1   Introduction

Lightweight materials are very attractive to increase the energy efficiency caused by weight reduction in the aerospace industry. Nowadays, the application of these advanced materials starts to go well beyond the aerospace industry, particularly to the automotive and wind energy industries, as global trends toward CO_2 reduction and resource efficiency have significantly increased. According to a recent report of McKinsey & Company [HEU12], the use of lightweight materials will significantly grow across industries, being currently about 80% of the total material share in the aerospace industry and expected to increase from 30 to 80 % by 2030 in the automotive industry. While the main drivers for the use and development of lightweight materials in the aerospace industry are the need to reduce fuel consumption as related costs and the need to increase passenger/cargo load per flight, the automobile industry is runned to the CO_2 emissions regulation. Last, but not least, the wind industry requires extreme lightweight materials in the long rotating blades, which has to resist high stresses.

To reinforce lightweight materials, carbon fibre is currently one of the most attractive materials due to its high potential for weight reduction in certain applications and its well stablished industrial scale processing. In spite of the increased production of carbon fibres, their current costs continue to be high. However in the next two decades it is expected that the costs of carbon fibres for automotive applications reduce from € 42/Kg today down to € 23/Kg in a conservative cost scenario [HEU12]. This will be mainly driven by the development of a less expensive precursor material to produce the carbon fibres and a reduction in the processing costs for fibre reinforced composites for pre- and part forming of 60 to 80 %.

In a parallel scenario, the demand of lightweight thermostructural materials for the industry also represents a way to create advanced technologies such as more efficient turbines, heat exchangers, propulsion, fusion reactors and Ultra High Temperature Ceramic (UHTC) parts for supersonic jets. In this manner, ceramic fibres play an important role to realize the fabrication of such materials. Research activities in this field led over the last 50 years to the development of commercially available Chemical Vapour Deposition (CVD) SiC fibres [CHE99, FLO14 , NUT85] and three generations of SiC fibres based on polymer derived ceramics (PDCs) [BUN06, DIC05, FLO14, MOT09]. In comparison to carbon fibres, high performance non-oxide ceramic fibres comprise not only superior mechanical properties, such as tensile strength > 2 GPa and stiffness, but also thermal stability and oxidation resistance at temperatures over 800 °C, which are essential for the reinforcement of new materials based on metallic (MMCs) and ceramic matrices (CMCs).

For MMCs applications, such as combustion engines and high efficient turbines, Titanium Matrix Composites (TMCs) reinforced with SiC fibres are promising candidates, as they combine the high strength, stiffness and creep resistance of SiC monofilaments with the high ductility, toughness and corrosion resistance of titanium alloys [HER04, LEY03]. These types of MMCs are better reinforced with CVD fibres having diameters > 100 μm to withstand thermal load in processes such as Hot Isostatic Pressing (HIP) and possible reactivity with the alloy matrix. Because SiC fibres are generally reactive with titanium alloys at high temperatures, fabrication processes that allow a controlled chemical reaction with the metal matrix, mainly dominated by diffusion, such as matrix-coated fibre technique enables the formation of a strong fibre-matrix interface and good adhesion. This good adhesion is necessary for the efficient load transfer from matrix to SiC fibres. The major obstacles for the application of TMCs in the industry are the high material costs of monofilament SiC fibres. Commercially available CVD SiC fibres are one of the most expensive ceramic fibres with prices up to ~€ 8000/kg (11000 U$/kg) [FLO14, LEY03, MAR84].

In contrast, the continuous processing of fibres from precursor route is still the most attractive method for the manufacturing of cost-effective non-oxide ceramic fibres. In this method polymer fibres are spun by conventional techniques, such as melt or dry-spinning, by using a preceramic polymer. Common types of polymers are polycarbosilanes (SiC systems), polyorganosilazanes (SiCN systems) and polyborocarbosilazanes (SiBCN systems). The polymer fibres are subsequently cured and finally pyrolysed into polymer derived ceramic fibres at temperatures higher than 1000 °C. Ceramic fibres derived from SiCN systems, such as polysilazanes, comprise good oxidation stability up to ~1500 °C (due to the nitrogen content) and also corrosion resistance in acids and bases. Beside this they offer a remarkable cost reduction, due to the availability of cheap educts, use of low e-beam doses for their curing and relatively simple processing [CHO00, HAC05].Two most promising and most used precursors in the SiCN system are currently KiON ML33 and HTT1800. These precursors are liquid oligosilazanes differing itself especially in terms of reactive functional groups. Until 2012 they were manufactured by Clariant AG, but in 2013 Clariant sold the precursor production to the company AZ-EM. In 2013 the prices of KiON ML33 and HTT1800 were quoted to be € 158/kg and € 178/kg, respectively. ML33 and HTT1800 open new opportunities to cost effectively process large diameter amorphous ceramic SiCN fibres, which until now were only produced by chemical vapour deposition of silicon precursors on a carbon or tungsten core.

2 Problem statements

Similar to carbon fibres, first studies on the processing of non-oxide ceramic fibres were directed to selective properties for the suitable reinforcement of MMCs and CMCs. The main purpose was the processing of high performance fibres with similar creep resistance and oxidation stability at temperatures over 1100 °C as technical monolithic ceramic, such as SiC. This was achieved with the development of precursors, such as polycarbosilanes, and the improvement of curing and pyrolysis techniques. However the high costs for the raw materials and fibre processing routes, such as chemical vapour deposition (CVD) route, makes difficult the acceptance of these high performance fibres in the market.

To allow non-oxide ceramic fibres to compete with other high performance fibres, the current researches are mainly focused on the development of new synthesis routes for tailored precursors and more cost-effective routes for the fibre processing. For polymer derived ceramics (PDCs) the cost factors are connected to the critical non-technical requirements, which are the price and availability of the starting materials, and the complexity of the processing route [DIC12a, HAC05, KIT10a].

One of the most challenging tasks in the processing of polymer derived ceramic fibres is the synthesis of a suitable preceramic polymer. Linear, high molecular weight organic polymers can be used to prepare organic fibres, but the same type of polymer is not suitable to produce ceramic fibres because of the easy fragmentation of the polymer into volatile products during the pyrolysis. In contrast, appropriate preceramic polymers for spinning are generally cross-linked, network-type with low molecular weights (< 10000 g/mol). This results in rather fragile green (polymer) fibres, being more difficult to handle them during the pyrolysis to ceramic fibres. Therefore, the successful processing of polymer derived ceramic SiCN fibres depends on the success of each of its processing steps, from the synthesis of the preceramic polymer to the pyrolysis of the fibres.

In the specific case of ceramic fibre processing via melt spinning, which is less expensive/complex than dry or wet spinning, some problems arise by using commercially available oligosilazanes such as ML33 and HTT1800. Their chemical and physical properties need to be tuned for the processing, because both ML33 and HTT1800 are liquid precursors. They also differ itself in terms of functional groups, which implies different melt spinning and curing behaviours. Therefore, physical and chemical modifications in the polymers, especially the rheological behaviour, interconnected to the molecular weight and thermal stability of these precursors are critical properties, which will decide about the failure or the success in the production of green (polymer) fibres. Additionally, the processing of thicker ceramic fibres from the precursor route implies cost reductions, but also a material with more

defects/voids if compared to fibres from the Chemical Vapour Deposition (CVD) route. This is a very unique challenge as the number and size of defects/voids in the fibres is related to the diameter.

3   Objective

The main objective of this work is the development of amorphous ceramic SiCN fibres with diameter > 70 µm from two commercially available liquid oligosilazanes, named ML33 and HTT1800, for application as reinforcement in metal matrix composites (MMCs), notably Titanium Matrix Composites (TMCs). The diameter of the ceramic SiCN fibres was chosen to be higher than 70 µm based on commercially available CVD SiC fibres (diameters ranging from 78 µm (SCS-9A) up to ~140 µm (SCS-6, SCS-Ultra and Sigma)). More details about these fibres will be discussed in Chapter 4.2.

To successfully achieve the processing of ceramic SiCN fibres, each step in the manufacturing chain of ceramic fibres from precursor route (see Fig. 1) needs to be feasible. Therefore, a set of goals from the synthesis of the preceramic polymer to the pyrolysis of the fibres was implemented and are displayed below:
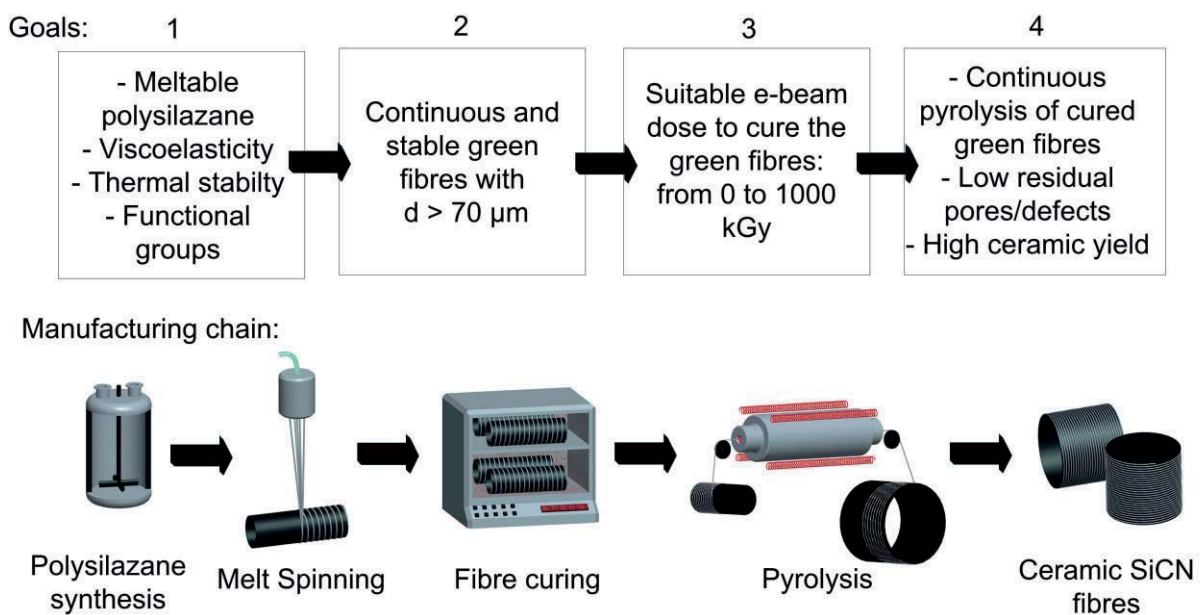
Fig. 1: Manufacturing chain of ceramic fibres from precursor route

To be suitable for the processing of ceramic SiCN fibres, the preceramic polymer must be processable by conventional polymer processing techniques. In this work melt-spinning is preferable against dry-spinning, due to the formation of green monofilaments with better mechanical properties and handleability, and to economical factors, such as the absence of solvent in the spinning process. The preceramic polymer must be stable at room temperature, fusible, forming a stable melt, and viscoelastic to allow the spinning of green (polymer) fibres. Another requirement is that the polymer contain latent reactive functional groups. This allows

the polymer to be cross-linkable to enable the green fibre to keep its shape after curing and during the early stages of the pyrolysis. Additionally it minimizes the evolution of volatiles during the pyrolysis and increases the ceramic yield of the polymer after the pyrolysis, which should be at least 60 to 75 wt.%.

For this reason, the first goal was to develop a simple and reproducible cross-linking reaction, allowing a controlled increase of the molecular weight of the oligosilazanes. This selective cross-linking reaction should lead to a meltable polysilazane with thermal stability and viscoelasticity, properties that play an important role for the melt spinning of continuous green fibres with reduced defects. Chemical, thermal and rheological characterizations, such as GPC, TGA and oscilatory rheometry, are essential tools to analyse the quality of the synthesised polymers.The liquid ML33 and HTT1800 oligosilazanes were selected as precursors for the processing of the thick ceramic fibres due to their reactive functional groups Si-H and N-H (and also Si-vinyl in HTT1800). These reactive groups are responsible for the controlled chemical cross-linking to a meltable polymer, further curing to an infusible polymer and, consequently, the formation of a material with high ceramic yield after the pyrolysis.

The second goal was the processing of continuous and stable green fibres by melt spinning technique. For the development and optimization of a reliable continuous processing of ceramic fibres with diameter around 100 µm, the chemical and physical properties of the precursor together with the mechanical stability of the uncured and cured green fibre must be well understood. By using a lab-scale melt spinning equipment, the parameters for the processing of the fibres, such as temperature and pull velocity can be optimized to reduce defects or flaws in the green fibres. Fibres with up to 150 µm diameter should be prepared. The mechanical stability of the green fibres is a crucial step to the success or failure in the pyrolysis of large diameter ceramic fibres. Factors such as surface flaws and internal porosity are important characteristics, which will determine the mechanical properties of the fibre.

To make the polymer and consequently the green fibre infusible, the application of high-energy irradiation is necessary. Having this in mind, electron beam irradiation was used to cross-link the green fibres before pyrolysis into ceramic fibres. But as the electron beam irradiation is a high cost technique, the influence of the irradiation doses in the cross-linking needed to be investigated, regarding the reduction of the necessary electron-beam dose. Simultaneously the curing process with electron beam irradiation makes the green fibres not just infusible, but also increases their mechanical properties. Therefore the tensile strength of the cured green fibres was tested to verify the influence of the reactive functional groups of the polysilazane in the mechanical properties of the fibre.

The last goal to be reached was the convenient pyrolysis of the cured green fibres in protective atmosphere. Pyrolysis temperature, residual porosity/defects and chemical composition of the large diameter amorphous ceramic SiCN fibres will influence their mechanical and thermal properties. The tensile strength, creep and oxidation resistance of these ceramic fibres was evaluated by SEM microscopy and standard tests, including tensile strength measurements, Bend Stress Relaxation (BSR) and oxidation tests.

4   Literature Review

4.1   Preceramic Polymers

4.1.1   History of Preceramic Polymers

The synthesis of organosilicon systems dates back to 1900s. At this time, Kipping, considered one of the founders of the silicon chemistry, synthesized many organic derivatives of silicon, which led to the development of the first silicone structures [KIP901, KIP907, KIP37]. Some years later Stock and Somieski described the preparation and reactivity of dichlorosilane (H_2SiCl_2), a fundamental educt used for the synthesis of a variety of preceramic polymers, i.e. the ammonolysis of dichlorosilane to prepare a mixture of oligosilazanes [STO21]. In 1948 Brewer and Harber carried out the ammonolysis of a dichlorodimethylsilane (($CH_3)_2SiCl_2$) solution in benzene with gaseous ammonia to synthesize a non-volatile oligocyclosilazane. Additionally, they prepared a viscous cyclosilazane oil by ammonolysis of dichloromethylsilane (CH_3SiHCl_2).This cyclosilazane turned to be a porous and brittle resin after destructive distillation in nitrogen [BRE48]. But it was not until 1956 that the first synthesis of a SiC based ceramic material derived from a thermal treatment of polycarbosilane precursors was conducted by Fritz [FRI56]. Following all these findings, in the 1960s Andrianov, Fink and Wannagat concentrated their researches in the synthesis and characterization of silicon-nitrogen compounds, in particular defined cyclic molecules, such as cyclodisilazanes. Their works led to the synthesis of preceramic polymers, which turned to be attractive for the production of non-oxide ceramics. [AND63, FIN64, WAN64]

Later on, with the development of the Müller-Rochow synthesis for the industrial production of dichlorodimethylsilane by a catalyzed reaction of methyl chloride with silicon metal, more opportunities arised to synthesize preceramic polymers. In addition to dichlorodimethylsilane, Rochow et al. also worked on the synthesis of cyclosilazanes and their posterior polymerization with ammonium halides, in particular ammonium bromide, which catalyse the reaction to cyclic and linear polysilazanes [LIE64, KRÜ62, KRÜ64, RED64].

Attempts to produce ceramics from organosilicon systems were published in scientific reports of Ainger and Herbert, Chantrell and Popper, and also Fink [AIN65, CHA65, FIN66b, FIN67a, FIN67b, FIN68, FIN69]. But the industrial application of ceramics from preceramic polymers was only introduced in the 1970s, when Verbeek and Winter managed to produce polyorganosilazanes by ammonolysis or aminolysis of dichlorodimethylsilane or trichloromethylsilane. The synthesized polyorganosilazanes could be processed in stable green bodies. After pyrolysis of the green bodies at temperatures higher than 1000 °C amorphous SiCN ceramic

materials, such as small-diameter ceramic SiCN fibres for high temperature applications, were yielded [MAN74, VER73]. Almost at the same time, Yajima reported the synthesis of polycarbosilanes and its application as a precursor for the processing of ceramic SiC materials, in particular ceramic SiC fibres [YAJ75a, YAJ75b].

The result of all the works cited in Chapter 4.1.1 are the fundaments of the synthesis of a large variety of preceramic polymers, such as polysiloxanes, polysilanes, polycarbosilanes and poly(organo)silazanes. These polymers are suitable for the processing of polymer derived ceramics (PDCs), i.e. high performance fibres, ceramic matrix composites, porous components and coatings which are suitable for high temperature applications [COL10a, COL10b, GRE00].

4.1.2 Synthesis of polysilazanes for precursor derived ceramics (PDCs)

The usual method to produce polysilazanes is the ammonolysis and aminolysis of halogenosilanes. The most preferable educts are chlorosilanes, which are products of the Müller-Rochow synthesis. In many cases they are byproducts in the silicone industry, which makes them inexpensive. Additionally, chlorosilanes have the advantage of being readily available and easily purified by distillation, which makes it attractive to produce different types of preceramic polymers, including polysilanes, polysilazanes and polycarbosilanes.

Similar to the synthesis of polysiloxanes, instead of reacting the chlorosilane with water for hydrolysis of Si-Cl bonds and formation of Si-O-Si groups, ammonia or amines are used to create Si-N bonds with the formation of solid ammonium chloride (NH_4Cl) salt as by product.

The Si-N bond is not as stable as the counterpart Si-O bonds, and tends to be cleaved under various conditions, which undergoes disproportionation reactions. Therefore, many different synthesis routes were reported to produce oligomers and polymers, which have not only a minimum stability for the processing of the polymer material, but also a remarkable ceramic yield after the thermal treatment.

One breakethrough in the development of preceramic polymers was the synthesis of perhydropolysilazane (PHPS) for the processing of Si_3N_4 ceramics. PHPS is synthesized by the *ammonolysis reaction* of dichlorosilane (H_2SiCl_2) in benzene, dichloromethane, diethyl ether or paraffinic solvents, according to Eq. 1. [SEY83, SEY84, STO21].

PHPS

$$\text{Cl-Si-Cl} \xrightarrow[\text{-NH}_4\text{Cl}]{\text{+NH}_3} *\left[\text{Si-N}\right]_n*$$

(1)
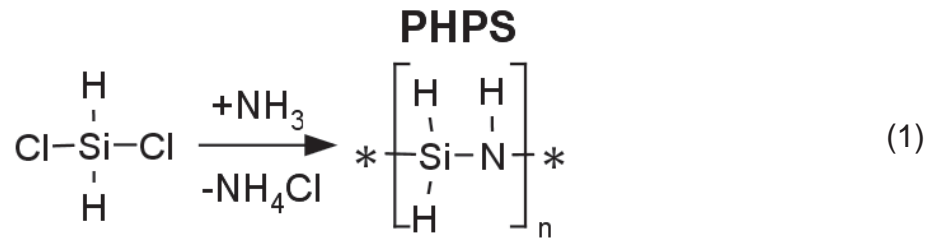
H_2SiCl_2 is a hazardous gaseous compound, due to its easy disproportionation with formation of SiH_4 and $SiCl_4$, making it very sensitive to moisture and oxygen. Furthermore, depending on the application, PHPS needs specific rheological properties and high ceramic yield, generally > 85 %. To achieve these properties, it is essential to control the molecular weight, elemental composition and branching structure.

Arai and Isoda [ARA89] synthesized PHPS by the ammonolysis of an adduct between dichlorosilane and pyridine and discovered that the addition of pyridine offers several advantages. Some of these advantages include the stabilization of the dichlorosilane, increase in molecular weights, catalytic activity in the thermal cross-linking for Si-H/N-H dehydrocondensation and disproportionation of NHSi groups, and beneficial introduction of a very small percentage of carbon in the ceramic [ARA87b, FUN89].

In the past, PHPS, industrially produced from the company Tonen in Japan, was used to produce continuous silicon nitride fibres [ARA87a], ceramic matrix composites [AOK92, SAT92] and ceramic coatings. The main industrial application of PHPS is currently concentrated in the processing of functional coatings, especially as dielectric coating for electronic applications, but also for solar, automotive and building materials, and is commercially available from the company AZ-EM, Wisbaden, Germany.

As stated by Aylett [AYL68], polysilazanes without carbon substituent are less stable due to SiH-NH linkages, which lose hydrogen easily, making the processing of some ceramic materials such as ceramic fibres unfavorable. Moreover because pure Si_3N_4 crystallizes above 1200 – 1300 °C, the mechanical stability of ceramic fibres from polysilazanes is weakened, leading to a catastrophic reduction of their mechanical properties above 1300 °C. Funayama [FUN90] reported this behaviour for stoichiometric Si_3N_4 fibres prepared from PHPS and also the reduction of the crystallization temperature of Si_3N_4 due to the presence of free silicon [PRO78]. But with the addition of a second refractory phase, such as carbon, the crystallization is delayed. Hence, a lot of attention was given for the development of SiCN precursor systems, such as polycarbosilazanes and polyorganosilazanes.