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Advances in organoelement chemistry for the development of new materials

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With the development of organoelement chemistry, polymer-to-ceramic technology based on the pyrolysis of organoelement ceramics-forming polymers (oligomers) acquires increasing interest. The organoelement ceramics-forming polymers are primarily organosilicon polymers (oligomers) – poly(oligo) carbosilanes and oligocarbosilanes modified by refractory metals (Zr, Hf and Ta), on whose pyrolysis carbide ceramics are formed. The use of polycarbosilanes and metal-containing carbosilanes in ceramics composite technology makes it possible to obtain binary and more complicated carbide ceramics with the uniform distribution of the elements at the molecular level and with the controlled structure, which allows one to enhance the quality of the final material.

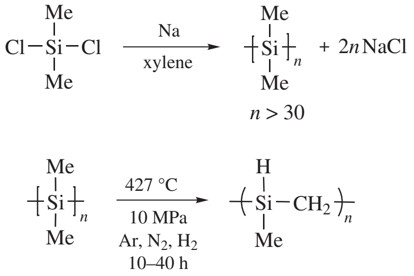
Traditional materials (metals and alloys on their basis) do not meet the increased current demands of promising technology and technical requirements imposed on the development of different products, which work under extreme conditions. The creation of new highly functional materials with a set of properties superior to the physicomechanical characteristics (strength, thermal resistance, corrosion resistance, radiation stability and thermal-fatigue life) becomes an important task. This problem can be solved with the use of ceramics matrix composites as one of the most promising classes of composite materials.[1–7]

Technical ceramics traditionally obtained by the sintering of oxide, carbide, nitride and silicide powders possesses unsatisfactory strength and heat resistance because of the presence of coarse grains (more than several micrometers), structural phase transitions at temperatures above 1000 °C and the polydisperse composition with coarse inclusions.

Ceramic materials suitable for operation under extreme conditions, for example, under the simultaneous action of high temperatures, mechanical loads, corrosive and abrasive media contain the compounds of aluminum, silicon, zirconium, hafnium and yttrium (usually, the high-purity oxides, carbides or nitrides of these elements). Therefore, the development of the chemistry of organoelement (organometallic) polymers and oligomers and their use as the precursors of ceramic compounds for the production of unique thermoresistant composition ceramic materials acquires increasing importance.[8–15]

The C/SiC and SiC/SiC oxygen-free ceramic composite materials are currently of priority for science-intensive branches of technology.[1–8] For this reason, the synthesis and characterization of polycarbosilanes (PCSs) as ceramics-forming oxygen-free organosilicon polymers (oligomers) are under intensive development. They are starting materials for the preparation of important ceramic composite components such as coreless fibers, matrix materials and the separate layers of complex interphase coatings and external barrier coatings.[16–28]

Yajima and coworkers[29–31] pioneered in the chemistry and technology of PCSs in the 1970s. They obtained polydimethylsilane (PDMS) according to the Wurtz reaction from dimethyldichlorosilane and sodium metal in xylene and then subjected it to thermal rearrangement at a high pressure (Scheme 1).



Scheme 1

The following structural model of PCSs as linear-cyclic molecules with a comparatively low molecular weight (800–2000) was proposed.[31]

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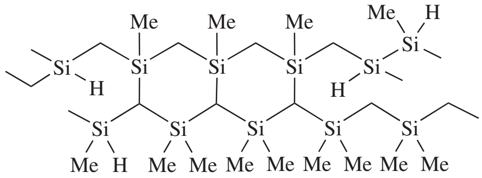
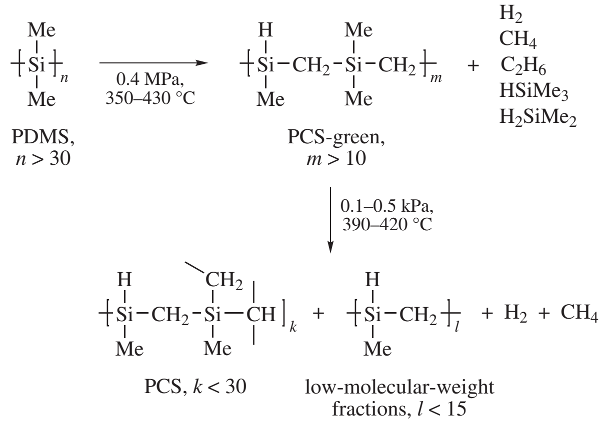


PCSs preparation method

Methods for the preparation of PCSs were developed by Tsirlin *et al.*[32,33] Accessible starting reactants and standard chemical equipment were used for the production of PCSs under milder conditions.

PCS was synthesized in a laboratory setup in accordance with Scheme 2.

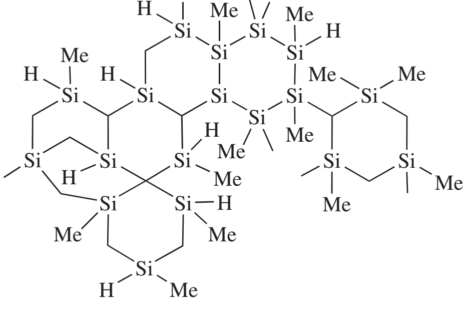


Scheme 2

The standard identification of the composition and structure of PCS by elemental analysis, IR spectroscopy and ^{1}H, ^{29}Si and ^{13}C NMR spectroscopy was supplemented with studies using GPC, the viscometry of dilute solutions and small-angle X-ray scattering (SAXS). An analysis of experimental data, in particular, the low values of the intrinsic viscosity of PCS samples in different solvents in comparison with sufficiently high molecular weights (from 3500 to 30000 a.m.u.) determined from light scattering data, made it possible to make a conclusion on the globular nature of PCS molecular formations. The conclusions are consistent with the results of the SAXS of dilute PCS solutions: the hydrodynamic diameter of spherical globules is 1.0–7.6 nm. The coincidence of the hydrodynamic radius and the radius of inertia suggests the nearly spherical shape of molecular globules with a rigid polycyclic structure.[34]

This conclusion explains the low viscosity of melted ceramics-forming carbosilanes and the difficulty of controlling the cross-linking processes of the samples in the course of heat treatment.

Based on the results of the studies, a fragment of the molecular structure of the ceramics-forming carbosilane can be represented by the following formula.



The ceramics obtained from ceramics-forming PCS possesses natural nanosized polycrystalline structure. In this case, the initial size of crystallites does not exceed 5–10 nm and the structure possesses high strength. However, an exposure at high temperatures initiates the growth of crystallites, which becomes noticeable at 1200–1300 °C (to 20 nm) after an exposure for tens of hours and sharply progresses at 1300–1400 °C (to 40–100 nm or more).[35] Furthermore, ceramic materials based on PCSs very frequently contain oxygen and free carbon (to 10 wt% each), and an active reaction between them comes into play at a temperature of 1100–1200 °C. These two phenomena disrupt the homogeneity and density of a pseudoamorphous ceramic structure and lead to the loss of the strength of both the fiber obtained from PCS and the material as a whole. This sufficiently low operating temperature considerably restricts the areas of application of the material.[9,13,35–37]

Modified PCSs

In order to develop PCSs for high-temperature composite materials, it was proposed to modify them by the introduction of different metals into the polycarbosilane matrix. Methods for the modification of PCSs with both metals and organometallic compounds were published. In this case, a wide range of metals from aluminum to refractory metals were used.[8–15,35–50]

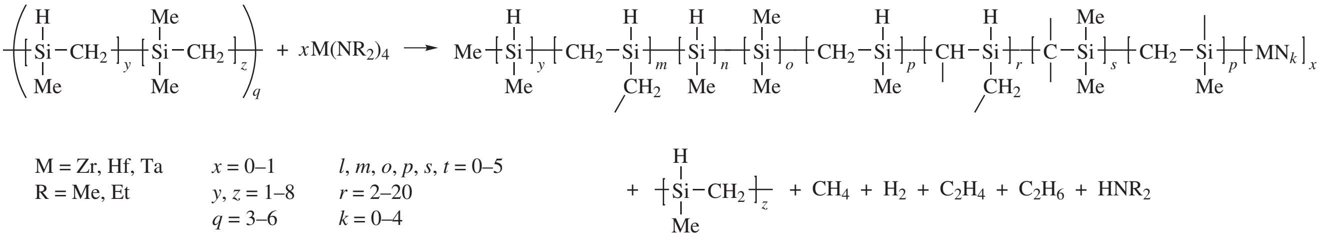
The studies performed in 2005–2012 showed that the alkylamide compounds of refractory metals (Zr, Hf and Ta), which do not contain oxygen and chlorine impurities harmful for SiC ceramics, are the most effective modifiers of carbosilanes.[51–53] It is important that crude polycarbosilane, which is the main product of the thermal rearrangement of polydimethylsilane at the first stage of the production of polycarbosilane (starting material for the manufacture of silicon carbide ceramics including silicon carbide fibers), can be modified with the aid of the alkylamide compounds of zirconium, hafnium and tantalum. The crude polycarbosilane is always separated and purified before the second stage (vacuum polycondensation with the distillation of low-boiling fractions and the production of final polycarbosilane). The introduction of alkylamide modifiers at this stage makes it possible to effectively include the production of nanometal carbosilanes into the general processing line with the simultaneous release of unmodified and modified carbosilane at the second stage. It is also important that the processes of the preparation of nanometal carbosilanes are highly competitive with the production of polycarbosilane in terms of efficiency because of shortening the process time and increasing the yields of polymers and ceramics. As a result, we considered this method as an optimum one for the production of nanometal polycarbosilanes (nano-MPCSs) with the use of the alkylamide compounds of zirconium, hafnium and tantalum and recommended it for industrial implementation.

The general reaction scheme of the cocondensation process can be represented as follows (Scheme 3).

The proposed method for the synthesis of nanometal carbosilanes allows one to obtain fusible soluble modified organosilicon oligomers with a homogeneous distribution of nanosized (5–20 nm) metal-bearing particles in an oligomer matrix (Figure 1). These oligomers possess high capability for fiber and film formation from the fusions or solutions; they are solidified upon thermochemical treatment, and they give a high yield of a ceramic residue upon pyrolysis (to 80 wt%).

The appearance of oxygen in the EDS spectra in the determination of the elemental composition of nano-MCS is explained by the high chemical activity of nano-MPCS toward oxygen and the moisture of air.

It was found that all of the synthesized nanometal carbosilanes possess fiber-forming properties. From them, polymeric fibers



M = Zr, Hf, Ta
R = Me, Et

x = 0–1
y, z = 1–8
q = 3–6

l, m, o, p, s, t = 0–5
r = 2–20
k = 0–4

$+ CH_4 + H_2 + C_2H_4 + C_2H_6 + HNR_2$

Scheme 3

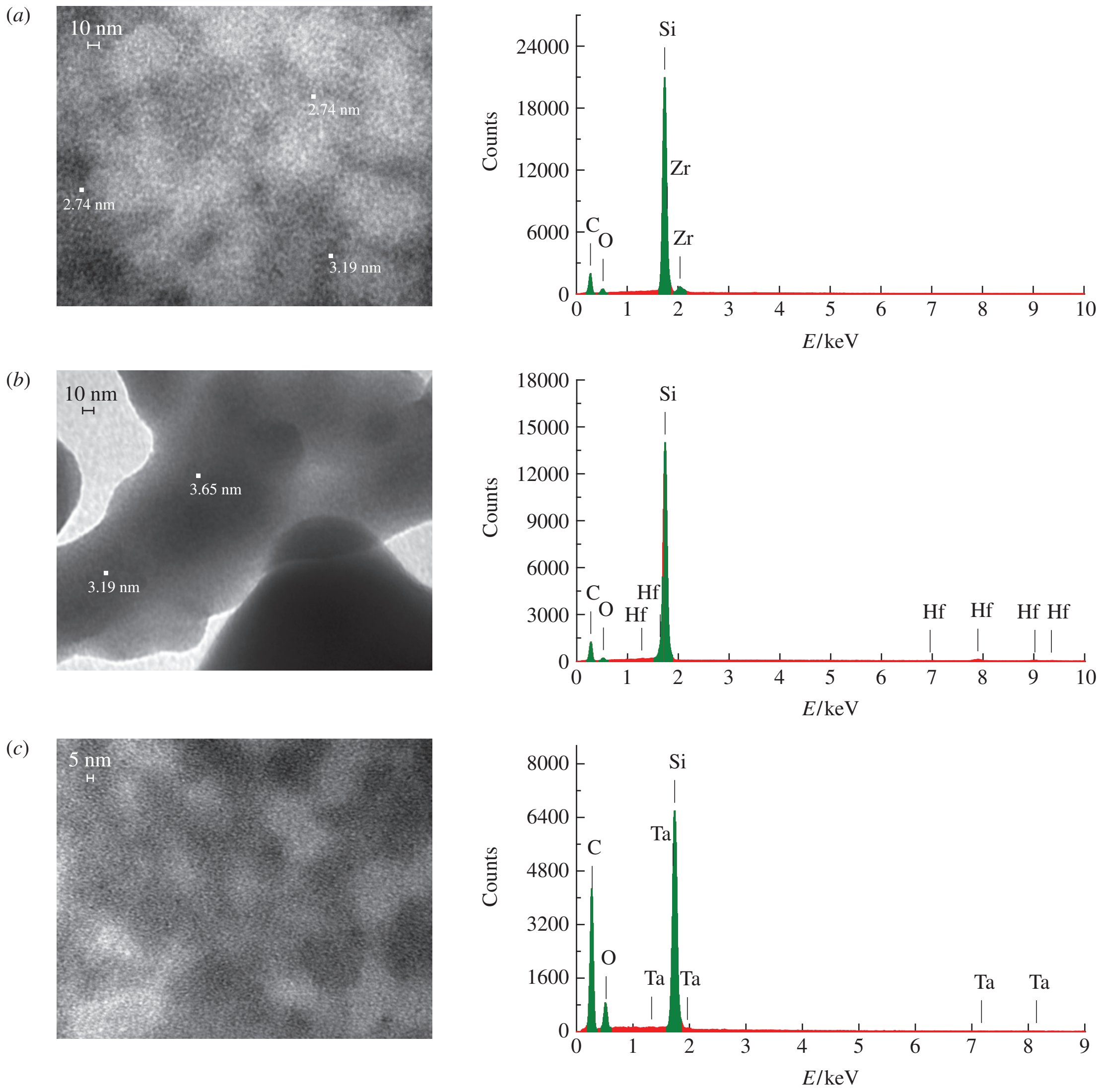


Figure 1 TEM micrographs and EDS spectra of nano-MPCSs: (*a*) nano-ZrPCS, (*b*) nano-HfPCS and (*c*) nano-TaPCS.

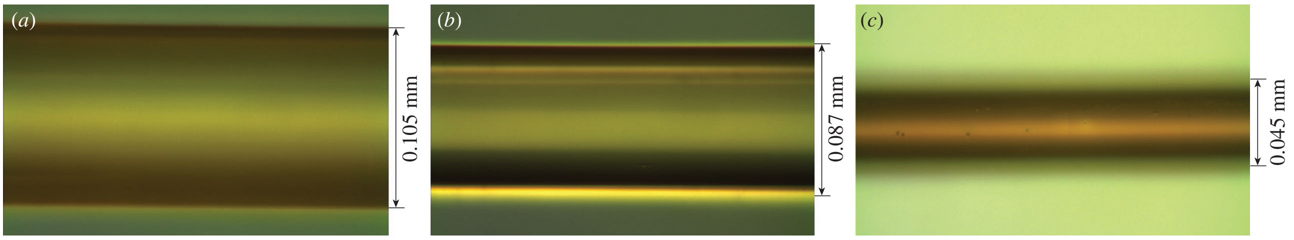
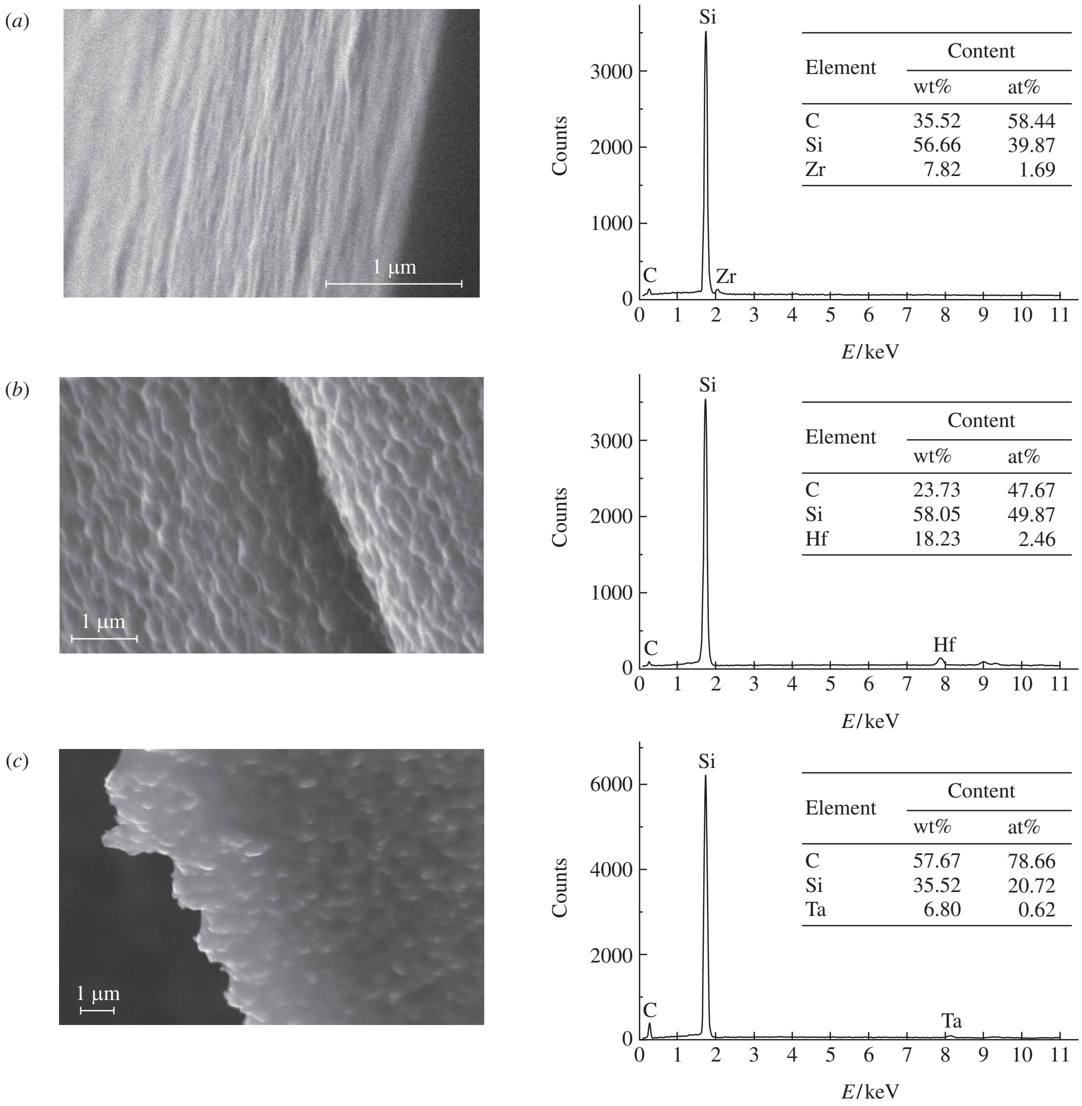


Figure 2 Photographs of coreless fibers from nanometal polycarbosilanes: (*a*) polymeric, (*b*) hardened and (*c*) pyrolyzed. Reproduced with permission from ref. 56. © 2014 Akademizdattsentr 'Nauka'.

were obtained [Figure 2(*a*)]; the consolidation [Figure 2(*b*)] and pyrolysis [Figure 2(*c*) of them led to the formation of silicon carbide fibers modified by refractory metal compounds.

The elemental composition and surface morphology of nano-MCS ceramics were determined by scanning electron microscopy (SEM) with EDS (Figure 3).



(a)

Element	Content	
	wt%	at%
C	35.52	58.44
Si	56.66	39.87
Zr	7.82	1.69

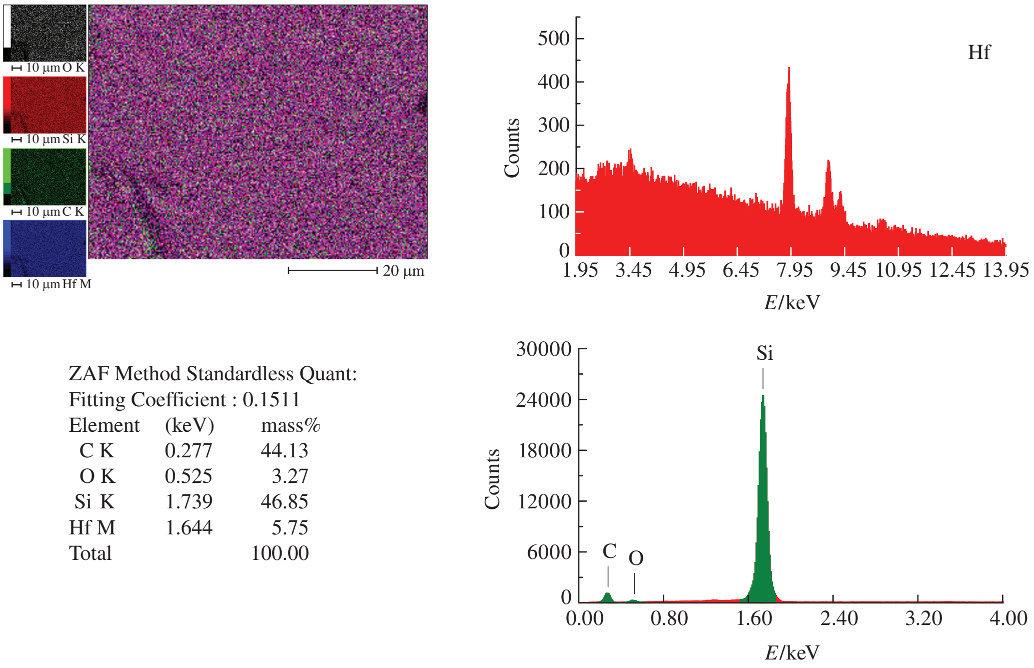
(b)

Element	Content	
	wt%	at%
C	23.73	47.67
Si	58.05	49.87
Hf	18.23	2.46

(c)

Element	Content	
	wt%	at%
C	57.67	78.66
Si	35.52	20.72
Ta	6.80	0.62

Figure 3 SEM/EDS: image of the surface and the elemental composition of nano-MCPS ceramic samples.



ZAF Method Standardless Quant:
Fitting Coefficient : 0.1511

Element	(keV)	mass%
C K	0.277	44.13
O K	0.525	3.27
Si K	1.739	46.85
Hf M	1.644	5.75
Total		100.00

Figure 4 SEM with EDS and mapping: the distribution of elements on the surface and the elemental composition of ceramics from nanohafnium carbosilane. Reproduced with permission from ref. 56. © 2014 Akademizdattsentr ‘Nauka’.

It was established that the pyrolysis of nanometal carbosilanes in an inert atmosphere at 1100 °C affords nanocrystalline (the crystallite size $D \sim 2$ nm) metal-bearing silicon carbide ceramics with an ultradispersed homogeneous structure, which is confirmed by SEM data with mapping according to the distribution of elements. For example, Figure 4 shows the SEM data for a sample of ceramics from nanohafnium carbosilane.

Conclusion

The use of ceramics-forming nanometal carbosilanes for the formation of the components (reinforcing fibers, coatings on them, matrices, powders, *etc*.) of new ceramic composite materials will make it possible to solve the problem of the development of ceramic composites with prolonged durability at temperatures higher than 2000 °C in oxidizing and other corrosive environments.[54–56]

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