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Laser synthesis of nanostructured ceramics from liquid precursors

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Abstract

The free-form net shape laser synthesis of nanostructured ceramics from liquid precursors enables a residual stress-free production of high temperature resistant ceramic units and components for the use in microsystem engineering. Due to the use of molecular compounded liquid, ceramic precursors the resulting ceramic components show outstanding properties, for example high purity and a nanostructured material design.

The use of pulsed lasers enables a defined input of energy required to pyrolyse the precursor material into a crystalline ceramic, so the active volume can be reduced significantly compared to other processes, for example pyrolysis by furnace.

In this paper several methods for a further minimization of the active volume are presented. The investigations determined different factors affecting the process. Realizing selective experiments allows a determination of their influencing level and the definition of a working area to produce three-dimensional components with high aspect ratio.

By several studies, e.g., scanning electron microscopy, transmission electron microscopy as well as X-ray diffraction analysis, the atomic structure and composition of the created components were analyzed and valued, so the different reaction processes can be described extensively.

Keywords: Laser-assisted pyrolysis; Preceramic polymers; Nanostructured ceramic; Rapid manufacturing

1. Introduction

The continually miniaturization of mechanical components in all areas of every-day life is one of the major challenges in scientific research and industrial application. Hence the focus is fixed on the development of functional mechanical components with reduced dimensions.

Above all else ceramic materials gained an important role due to their outstanding properties, e.g., temperature and chemical resistance as well as high strength and hardness. However, the size of the ceramic components is often restricted by several factors. Usually ceramic components are made of mechanically compressed and subsequently sintered ceramic powders. Moreover sintering supplies are often necessary to support the diffusion process within the ceramic powder. Powder sizes as well as the size of the matrices are still restricting factors preventing the use in microsystem engineering. Other possibilities, e.g., laser sintering/melting [1–3] enable free-form and high flexible processing of ceramic components indeed, but there are still subsequent sintering processes in oven and further finishing processes necessary.

The pyrolysis of silicon organic polymers offers a completely different possibility to fabricate ceramic components. Due to the bottom-up strategy the use of chemical substances with high purity as precursor materials for a subsequent pyrolysis is possible.

However, up to now only coatings or thin fibres can be processed well due to the degassing behaviour at pyrolysis reactions. Bulk ceramics are only producible using slow heating rates and long dwell times. Moreover residual stresses within the components, long processing times and the necessity of a mould are still restrictions for this process.

Thus the laser-assisted pyrolysis of liquid silicon organic polymers offers high potential for free-form fabrication of dense and residual stress-free ceramic components.

2. Literature overview

The pyrolysis of silicon organic polymers has a long scientific history. After the first synthesis [4] and decomposition [5] further fundamental investigations had been conducted by

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Burkhard [6], Fritz et al. [7] and Kumada [8]. In the early 1960s Popper was the first who pave the way for industrial applications using pyrolysis of preceramic polymers [9]. Especially the investigations of Yajima et al. enabled the establishment of a complete new branch of industry [10–15]. After these initiations the pyrolysis of preceramic polymers into ceramic materials gained significant scientific and industrial interests.

Nowadays precursor pyrolysis is established in scientific research as well as in some industrial applications. However, several restrictions prevent the processing of bulk ceramic components as degassing during the pyrolysis process promotes porosity and residual stresses within the components. Riedel et al. developed a process for producing dense bulk ceramic parts using slow heating rates, which allow degassing during conversion [16]. Concerning high process efficiency, the reduction of processing time as well as higher process flexibility are challenging aims. For this reason laser pyrolysis seems to be a promising way to achieve higher process efficiency and flexibility as well. The high potential of this process had been identified by several research groups [17–31]. Besides high flexibility and defined input of energy, laser-assisted pyrolysis allows the reduction of residual stresses within the components by minimizing the active volume significantly. However, laser pyrolysis is commonly used in combination with precursors in a powdery state, so the laser-assisted pyrolysis using liquid precursor material is a relatively new method [21].

3. Pyrolysis process for heating in furnace

The pyrolysis process is divided into several steps as shown in the flow chart in Fig. 1. After synthesizing the polymer from monomer units, the resulting precursor is cured into a solid preceramic network by thermal crosslinking within a temperature level of 400–500 K. During crosslinking reductive amination and dehydro-interlinking reactions occur using a polysilazane precursor. At elevated temperatures the cured solid polymer is decomposed into an amorphous covalent ceramic material by ceramization, which means loss of organic groups, for example methyl groups. Depending on the precursor material the ceramization process take place within a temperature level of 700–1300 K. Above this temperature level the ceramic material is converted into a crystalline ceramic material.

Due to the high active volume increasingly crack formation occurs. Moreover the degassing leads to a high porosity within the component.

4. Process setup

Aim of the process setup is to minimize the active volume significantly. Diverse preliminary investigations had shown that the energy of the laser, necessary for the conversion process, leads to an unintended crosslinking out of the focal area and an increase of the active volume. Basic idea of the process setup is to split the laser beam and recombine it in the focal area to minimize the active volume. Only in the recombination area the energy level is high enough to start the pyrolysis reactions. As shown in Fig. 2 the optical setup is build up by diverse beam splitters, mirrors and focal lenses. The setup is mounted on a LASAG FLS 542 pulsed Nd:YAG laser with Gaussian shape (TEM_{00} mode).

For processing within the laser pyrolysis process the liquid preceramic polymer has to show features like low absorbance at laser wavelength and stability under regular working conditions. High chemical purity, good modification possibilities and commercial availability are further intended characteristics. For

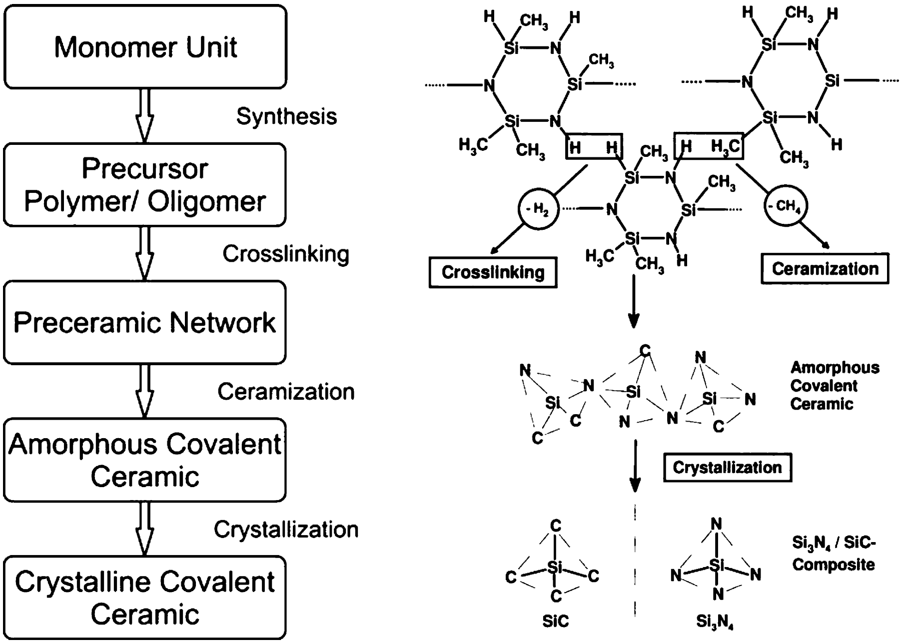

Fig. 1. Material design by molecular architecture [33] (left side) and pyrolysis of a polysilazane precursor in detail [34] (right side).