \rightarrow \text{Si–O}–\text{Si} + \text{H}_2\text{O} \quad (4) \\
\text{Si–OH} + \equiv \text{Si–NH}–\text{Si} & \equiv \rightarrow \equiv \text{Si–O}–\text{Si} + \text{NH}_3 \quad (5) \\
\equiv \text{Si–OH} + \equiv \text{Si–NH}–\text{Si} & \equiv \rightarrow \equiv \text{Si–O}–\text{Si} + \text{NH}_3 \quad (6) \\
\equiv \text{Si–OH} + \text{NH}_3 & \rightarrow \equiv \text{Si–O}–\text{Si} + \equiv \text{Si–NH}_2
\end{align*}
\]

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 SiN0.45O0.55.15

Preliminary results 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).

\[
\begin{align*}
\text{MgO} + \text{SiO}_2 & \rightarrow \text{MgSiO}_3 \\
2\text{MgO} + \text{SiO}_2 & \rightarrow \text{Mg}_2\text{SiO}_4
\end{align*}
\]

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. 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. 2. XRD analysis of the MgO/PHPS samples after pyrolysis at 900 and 1100°C for 2 h in air. [MgS2O3 (84-007-7321), MgSiO3 (90-065-0610), MgO (90-041-0439)]

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.
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 MgSi3.2O4.9. Therefore we conclude, that the interphase is composed of a mixture of MgSiO3 and SiO2. The fine grained structure is composed of 30 at.% Mg, 15 at.% Si and 55 at.% O. The resulting normalized composition of Mg2SiO4 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 Mg3SiO4 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 Mg3SiO4 composite ceramics based on MgO/PHPS powder mixtures.

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