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Nano-structured metal-containing polymer precursors for high temperature non-oxide ceramics and ceramic fibers—syntheses, pyrolyses and properties

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Abstract

Nano-structured metal-containing ceramic polymer precursors have a potential for progress in the field of polymer-derived ceramics. In this paper the synthesis and characterization of nano-metallopolycarbosilanes (nMPCS) and their transformation into ceramic materials are reported. The formation of metal nano-particles via fast thermolysis of metal- containing compounds in polymer solution or melt previously developed by the authors was applied to preceramic polymers. Tetrabenzyltitanium, tetrabenzylzirconium, bis(cyclopentadienil)dichloride-titanium and zirconium as well as tetrachlorides of these metals and tetrakis(diethylamino)zirconium were used for the introduction of metal nano-particles. The products were characterized by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), differential-thermal analysis (DTA), gel-penetration (GP)-chromatography, X-ray diffraction (XRD), scanning electron microscopy (SEM) and other special analyses. The results of these studies may be useful for the fabrication of non-oxide ceramic fibers, interphase coatings and high temperature ceramic matrix composite (HT-CMC) matrices. Cp_2ZrCl_2 and $Zr[N(C_2H_5)_2]_4$ provided nano-particles with diameters of 2–4 nm and turned out to be the most suitable compounds for the preparation of ceramic matrices. Besides, they open a new way of oxygen-free curing. Coreless fibers were obtained from nZrPCS with up to 3 mass% of metal. Future investigations will be focused on optimization of the oligocarbosilanes used as starting materials and the development of less reactive polycarbosilane (PCS)–metal-containing compound (MCC) systems.

Keywords: Chemical properties; Fibers; Nanocomposites; Nanometallopolymers; SiC

1. Introduction

Among different directions for further progress in the field of polymer-derived ceramics is the application of metal-containing precursors including nano-structured metal containing polymers. These polymers are essentially homogeneous (monophase) and form an ultra fine ceramic structure stable at high temperatures. Besides that, active metal nano-particles (MNPs), which are formed during the synthesis step, work as acceptors of residual oxygen and initiators of oxygenless curing processes, improve sintering activity, and are responsible for special magnetic, electrical and thermophysical properties at high temperatures.

The study on ceramic polymer precursors for components of high temperature ceramic matrix composite matrices (HT-CMC) reported here is based on the previous research of the authors on linear organic polymers (polypropylene, for example). MNPs formed via fast thermolysis of metal-containing compound (MCC) systems in polymer solution or melt at temperatures above the corresponding temperature of decomposition.[1] This method was applied to ceramic polymer precursors as polymer matrices for MNPs.

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In the past decade, many new valuable ceramic polymer precursors were proposed and synthesized. [2–6] Nevertheless, the polycarbosilanes (PCSs) are still the most important among non-oxide polymer precursors. These polymers satisfy the crucial criteria for economic feasibility and offer possibilities for further improvement. We used in our research a modification of Yajima's method for synthesizing PCSs via polydimethylsilane (PDMS) but without high pressure and initiators.[7] The process of PDMS to PCS transformation is based on thermal decomposition, rearrangement and polycondensation. During this transformation less stable –Si–Si– units rearrange into more stable –Si–CH_2–Si– units with reactive Si–H and Si–C side groups. Previously the processes of the intermediate product formation and its activation by Zr, Ti and Fe containing MCCs were studied,[8,9] and the products were preliminary characterized.[10] Very similar properties (structure, composition, and size distribution) of iron nanoparticles (up to 5 mass.%) were obtained by pyrolysis of $Fe(CO)_5$ in linear organic polymers and in PCS. But a significant influence of the polymer matrix, the MCC metal and ligand type on the polycondensation process was found. Besides, important changes of the polymer structure were detected. Thus, new aspects were discovered in the study of nano-metallopolymer precursors.

In this paper we report recent results on syntheses, transformation and characterization of nano-metallopolycarbosilanes (nMPCS),[11] which are to be used for non-oxide ceramic fibers, interphase coatings and matrices of HT-CMCs.

2. Experimental procedure

Tetrabenzyltitanium, tetrabenzylzirconium [$M(CH_2C_6H_5)_4$ = MBz_4], bis(cyclopentadienyl)di-chloride-titanium and zirconium [$(C_5H_5)_2MCl_2$ = Cp_2MCl_2], the tetrachlorides of these metals (MCl_4) and tetrakis-(diethylamino)zirconium {$Zr[N(C_2H_5)_2]_4$ = $Zr[NEt_2]_4$} were used as MCCs for the introduction of metal nano-particles. $TiBz_4$ and $ZrBz_4$ were synthesized according to Zucchini et al.,[12] $Zr[NEt_2]_4$ by analogy with Bradley and Thomas,[13] the commodity compounds Cp_2TiCl_2 and Cp_2ZrCl_2 (>98 mass%) and the chlorides were used. $TiCl_4$ and $ZrCl_4$ were double distilled and sublimated, respectively.

The specimens of nMPCS were synthesized by introducing the MCC solutions in low boiling point solvents (hexane, tetrahydrofuran) into the PCS-oligomer melt or solution. This oligomer starting material {[–$Si(CH_3)_2$]$_x$[–$Si(CH_3)H$–CH_2–]$_y$}$_n$, with x, y = 1–8, n = 2–6, M_n = 300–600 was obtained by partial rearrangement of a PDMS $[Si(CH_3)_2]_n$ with $n>30$. For the nMPCS synthesis a standard laboratory reactor equipped with an extra fast-acting mixer was used. The MCCs were introduced dropwise at temperatures from RT to 380 °C under an inert atmosphere. Subsequently, the finished reaction mixture was filtered and the volatile fractions were distilled off. All these operations were carried out in a glove box filled with inert gas. The thermomechanical properties of the polymer samples were evaluated with respect to the temperatures of softening (T_{soft}), good spinning behavior (T_{spin}) and melting (T_{melt}). The chemical composition of the finished product was determined.

The products were characterized by X-ray photoelectron spectroscopy (XPS) (metal contents), thermogravmetric analysis, differential scanning calorimetry, differential-thermal analysis (TGA, DSC, DTA) (pyrolysis data), infrared (IR)- and nuclear magnetic resonance (NMR)-spectroscopy (chemical structure), gel penetration (GP)-chromatography (molecular mass data), small angle X-ray scattering (SAXS), X-ray diffraction (XRD), X-ray radial electronic density distribution technique (X-ray RED), extended X-ray absorption fine structure (EXAFS), wave dispersive X-ray analysis (WDXA), SEM and transmission electron microscopy (TEM) (structural investigations of nMPCS and ceramic products). Details of these analyses were published elsewhere.[10]

3. Results and discussion

3.1. MCC thermolysis

The literature data for the thermal stability of the MCCs used in this study are not complete, systematic and methodically clear.[14,15] The temperatures of decomposition onset have been estimated, but are not supported by specific experimental data for each MCC.

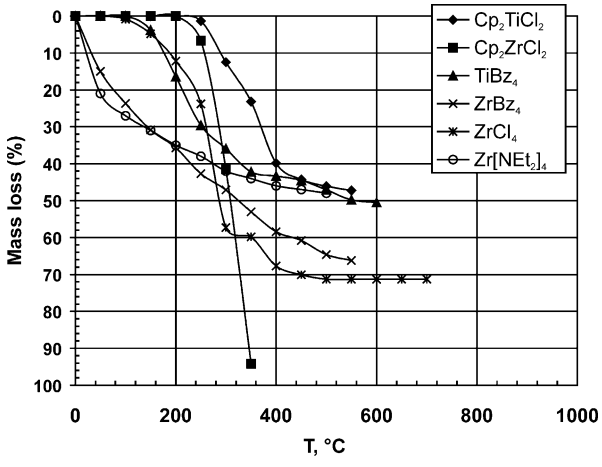

Fig. 1. TGA data for the organometallic compounds used in this study.

Therefore, TGA experiments were carried out under inert atmosphere in order to investigate the pyrolysis behavior of the MCCs. This is a useful technique although it differs from the real pyrolysis conditions in the PCS melt or solution. The data in Fig. 1 show significant differences between the theoretical decomposition according to the scheme $ML_n \rightarrow M + nl$ and the experimental results with respect to the amount of solid residues. These data (theoretical/experimental ratio, mass %) are accordingly: $ZrCl_4$—39.1/28.0; Cp_2TiCl_2—19.3/54.0; Cp_2ZrCl_2—31.2/<5.0; $TiBz_4$—11.7/50.0; $ZrBz_4$—20.0/34.0. The lower yields for Cp_2ZrCl_2 and $ZrCl_4$ can be explained by partial evaporation, while in other cases the products of ligand decomposition increased the amount of residual solids. $TiBz_4$ and $ZrBz_4$ decomposed at 200–600 °C and show very small ratio. At the same time the literature data[11] indicate that in solution M–C-bond dissociation takes place to form the metal atoms and benzyl radicals, which react to generate dibenzyl and toluene:

$$\begin{aligned} xM(CH_2C_6H_5)_4 \rightarrow\ & 4x\cdot CH_2C_6H_5 + [\text{–M–}]_x \\ \rightarrow\ & (C_6H_5CH_2CH_2C_6H_5) \\ & + 2CH_3C_6H_5 \end{aligned} \quad (1)$$

There are data on $ZrBz_4$ decomposition photolytically even at room temperature. A complete separation of the ligands was also found in some of our experiments. Toluene and dibenzil were detected in the reaction product in a ratio of 1:2.[10] These results indicate that the conditions of MCC introduction should avoid the evaporation of the metal complexes and provide sufficient time and temperature for efficient decomposition and nano-particle formation.

3.2. The role of MCCs and their decomposition products in the PDMS to nMPCS transformation

The transformation of PDMS to PCS was carried out at 300–400 °C during 25–30 h.[8] Linear PDMS, $[\text{–}Si(CH_3)_2\text{–}]_n$ transforms gradually by dissociation, Kumada-rearrangement and polycondensation reactions into highly branched PCS with ≡Si–CH_2–Si≡ as well as $(\equiv Si)_3C$–H units and reactive ≡Si–H groups. The latter are necessary for further polymer curing. Depending on the time of MCC introduction the decomposition products may react with any of the intermediate pyrolysis products and influence structure and properties of the PCS matrix and the metal nanoparticles.

In order to get a better understanding of these processes analyses of gaseous, liquid and solid products were carried out. The obtained data are shown in Table 1.

An environment of alkyl groups, as it is present in the PDMS polymer, obviously lowers the temperature of decomposition for such stable MCCs as the chlorides are. The formation of HCl, a diminishing number of Si–H groups in nMPCS in comparison with PCS (from 0.65 to 0.2–0.4 mass.% for MCl_4), and the presence of M–Si bonds in nMPCS (see the data of structural analyses below) suggest that the following reactions take place:

$$\equiv M-Cl + H-Si \equiv \rightarrow\ M-Si \equiv + HCl \quad (2)$$

$$\equiv Si-CH_3 + Cl-M \equiv \rightarrow \equiv Si-CH_2\text{–}M \equiv + HCl \quad (3)$$

$$\equiv Si-CH_2\text{–}Si \equiv + Cl-M \equiv \rightarrow \quad \begin{array}{l} \qquad Si \equiv \\ \qquad\ | \\ \equiv Si-CH \\ \qquad\ | \\ \qquad M \equiv \end{array} \quad (4)$$

Another important point is the chlorine content in nMPCS. According to TGA, DTA and IR-spectroscopy data the thermolysis of solid Cp_2ZrCl_2 in the closed vessel with an inert gas gives gaseous, liquid and solid products. The latter is a complex polymeric material, containing the metal as well as carbon and chlorine. Of the Cl 67–85 mass.% are evolved as HCl during the synthesis of nMPCS with MCl_4. A simple reaction scheme is shown in Eq. (5)

$$\begin{array}{l} -Si \equiv \rightarrow\ [ZrCl] + \equiv Si-Si \equiv \\ \qquad\qquad \downarrow \\ \qquad\qquad [ZrCl]_n(\text{cluster}) \\ \quad + 3HCl \end{array} \quad (5)$$

Many cluster subhalogenides of zirconium with the Zr:Cl-ratio <1:2 are known.[16] Our structural analyses confirmed the presence of Zr containing nano-particles with a similar Zr:Cl-ratio. An idealized structure is shown in Fig. 2.

The most suitable of the studied MCC turned out to be Cp_2ZrCl_2. It forms at 300–380 °C a well dissolving polymer, which melts at 200–240 °C, contain many Si–H groups and about 3 mass % of metal. Nevertheless, the content of Cl atoms is directly and of Si–H groups is inversely proportional to the quantity of introduced metal. Low temperature synthesis required longer reaction times but provided an increased metal content.

The spectral study showed that possibly the transformation of cyclopentadienil ligands plays an important role in the processes of nano-particle formation. It is known that the metal-cyclopentadienil bond is more reactive than the other bonds in the MCCs. Therefore

Table 1
The conditions of nMPCS syntheses and some characteristics of the final products

Synthesis number	MCC	Introduced initially (mass%)		Experimental conditions		Content in nMPCS (mass%)				Yield (PCS) (mass%)
		MCC	Metal	T,°C	t, h	H at Si	Metal	Cl	Cl/M (at.%)	
1	Abs. (base PCS)			350–400	30.0	0.65	Abs.	–		65
2	$TiBz_4$	10.0	1.16	330–380	2.5	0.90	1.4	–		75
3	$TiBz_4$	26.0	3.01	330–350	3.0	0.75	3.5	–		78
4	$ZrBz_4$	10.0	2.00	340–380	12.0	0.70	1.4	–		64
5	$ZrBz_4$	12.5	2.50	340–380	8.0	0.65	2.4	–		62
6	$TiCl_4$	1.5	0.38	310–320	2.5	0.36	no anal.	5.8		62
7	$TiCl_4$	3.8	0.95	330–350	1.0	0.28	no anal.	5.6		51
8	$ZrCl_4$	1.5	0.59	300	0.8	0.19	no anal.	6.3		91
9	$ZrCl_4$	2.6	1.01	300	1.0	0.27	no anal..	6.2		61
10	Cp_2ZrCl_2	1.8	0.56	300–380	6.0	0.94	0.97	n.a.		56
11	Cp_2ZrCl_2	6.7	2.09	270–335	10.5	0.75	4.08	1.7	1.09	55
12	Cp_2ZrCl_2	8.7	2.27	270–350	15.0	0.80	4.70	2.7	1.25	83
13	Cp_2ZrCl_2	10.0	3.12	300–350	8.0	0.76	3.77	1.7	1.15	68
14	Cp_2ZrCl_2	10.0	3.12	275	22.0	0.62	5.90	2.7	1.18	57
15	Cp_2TiCl_2	4.0	0.8	265	13.5	0.74	0.95	1.8	2.4	55

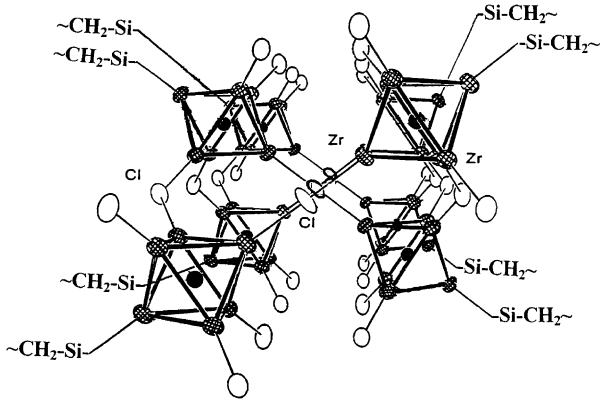

Fig. 2. Principal structure model of chlorine containing zirconium cluster (nano-particle).

this bond cleaves first. Moreover, its cleavage is facilitated by interaction with the polymer matrix. This is supported by our data: just after the end of MCC introduction the signals in IR- and proton NMR-spectra for Cp-rings were absent (Fig. 3). The results of our structural studies also show that after the separation of Cp-groups metal and chlorine containing fragments $[ZrCl_{<2}]_n$ transform to clusters in an analogues way as in the case of $ZrCl_4$ and form the same type of cluster structure (Fig. 2).

The cleavage of Cp-rings with the formation of–C–C–C– chains in the PCS structure was detected by IR spectroscopy using high concentrations of the Zr complex. These changes became evident in the area of Cp-ring C–H valence ($\nu_{c-h} = 2920$ cm^{-1}) and deformation ($\nu_{c-c} = 1460$ and 1320 cm^{-1}) vibrations, which were not found in the metal-free PCSs.

Cp_2TiCl_2 was too reactive to be really used for effective nMPCS synthesis. The introduction of less than 1 mass.% of Ti into the PCS oligomer mixture required a decrease of the maximal temperature to 265 °C to avoid a fast formation of insoluble and non-fusible polymers.

These results correlate well with the literature data for the energy of bond dissociation[17,18] (Table 2). The Cp–M bonds dissociate first, M-Cl bonds react later and not completely under the synthesis conditions.

$TiBz_4$ and $ZrBz_4$ form nMPCSs as well, but in the case of $ZrBz_4$ several percent of insoluble solids were formed. TGA data showed a mass loss of 50–60% and the termination of decomposition at temperatures as high as 500–600 °C. Thus, the yield with respect to the metals in MBz_4-derived nMPCS is about 50%. These results made it difficult to investigate the reaction behavior of the chlorine-free MCCs with $TiBz_4$ and $ZrBz_4$. It can be supposed that the metal nano-particles in this case contain less non-metal elements and are more active than in the case of chlorine containing MCCs, which increases the tendency to form insoluble products.

3.3. Structural analyses

3.3.1. PCS containing metal nano-particles (nMPCS)

Some of our results of structural analyses were discussed previously.[10,19] As to the structure and composition of nZrPCS, the available results allow drawing the following conclusions:

1. The XPS experiments have shown that the content of Zr on the surface of the nano-composite is much lower than in the volume. The surface layer contains oxygen. Ion etching of a surface up to the depth of 50 Å indicated an increase of the Zr content in the bulk of the samples.

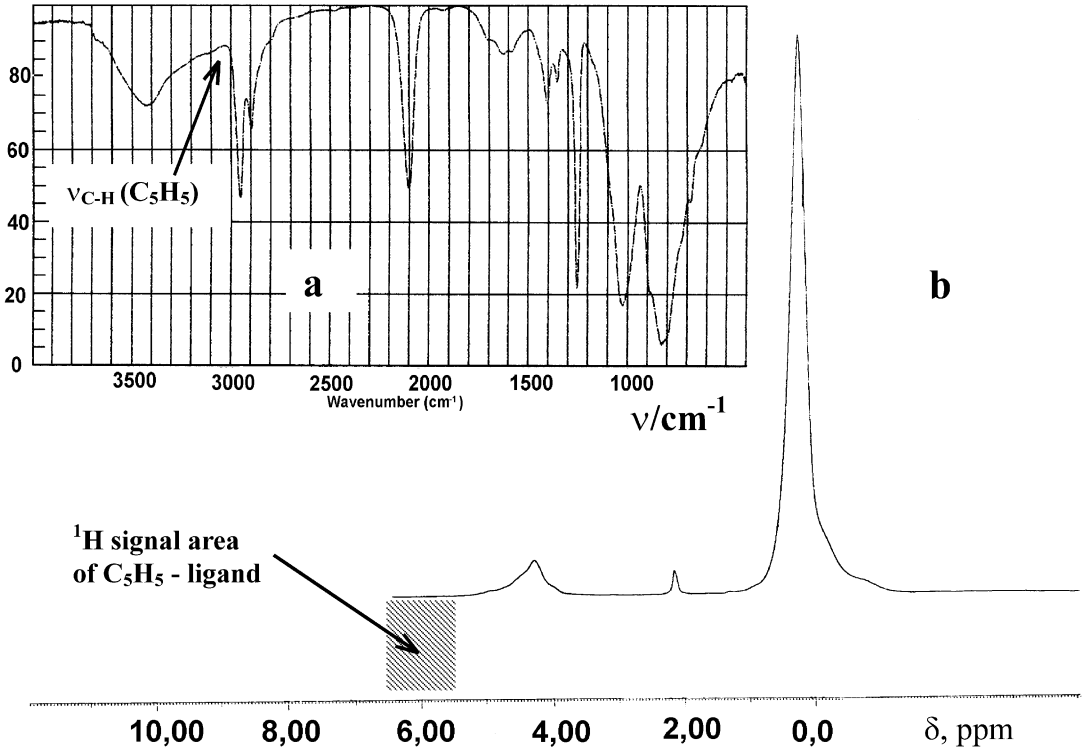

Fig. 3. Spectra of nZrPCS—reaction mass just after introduction of Cp_2ZrCl_2. (a) IR; (b) NMR. The Cp-ligand signals are absent in the marked zones.

Table 2
Energies of bond dissociation, which are relevant for MCCs used in our investigations

Bonds	Cp–Ti	Cp–Zr	Ti–Cl	Zr–Cl	$[Et_2N]$–Zr	Et–N
Energy of dissociation, kJ/mol	269.0	358.6	430.5	488.7	360.6	295.5

2. It has been found that X-ray RED, EXAFS and SAXS, which give information about the bulk volume, demonstrate the presence of metallic zirconium clusters. These clusters have diameters of ~20 Å and are connected to the matrix mainly with Zr–Si-bonds.
3. Zr–Zr (3.18–3.23 Å) and Zr–Cl (2.6–2.8 Å) distances measured by X-ray RED and EXAFS correlate well with the corresponding bond-distances in the Zr chloride clusters.

These results support the suggested model of Zr nanoparticles in a PCS matrix (Fig. 2). Zr–O-bonds were also detected, indicating a slight contamination with oxygen. The quantity of metal atoms in one particle, the fulfillment extent of internal "voids", the kind of atoms in these voids (H, C, Si), the kind of ligands (Cl, O), and the type of ligand-matrix bonding may of course vary from cluster to cluster.

3.3.2. Ceramics obtained from nMPCS

Ceramic materials were fabricated by pyrolysis of the nano-particle containing polymers by heat treatment in an inert atmosphere (Ar, N_2) up to 1200–1500 °C and structurally investigated.

The results for specimens with a Zr content up to 3 mass% and heated at 1100–1200 °C showed that $ZrSi_2$ was formed. The RED peak with $r = 1.87$ Å can be assigned to Si–C containing phases. The Zr–O phase was not found. In contrast nTiPCS showed a substantially different phase composition: after heat treatment Ti–C and Ti–O bonds were detected.

For specimens with 5–11 mass% of Zr annealed at 1500 °C qualitative phase analysis and an estimation of the size of coherent scattering area have been carried out. In all samples SiO_2 was discovered in small amounts (~1 mass%). Coarsely crystalline phases of zirconium oxide and solid solutions of carbides of silicon and zirconium have been observed in these samples with high zirconium content. The results suggest that

Table 3
Change of molecular mass, melting behavior and number of Si–H bonds during nZrPCS synthesis with $Zr[N(C_2H_5)_2]_4$

Specimen number	T, °C (0.25 kPa)	$M_n/M_w/M_z$	M_w/M_n	High molecular fractions (mass %)	Thermo-mechanical characteristics, °C			H at Si (H–Si), (mass %)
					$T_{soft.}$	$T_{spin.}$	T_{melt}	
5	280	760/1700/3700	2.24	1.3	105	120	185	0.65
6	290	810/1750/3900	2.16	1.3	130	150	230	0.75
7	330	1070/2240/4900	2.09	5.6	195	215	260	0.62
8	330	1240/2650/5900	2.14	6.4	210	230	265	0.63
9	350	1400/3900/10600	2.79	10.0	235	250	290	0.57

Table 4
Oxygen-free chemical curing of PCS with MCC

MCC	After 135 °C		After 280 °C		Comment
	Shape of fiber	T_{melt}	Shape of fiber	T_{melt}	
Cp_2ZrCl_2	Retained	No melting	Retained	No melting	Cured
$Cp_2Zr(CH_3)_2$	Retained	No melting	Retained	No melting	Cured
$Mo(CO)_6$	Retained	No melting	Slight. distorted	No melting	Incompl. cured
No MCC	Not retained	190–200 °C	Melted	190–200 °C	Not cured

only a fraction of the zirconium inside the PCS-matrix is in a highly dispersed state. The remaining fraction of zirconium crystallizes in the form of larger particles covered with an oxide film.

The X-ray diffraction phase analyses were confirmed by X-ray RED curves. From the data it can be concluded that highly dispersed solutions of the two carbides ZrC and SiC are the result of interactions of the nano-particles with the PCS matrix during the heat treatment.

At a concentration of about 1.0–1.5 mass % of the metal and less than 1 mass % of oxygen a slight stabilization of SiC phase was found by X-ray diffraction and TEM. Our future investigations will be focused on a more detailed analysis of the structure and properties of the ceramic materials obtained by pyrolysis of nMPCS.

3.4. Technological aspects of nMPCSs fabrication

It was noted previously [20] that nZrPCS with a residual concentration of Zr below 3% has some advantages over metal-free PCS. A more regular polymer structure, an increased Si–H group content, a narrow molecular mass distribution (MMD), about 10% higher ceramic yield and shorter reaction times are the main positive characteristics. Nevertheless, considering the fabrication of ceramic coreless fibers, important technological difficulties were encountered.

For the preparation and investigation of ceramic fibers the polymerization was carried out with the above mentioned MCCs and additionally with $Zr[NEt_2]_4$. The TGA data of the last compound are comparable to $ZrBz_4$ and $TiBz_4$, but the decomposition begins at lower temperature (Table 2, Fig. 1). It has a lower vapor pressure in the liquid state (0.007 kPa at bp = 120 °C) and contains no chlorine. The amount of MCCs was calculated for a Zr concentration of 3 mass % in the finished nMPCS polymer. Several samples were taken during the synthesis at different times and temperatures and analyzed with GPC, NMR- and IR-spectroscopy. The thermo-mechanical properties of the samples were also evaluated.

The most important results for the work with $Zr[NEt_2]_4$ are summarized in Figs. 4 and 5 and Table 3. The MMD changes with increasing reaction temperature. Gradually, a "tail" of high molecular mass is formed, which consists of a fraction of up to 10% at the end of the synthesis. This concentration is not tolerable to guarantee a stable spinning of fibers. However, Table 3 shows that M_n, T_{soft}, T_{spin}, T_{melt} are only just suitable for spinning and curing.

The NMR analyses showed that the interaction between the MCC and oligocarbosilanes (OCS) begins at 180 °C and finishes at about 300 °C. ^1H NMR spectra of the first specimen show in addition to the characteristic signals of $Zr[NEt_2]_4$ (CH_3 at 1.16 ppm and CH_2 at 3.39 ppm) signals of CH_3-groups at 1.08 ppm and for CH_2-groups at 2.59 ppm. This indicates the beginning of thermal decomposition of the MCC and diethylamine formation. Increasing the temperature up to 330 °C at 0.15 kPa is accompanied by the evolution of volatile oligomers and causes the MCC ligand signals to vanish, while Si–CH_3 and Si–H are still detected (Fig. 5).

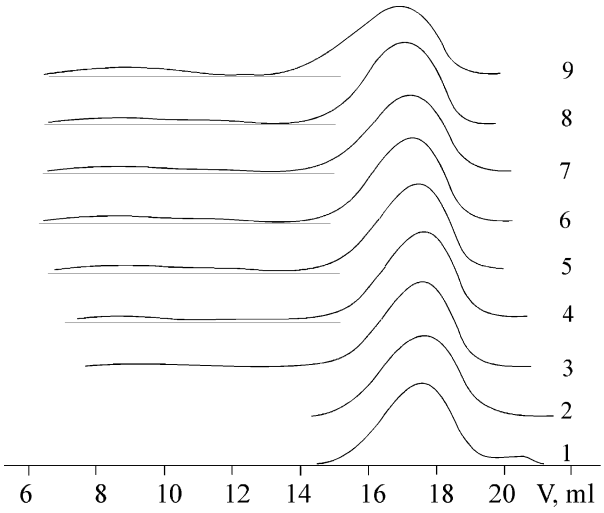

Fig. 4. Change of the MMD during the polymerization of nZrPCS. Curves 1–9 correspond to samples taken in the interval between 200 and 350 °C at 0.5 kPa.

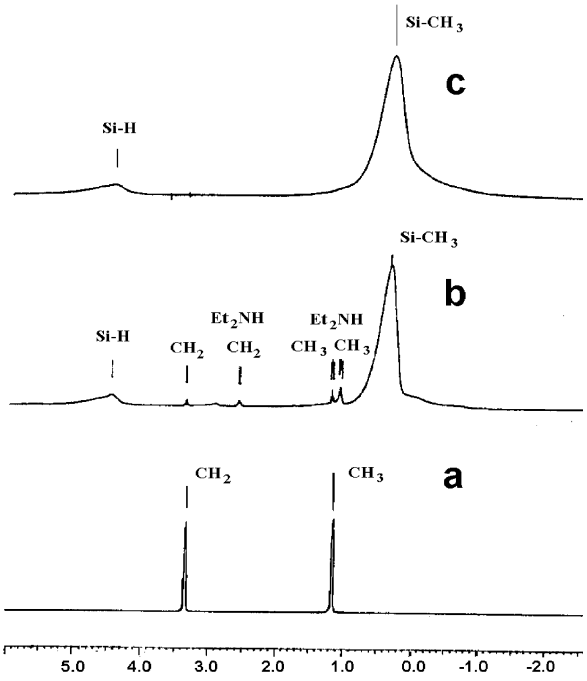

Fig. 5. Proton (^{1}H) NMR spectra of $Zr[N(C_2H_5)_2]_4$ and products of nMPCS synthesis. (a) $Zr[N(C_2H_5)_2]_4$; (b) $OCS + Zr[N(C_2H_5)_2]_4$–first probe; (c) $OCS + Zr[N(C_2H_5)_2]_4$—final probe.

One of the goals of our research is to find suitable conditions for oxygen-free curing of the polymer (green) fibers after spinning by the addition of MCCs. The experiments included heat-treatments of metal-free PCS fibers in the vapors of several MCC without any oxygen and moisture at about 40 °C for 24 h. Subsequently, the process of curing was carried out by heating under dry oxygen free nitrogen to 135 °C and then to 280 °C with a heating rate of about 6 °C/h. The criterion for sufficient curing was a constant shape of the fibers without signs of melting. Chromium and zirconium acetylacetonates, tetrabenzylzirconium, tetrabenzyltitanium, dicyclopentadienyldichloride- zirconium and titanium, bis(cyclopentadienyl)dimethylzirconium as well as the carbonyls of iron, chromium and molybdenum were used.

The results showed that several compounds are able to initiate the curing of PCS (Table 4), but their efficiency differs significantly from each other. According to this preliminary study only three of them gave rather satisfactory results: Cp_2ZrCl_2, $Cp_2Zr(CH_3)_2$ and $Mo(CO)_6$. These results provide a novel potential for an oxygen free chemical curing in the fabrication of ceramic fibers.

In order to improve the spinability of nMPCSs a series of syntheses with different heating rates and with different holding times at intermediate temperatures were carried out.

However, no sufficient improvement of the products was achieved, we succeeded to use the synthesized specimens of nZrPCSs for preliminary fiber spinning experiments (Fig. 6). The fibers were cured in N_2 containing a small amount of oxygen and heat treated up to 1000 °C.

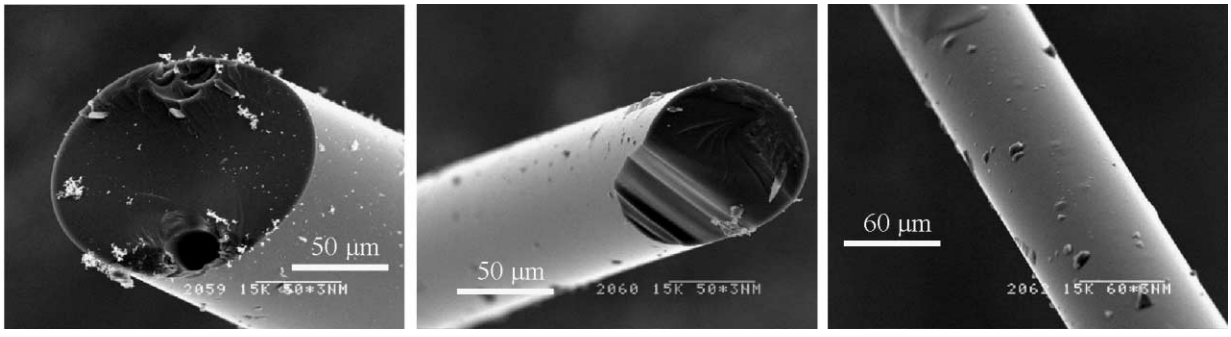

Fig. 6. SEM images of nZrPCS polymer fibers.

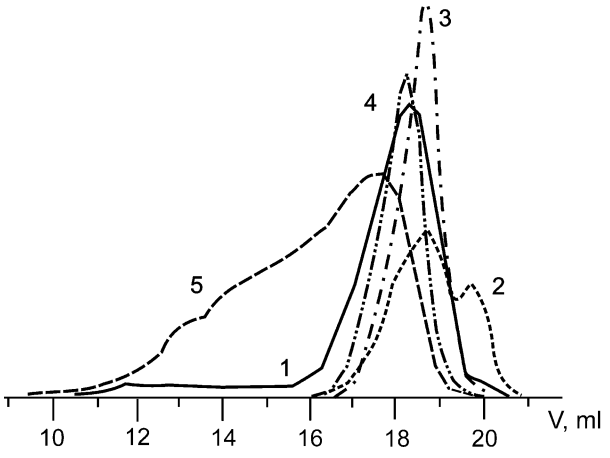

Fig. 7. Molecular mass distribution of the initial OCS and its fractions distilled up to 400 °C; 0.2 kPa. 1—OCS ($M_n/M_w/M_z$=450/10 000/280 000); 2—1 st fraction distilled up to 200 °C (18 mass%, 200/400/780); 3—2nd fraction distilled between 200 and 300 °C (25%, 320/420/580) and 4—3-d fraction distilled between 300 and 400 °C (25%, 480/640/890); 5—residue (32%, 1400/28 000/470 000).

The examination of OCSs in respect of the "tail"-problem showed that different fractions had very different MMD (Fig. 7), which depends in turn on the composition of the PDMS. This factor might show the way for controlling and improving the polymer properties in future studies. The main question to be answered is whether OCS has specific fractions, which are prone to interact with nano-particles forming large molecules, or a certain part of the nano-particles causes around itself the formation of the high molecular weight fractions. In the first variant a new way of the initial OCS fabrication would be needed. In the second variant, other less active MCCs and less active matrices should be used.

4. Conclusion

The results of this study revealed new data of the nMPCs fabrication process. These nMPCs contain nano-particles or metal clusters with diameters of 2–4 nm. A detailed investigation of the thermolysis of MCCs turned out to be very important. Cp_2ZrCl_2 and $Zr[N(C_2H_5)_2]_4$ are the most suitable additives in nMPCSs for the ceramic matrices of CMCs. Coreless fibers are obtained from nZrPCS with up to 3 mass.% of metal. At higher MCC concentrations the MMD of the polymer products are characterized by the presence of high molecular mass fractions. These "tails" form during the polymer synthesis and harm spinning process. On the basis of the received results optimized initial oligocarbosilanes and less active polycarbosilanes and MCCs should be used. But this problem requires further investigations.

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References

1. Kosobudsky, I. D., Gubin, S. P., New type of metallopolymers—metal clusters in polymer matrices (in Russian). *Visokomolekularnie coedineniya*, 1985, **27**, 689–695.
2. Baldus, H.-P., Jansen, M., Novel high-performance ceramics—amorphous inorganic networks from molecular precursors. *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 328–343.
3. Dressler, W., Riedel, R., Progress in silicon-based non-oxide structural ceramics. *Int. J. Refractory Metals Hard Materials*, 997, **15**, 13–47.
4. Kroke, E., Li, Y.-L., Konetschny, C., Lecomte, E., Fasel, C., Riedel, R., Silazane derived ceramics related materials. *Mater. Sci. Eng. R*, 2000, **R26**, 97–199.
5. Interrante, L. V., Rushkin, I., Shen, Q., Linear and hyperbranched polycarbosilanes with Si–CH_2–Si bridging groups: a synthetic platform for the construction of novel functional polymeric materials. *Applied Organometallic Chemistry*, 1998, **12**, 695–705.
6. Uhlig, W., Synthesis, functionalization and crosslinking reactions of poly(silylenemethylene)s. *Polym. Adv. Technol.*, 1999, **10**, 513–522.
7. Tsirlin, A. M., Fedorova, T. V., Florina, E. K., Popova, N. A., Gerlivanov, V. G., Method of Polycarbosilanes Fabrication. Patent of RF 2108348, 14 April 1998.
8. Popova, N. A., Lavruchin, B. D., Zagorevskii, D. V., Turkeltaub, G. N., Tsirlin, A. M. *et al.*, Low molecule products of polydimethylsilane pyrolysis. *Metalloorganicheskaya Chimiya*, 1991, **5**, 984–988.
9. Gubin, S. P., Kozinkin, A. B., Afanasov, M. I., Popova, N. A., Tsirlin, A. M. *et al.*, The Clusters in the polymer matrix. III. Composition and structure of Fe-containing nano-particles in ceramic polymer precursors. *Neorganicheskie Materially*, 1998, **35**(2), 237–243.
10. Gubin, S. P., Moroz, E. M., Voronin, A. I., Kriventsov, V. V., Tsirlin, A. M. *et al.*, Nanoparticles of Ti and Zr in organosilicon polymer ceramic precursors. *Mendeleev Commun.*, 1999, 59–60.
11. Tsirlin, A. M., Florina, Å. K., Popova, N. À., Borisenko, L. L., Gubin, S. P., Gerlivanov, V. G., Ismailova, E. A., Polycarbosilanes Containing Metal Clusters and the Method of their Fabrication. Patent/RF No. 2125579, 27.01.1999.
12. Zucchini, U., Albizzati, E., Giannini, U., Synthesis and properties of some titanium and zirconium benzyl derivatives. *J. Organomet. Chem.*, 1971, **26**, 357–372.
13. Bradley, D.Ñ., Thomas, I. M., Metallo-organic compounds containing metal-nitrogen bonds. Part 1. Some dialkylamino-derivaitives of titanium and zirconium. *J. Chemical Society*, 1960, **10**, 3857–3861.
14. Nesmeyanov, A. N., Nikitina, T. V. *et al.*, *The methods of organoelement chemistry*. Nauka, Moscow, 1974.
15. Cardin, D. J., Lappert, M. F., Raston, C. L., *Chemistry of organo-zirconium and Hafnium Compounds*. John Wiley and Sons, New York, 1986.
16. Zhang, J., Corbett, J. D., Two families of centered zirconium

cluster phases with $M_{1,2}M'Cl_6{*}Zr_6Cl_{12}Z$ compositions. *Inorg. Chem*., 1993, **32**, 1566–1572.
17. Telnoi, V. I., Rabinovich, I. B., Thermochemistry of organic compounds of transitional metals (in Russian). *Uspechi Chimii*., 1977, **46**, 1337–1367.
18. Baev, A. K., Mikhailov, V. E., Thermochemistry of alkylamide compounds of the metals of titanium, vanadium and chromium sub-groups (in Russian). *Zhurnal fizicheskoi chimii RAN*, 1989, **LXIII**(7), 1713–1724.
19. Kriventsov, V. V., Zyuzin, D. A., Bogdanov, S. V., Moroz, E. M., Gubin, S. P., Tsirlin, A. M., Popova, N. A., EXAFS and X-ray RED study of polymetalcarbosylanes. *Nuclear Instruments and Methods in Physics Research*, 2000, **A 448**, 314–317.
20. Kroke, E., Riedel, R., Tsirlin, A. M., Gubin, S. E., Moroz, E. M. et al. High temperature stable ceramic composites derived from nano-metallopoly(boro)silasane precursors. In *Proc. of the 12th Int. Conf. ICCM-12, 1999*, CD, No.556.