



Synthesis and high-temperature oxidation of a polymer-derived Mo-SiN based ceramic composite



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ABSTRACT

Si_3N_4 ceramics strengthened with molybdenum silicides seem to be potential candidates for (ultra-)high temperature applications. While Mo_5Si_3 exhibits a higher melting point and a better creep resistance than MoSi_2 , its oxidation resistance is inferior due to accelerated pest oxidation at 700°C in air.

In order to protect $\text{Mo}_5\text{Si}_3/\text{Si}_3\text{N}_4$ ceramic composites from pesting, in this work a composite material was developed using the inorganic precursor PHPS loaded with Mo particles as active filler. After pyrolysis, the resulting ceramic composite was coated with PHPS to generate a protective SiO_2 layer before the oxidation of Mo_5Si_3 starts.

The results demonstrated the in-situ formation of the silicide phase during pyrolysis at temperatures up to 1500°C via solid-state reaction of the formed amorphous SiN phase and the Mo particles. As intended, the coated $\text{Mo}_5\text{Si}_3/\text{Si}_3\text{N}_4$ ceramic composites exhibit a remarkably increased oxidation resistance up to 700°C compared to the uncoated material.

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1. Introduction

Composite ceramics based on Si_3N_4 strengthened with molybdenum silicides seem to be potential candidates for structural applications at high-temperatures and ultra-high temperatures due to their good temperature oxidation resistance as well as a high fracture toughness or remarkable high temperature strength [1–3]. Especially, Mo_5Si_3 exhibits a higher melting point compared to MoSi_2 and appears more creep resistant due to its complex unit cell. Almost no research was directed towards Si_3N_4 reinforced with Mo_5Si_3 [1,4]. This can be attributed to aspects like an increased density or a thermal expansion anisotropy in c-direction of the unit cell, which is twice higher than in a-direction [5]. Furthermore, the oxidation resistance of Mo_5Si_3 is inferior compared to MoSi_2 and it undergoes accelerated pest disintegration in the temperature range from 400 to 700°C [6–9]. This means that a protective SiO_2 scale does not form fast enough to completely cover the Mo_5Si_3 grains to prevent the composite from further oxidation [6] resulting in component failure in a catastrophic manner.

The conventional processing of Si_3N_4 ceramics strengthened with molybdenum silicides is based on several ways e.g. powder

preparation techniques via combustion synthesis [10], mechanical alloying [11], pressure assisted sintering [9] and infiltration methods [1].

The route of polymer-derived ceramics (PDCs) is an interesting alternative towards conventional manufacturing methods offering advantages like reduced processing temperatures or simplified shaping [12–14]. Recently published work on the processing of ceramic composites based on organopolysilazanes loaded with refractory metal particles demonstrated the benefits and the potential of the PDC technique [15,16]. By adjusting the polymer/filler ratio, the phase composition and the microstructure of the resulting composites can be tailored and designed in a unique way.

The scope of the present work is the processing of $\text{Mo}_5\text{Si}_3/\text{Si}_3\text{N}_4$ composites derived by the polysilazane PHPS loaded with molybdenum particles. During pyrolysis of the precursor up to 1500°C in nitrogen atmosphere both the silicide phase and the Si_3N_4 ceramic phase should form.

As it is reported in the literature, ceramic coatings based on PHPS are very effective to protect metal surfaces from oxidation up to 1000°C by forming a SiO_xN_y layer [17]. Therefore, subsequent infiltration and coating of the generated $\text{Mo}_5\text{Si}_3/\text{Si}_3\text{N}_4$ composite with PHPS should reduce the pest disintegration at temperatures up to 700°C .

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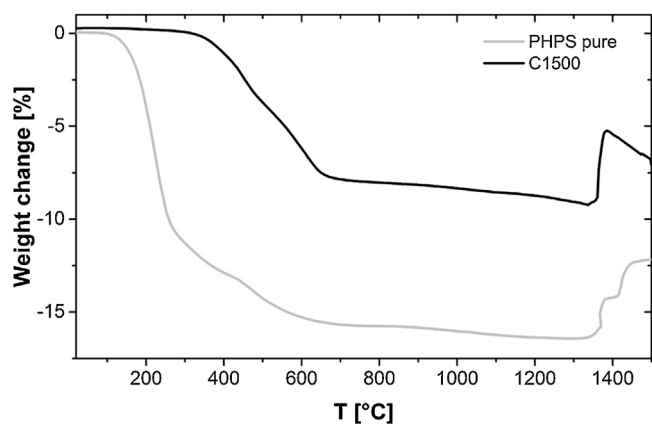


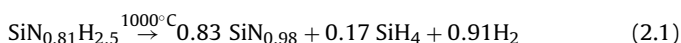
Fig. 1. TG analysis of PHPS powder (<63 μm) and the composite material after pyrolysis up to 1500 °C in nitrogen atmosphere.

2. Experimental

2.1. Materials

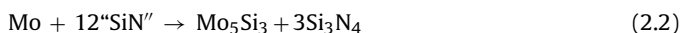
For this work a liquid perhydropolysilazane (PHPS-NL 120-20, Merck KGAA, Germany), which is commercially available as a solution of 20 wt.% of PHPS in di-*n*-butyl ether, was used. The solution includes already a palladium catalyst to reduce the temperature necessary for thermally cross-linking of the precursor. The structure of the PHPS polymer is composed of a Si backbone including highly reactive Si-N_(x) and Si-H_(x) ($x = 1-3$) groups.

As Fig. 1 shows, the conversion of the PHPS polymer to an amorphous ceramic occurs in the range from 200 to 700 °C accompanied by a weight loss which can be attributed mainly to the evaporation of oligomers and gaseous SiH species as well as hydrogen resulting from the pyrolysis process [17]. The ceramic yield is about 85 wt.% after pyrolysis at 1000 °C. The chemical composition of PHPS in the initial state and after pyrolysis can be described by Eq. 2.1 and is based on elemental analysis of the initial precursor polymer and the ceramic residue after pyrolysis at 1000 °C in nitrogen atmosphere [17].



The Mo/PHPS volume ratio used for the present work is listed in Table 1. Molybdenum powder (Alfa Aesar, USA) with a particle size of 3–7 μm and a purity of 99.95% was used as active filler.

As the Si:N ratio of the PHPS precursor after pyrolysis at 1000 °C in nitrogen atmosphere is already 1:1 and of the desired phase composition basing on the resulting Mo₅Si₃/Si₃N₄ composite ceramic, the Mo/PHPS ratio was calculated by the chemical reaction according to Eq. 2.2.



By choosing an increased amount of PHPS in the starting composition instead of the stoichiometric ratio for Mo₅Si₃ formation, we expect on the one hand a fully conversion of the Mo particles

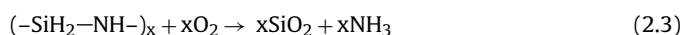
to the respective silicide phase. On the other hand, the composite microstructure should be composed of homogeneously distributed silicide particles within a Si₃N₄ phase.

2.2. Processing and sample characterization

Both the coating of the powders with the precursor and the cross-linking was performed in a Schlenk flask at 135 °C for 4 h. As it is reported in the literature, PHPS is highly reactive with hydroxyl groups due to the large number of Si–H bonds [17,18]. We expected, that this reactivity result in a good adhesion between the silazane and the Mo filler particles, which is a precondition for a quantitative reaction of the components. After removing the solvent, the dried and solid Mo/PHPS mixture was removed from the flask, grinded and compacted to cylindrical specimen with a diameter of 13 mm and a height of 4 mm by uniaxial pressing at 100 MPa in inert atmosphere. For comparison, the pure PHPS polymer was also cross-linked like the composites and subsequently grinded and sieved to achieve a particle size smaller than 63 μm .

The pyrolysis of the samples was performed in a TGA device (L81 A1550, Linseis, Germany) at temperatures of up to 1500 °C under flowing nitrogen (purity 5.0) applying a heating rate of 5 K/min and annealed for 1 h at the maximum temperature.

In order to increase the oxidation resistance of the composite materials, the pyrolyzed cylindrical specimen were dip-coated (C1500i) with a PHPS/dibutyl ether solution (20/80 wt.%) using a hoisting apparatus. According to Günthner et al. [17] subsequent annealing of PHPS based coatings in air at 110 °C results in the formation of a protective SiO₂ scale via the reaction described in Eq. 2.3.



The samples C1500ii were dip-coated again after the annealing process at 110 °C in order to increase the coating thickness and to achieve a uniform coating.

The hoisting speed was set for each experiment to 0.5 m/min resulting in a coating thickness of about 1 μm .

All samples were oxidized in the TGA device at 700 °C for 10 h in high-purity air using a constant flow rate of 5 l/min and a heating rate of 20 K/min.

Crystalline phases were detected by X-ray powder diffraction analysis (D8 ADVANCE, Bruker AXS, Karlsruhe, Germany) using monochromatic CuK α radiation. The phase composition was determined via quantitative Rietveld refinement using the evaluation software TOPAS (V4.2, Bruker AXS, Karlsruhe, Germany) and PDF-4+ 2013 structural database for crystallographic information. The microstructure of the pyrolyzed composite materials 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 and reaction zones within the filler particles and the amorphous SiN matrix. The density of the pyrolyzed samples was measured using a He-pycnometer (AccuPycII 1340, Micromeritics, Germany).

Table 1

Composition, ceramic yield after pyrolysis at 1000 °C in nitrogen atmosphere and heat treatment of the investigated samples.

Material	Mo/PHPS ratio		Ceramic yield (1000 °C) [%]	Heat treatment [°C]	Atmosphere
	[vol.%]	[wt.%]			
PHPS pure	0/100	0/100	84	1000	N ₂
C1000	8/92	43.5/56.5	84	1000	N ₂
C1500	8/92	43.5/56.5	93	1500	N ₂
C1500i, C1500ii	8/92	43.5/56.5	–	700	air

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