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Journal of the European Ceramic Society 25 (2005) 521–528

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The peculiarities of transformation of organosilicon polymer into ceramic products under mechanochemical treatment

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Received 24 September 2003; received in revised form 16 January 2004; accepted 25 January 2004

Abstract

The effect of mechanical treatment on polygermasilethyne for different periods of time was studied. The structural and chemical transformations of polygermasilethyne into ceramic products induced during a high-energy ball milling were investigated by infrared and Raman spectroscopy, thermal analysis, X-ray analysis, as well as scanning electron microscopy analysis with using EDS spectrometer. It was shown that high-energy mechanical treatment leads to the cross-linking process including the formation of new covalent bonds between molecules and rigid three-dimensional network. Simultaneously an amorphous solid network is converted to nano- and microsized inorganic phases, namely, silicon carbide, carbon and germanium-containing phase.

Keywords: Milling; Precursors-organic; SiC; Structural applications; Preceramic polymers

1. Introduction

During the last 10 years organosilicon polymers have attracted much attention for their potential applications as precursors to ceramics with amorphous and nanocrystalline microstructure. The properties of polymer-derived ceramics can be varied in a wide range by tailoring the molecular structure, composition of the precursors and experimental techniques which are used to polymer–ceramics transformation.[1] Generally, polymer–ceramics transformation is carried out under thermal treatment. Thermolysis of organosilicon polymers was carefully studied by Corriu et al.[2] and Laine and Babonneau.[3] They showed that to obtain a ceramics with a high ceramic yield (70–90 wt.%) the cross-linking stage during thermal transformation of organosilicon polymers is necessary. Polymers that undergo cross-linking reactions will form stabilized network systems.[2,3] During thermolysis the network systems will hinder the fragmentation reactions. Usually, cross-linking process of polymers with different molecular structure and composition occurs in the temperature range of 200–400 °C. Further heating up to 1000 °C is necessary to convert the network structure into SiC-based ceramics.[2–8]

Recently, Cavaliery et al.[9] demonstrated, that solid-state mechanical milling of polymer materials represents a strategy for producing of polymer blends. The mechanochemical treatment resulted in considerable chemical and structural changes in polymers. One can expect that the combination of mechanical effects on organosilicon polymers will also induce chemical and structural changes and result in the formation new phases. Mechanical destruction of organosilicon polymers, especially, polysiloxanes was studied by Dubinskaya[10] and Balykova and Rode.[11] It was found that the mechanical effects induced radical chain scissions within polymer molecules and breaking of intermolecular bonds. Kinetics of breaking of bonds was depended not only on the stiffness of structure but molecular weight and milling conditions. It was shown that during the mechanical milling the chain scission and interchain cross-linking processes can occur simultaneously. Smith et al.[12] have shown that in dependence of the milling conditions of polyisoprene chemical cross-linking process is more possible than chain scission one. These works demonstrate that the effect of mechanical treatment on behavior of polymers can be profound.

In our previous works the thermolysis of polygermasilethyne (PGSE) was studied in detail.[7,8] The aim of

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doi:10.1016/j.jeurceramsoc.2004.01.014

this work is to study the peculiarities of physico-chemical changes that occur as a result of high-energy ball milling of unsaturated organosilicon polymer, containing germanium atom in main chain.

2. Experimental

2.1. Initial substances

Synthesis of polygermasilethyne $\{(\text{–SiMe}_2\text{C≡C–})_5\text{GeMe}_2\text{C≡C–}\}_n$ is described by Baklanova et al.[7] in detail. PGSE is a terra cotta amorphous powder soluble in chloroform to form dark-yellow solutions. The elemental composition of initial PGSE (wt.%) is 6.68H; 52.93C; 12.63Ge; 25.09Si; 2.67O. Stoichiometry is $\text{GeSi}_{5.15}\text{C}_{25.36}\text{H}_{38.40}\text{O}_{0.95}$.

2.2. Mechanochemical treatment

Polymer was mechanically treated in planetary high-energy mill (AGO-2) for 10, 20, 30, 40 min period of time. The apparatus was water cooled. All procedures with specimens obtained on different stages of mechanical treatment were conducted in dry box under flow of argon. The experimental conditions are listed in Table 1.

2.3. Analytical methods

TG-DTA of initial polymer and products derived on different stages of mechanical treatment was performed in flow argon in the temperature range of 20–1000 °C (MOM derivatograph, Budapest). The heating rate was 10 K/min. Infrared spectra were recorded in the 4000–400 cm^{-1} region with “Specord IR-75.” Samples for IR were mixed with KBr in an agate mortar and then pressed into pellets. Raman spectra were recorded with help of a Bruker RFS 100/S spectrometer equipped with a Nd:YAG laser operating at an exciting wavelength of 1064 nm, the laser output being 100 mW. The samples were prepared as mixture with KBr at a 1:100 ratio. For each spectrum, from 100 to 300 scans were accumulated. This was sufficient to obtain spectra with a low noise required for fitting procedure. The phase compositions of products were determined using X-ray diffractometry (DRON-3 St. Petersburg, Cu Kα radiation). The iron contamination was evaluated by atomic absorption in accordance with the GOST procedure. The germanium content was determined according to method developed by us.[7] Products derived at different stages of mechanical treatment were investigated using scanning electron microscopic (SEM) analysis (JEOL “JSM 820” equipped with energy dispersive spectrometer). The specific surface areas of mechanically treated samples were determined using BET method (Sorbi N.4.1, MET A) after outgassing at 90 °C for 1 h in He flow. Dissolutions tests were carried out on products derived at different stages of mechanical treatment. The soluble in chloroform fractions were filtered. The insoluble fraction was dried and weighted.

Table 1
Experimental conditions of high-energy ball milling of PGSE

Atmosphere and pressure	Argon, 2 atm
Jars volume	150 cm^3
Total ball weight	200 g
Ball diameter	5 mm
Ball and jar material	Hardened stainless steel
Mass charge	1.5 g
Acceleration	600 m/s^2

3. Results

3.1. Characterization of samples

While mechanical treating polymer grows dark and after 20 min of treatment became black powder. Immediately after milling the products of treated polymer were pyrophoric and sparked while scraped off the walls of jar. The samples mechanical treated for 10–40 min are insoluble in chloroform. The insoluble fraction consists about 95 wt.%. Specific surface areas determined for initial and the 10, 20 and 30 min treated polymer were about 1, 96, 158 and 105 m^2/g, respectively. As one can see, the mechanical treatment of polymer results in a sharp increase in specific surface area even for short period of time. The largest value is observed for sample treated for 20 min.

3.2. TG-DTA analysis

The TG-DTA analysis measurements for untreated polymer are described in detail by Baklanova et al.[7] DTA curve of PGSE exhibits a strong exotherm in the 220–280 °C region. This peak is accompanied by insignificant (about 1–2 wt.% mass loss). According to Corriu et al.[2] and Baklanova et al.[4,7] the appearance of this peak can be attributed to cross-linking process. In the 400–700 °C range the endotherm is observed. Simultaneously, the mass loss becomes substantial and reaches ∼15 wt.%. The 400–700 °C—temperature range corresponds to polymer degradation.

Fig. 1 presents DTA curves in the 200–300 °C regions for initial and 10 min treated polymer. One can see that no exotherm belonging to cross-linking process is observed for mechanically treated sample in this range. No exotherms are observed also for polymers mechanically treated for 20 and 30 min.

In the 400–750 °C ranges, DTA curves for polymer samples preliminary mechanically treated exhibit no noticeable peaks. However, significant mass losses within this region are determined. TG analyses of polymer preliminary mechanically treated for different period of time are shown in Fig. 2. One can see that mass losses are depended on treatment time. For the 10 and 20 min treated samples mass losses in this temperature region are 7.7 and 5.8 wt.%, respectively.

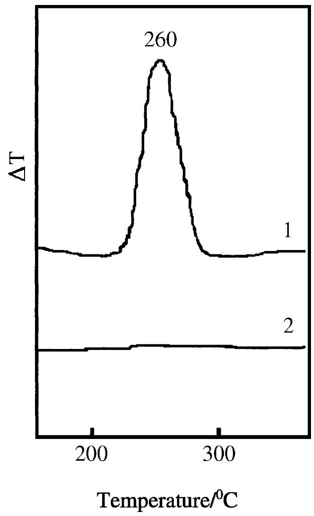

Fig. 1. DTA curves for untreated (1) and the 10 min treated (2) PGSE.

For 30 min mechanically treated polymer sample, the mass loss becomes insignificant (~0.5 wt.%). The temperature region of a sharp mass losses for preliminary mechanically treated polymer coincides with that of polymer degradation during thermal treatment.[7] It suggests that the mass loss of treated samples in this temperature region is also due to polymer decomposition. Endothermic peak regarding to polymer decomposition cannot be detectable for a variety of reasons. One of these reasons is that the endotherm intensity of initial polymer has low value. During the mechanical treatment, a part of polymer is decomposed so the endotherm intensity is decreased. At the same time the mechanical treatment results in change of particle size distribution and, therefore, leads to increase of width and to decrease of relative intensity of this peak. Besides, the other reasons likely to exist for smearing of a peak belonging to decomposition of polymer in DTA curves for preliminary mechanically treated samples.

Thus, the absence of exotherm corresponding to cross-linking for polymer preliminary mechanically treated and then heated and the dependence of mass losses on time of treatment is an evidence of intense transformation of polymer during mechanical treatment.

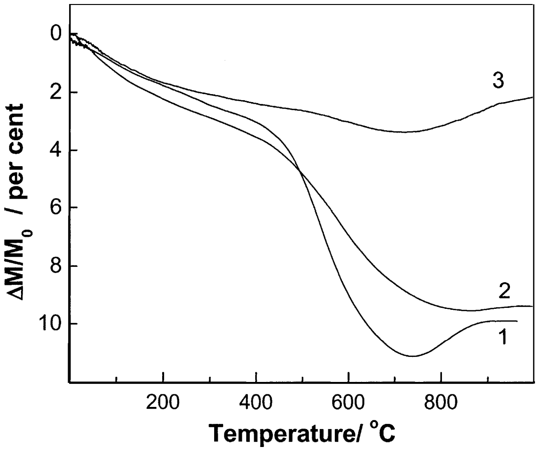

Fig. 2. TG curves of PGSE preliminary treated for 10 min (1), 20 min (2) and 30 min (3).

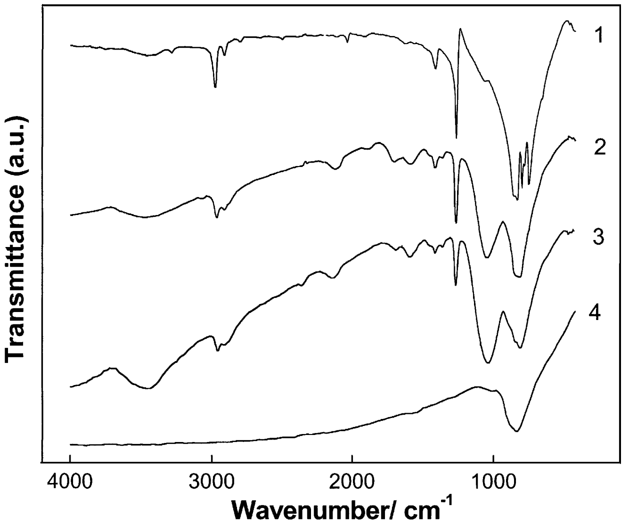

Fig. 3. IR spectra of initial polymer (1) and polymer treated for 10 min (2), 20 min (3), and 30 min (4).

3.3. *IR spectroscopy*

IR spectra of the initial polymer and those after mechanically treatment are represented in Fig. 3. One can see that in spectra of the 10 and 20 min mechanically treated polymers additional bands at about 1580, 1450, and 1350 cm^{-1} are revealed. The 1700–1300 cm^{-1} region in IR spectra is represented close-up in Fig. 4. According to Socrates,[13] the appearance of ~1580 cm^{-1} band can be assigned to aromatic –C=C– bonds. The appearance of ~1350 cm^{-1} band in IR spectra of thermolyzed organosilicon polymers is noted by many investigators.[2,3,7] This band can be attributed to vibrations of Si–CH$_2$–Si groupings which are formed as a result of cross-linking process. One can note that ~1450 cm^{-1} band (can be attributed to CH$_3$ bending as[13]) can be

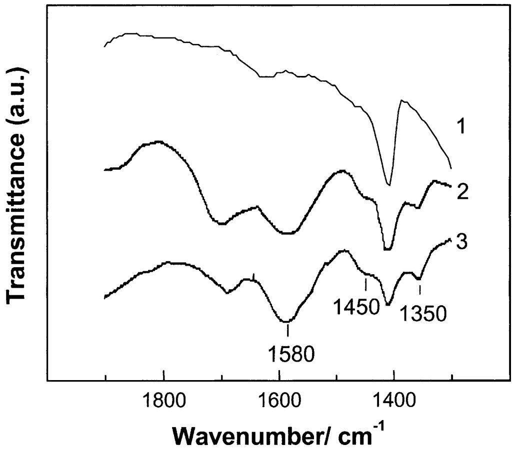

Fig. 4. IR spectra in 1700–1300 cm^{-1} region for initial polymer (1) and treated for 10 min (2), 20 min (3).

revealed in IR spectrum of mechanically treatment polymer only and it is absent in IR spectrum of thermolyzed PGSE. The intensities of above-mentioned bands are increased with increasing of time of mechanical treatment. One can see in Fig. 3 that an additional feature at ~2120 cm^{-1} is present which can be assigned to disubstituted –C≡C– groups. The reason for the appearance of this band likely to be the breaking symmetry of triple carbon–carbon bond as a result of cross-linking process and splitting of Ge–C≡C and Si–C≡C bonds during mechanical treatment. One can see (Fig. 3) that with increasing time of mechanical treatment the intensities of bands assigned to CH_3 stretching vibrations (2970 and 2910 cm^{-1}) and Si–CH_3 deformation vibration (1260 cm^{-1}) decrease. According to Socrates,[13] broad band centered at ~1700 cm^{-1} can be attributed to –C = O vibrations. Because of the mechanical treatment was performed in an inert gas in jar that was preliminary pumped and washed several times by inert gas the interaction of products of milling with oxygen-containing gases must be excluded. We suppose that the products of mechanical treatment can react with an air under storage resulting to formation of oxygen-containing phases.

In IR spectrum of the 30 min mechanical treatment product the only broad band centered at ~820 cm^{-1} is observed (Fig. 3). This band is assigned to Si–C stretching vibration in SiC_4 tetrahedral species.[2] One can note that an analogous IR spectrum was observed early for PGSE polymer thermolyzed at 800 °C.[7] Thus, disappearance of characteristic bands in spectrum of the 30 min mechanical treatment polymer and appearance of strong Si–C stretch band provide an evidence for the formation of SiC-based phase during mechanical treatment of polymer.

3.4. Raman spectroscopy

Raman spectra of the 10 and 30 min mechanically treated polymer are represented in Fig. 5a and b. One can see that in Raman spectrum of polymer-derived product (10 min mechanical treatment) all characteristic features of polymer are disappear, only a very broad band in the 1650–1000 cm^{-1} region is present. Computer deconvolution of spectrum allows us to reveal four broad bands at about 1200, 1370, 1510 and 1590 cm^{-1}. Spectrum of polymer derived product (30 min treatment) differs from above mentioned one in two clear bands at 1295 and 1600 cm^{-1} that can be attributed to bands of disordered (D) carbon and graphite (G), respectively.[14] The best peak-fitted model of Raman spectrum gives five bands at about 1195, 1295, 1415, 1540 and 1600 cm^{-1}. The 1140–1200 cm^{-1} band was detected in Raman spectra of deposited carbon films and glassy carbon and is assigned to disordered and hydrogenated sp^3-bonded carbon. The band at around 1540 cm^{-1} is attributed to the highly disordered sp^2-bonded carbon.[15,16] The band at ~1415 cm^{-1} is revealed in Raman spectrum taken only at 1064 nm wavelength of laser excitation.[8] The appearance of bands assigned to carbon suggests that the mechanical treatment of polymer for 30 min results in the formation of free carbon phase. One can note that an analogous Raman spectrum was observed for PGSE polymer thermolyzed at 800 °C. This is a temperature at which the organic–inorganic transformation of organisilicon polymers is completed.[7]

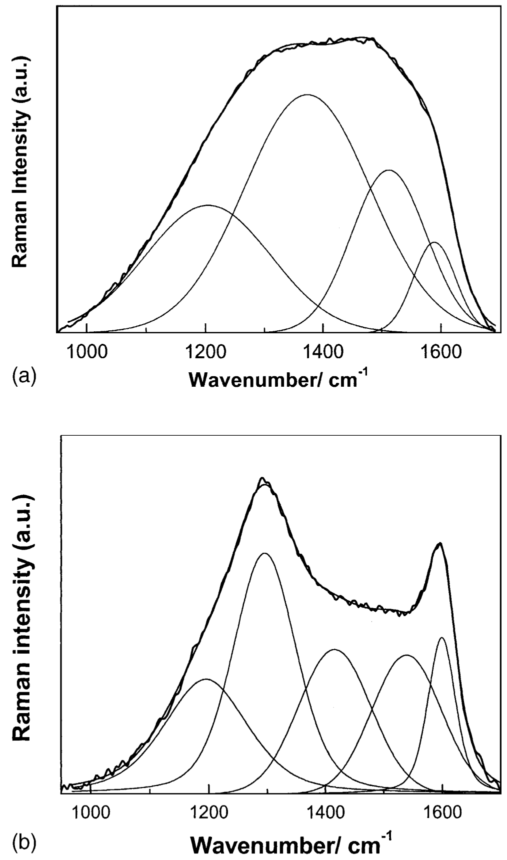

Fig. 5. Raman spectra of polymer treated for 10 min (a) and 30 min (b).

3.5. XRD analysis

X-ray diffraction patterns of products derived from polymer at 20 and 30 min of treatment are shown in Fig. 6. The polymer treated for 10 min gives only X-ray amorphous products. Beginning from 30 min in XRD patterns the peaks appear which can be attributed to β-SiC phase according to PDF (No. 29–1129).[17] Besides, a broad peak centered at about $2\Theta = 45°$ is present for products derived after the 20–40 min treatment. Its intensity is increased with time of mechanical treatment. The presence of this peak in XRD patterns is an evidence of appearance of Fe-containing phase.[17] The presence of Fe in polymer-derived products is confirmed by elemental analysis. According to elemental analysis data, the iron contents are 1.46 and 30.0 wt.% for the 10 and 40 min mechanical treatment, respectively. No peaks belonging to germanium phase were detected. However, according to chemical analysis of products derived at the 10 and 40 min mechanical treatment the germanium contents are 9.88 and 7.62 wt.%, respectively.

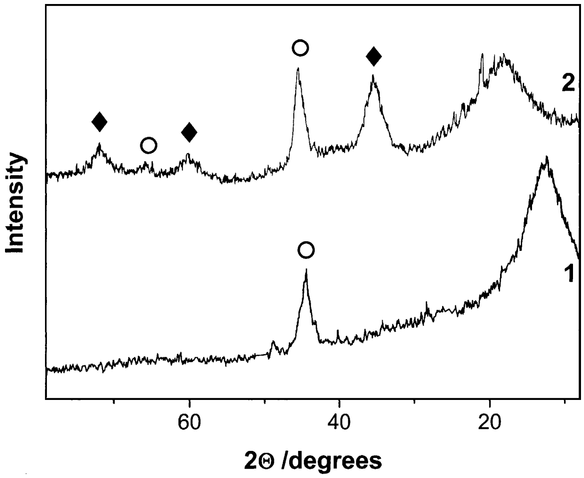

Fig. 6. XRD patterns for the 20 min (1) and 30 min (2) treated polymer. Reflections of (◆) SiC, (○) "FeGe."

Thus, from XRD and elemental analysis data it follows that in course of mechanical treatment the transformation of polymer occurs.

3.6. SEM analysis

SEM images of products derived from mechanical treated polymer are represented in Fig. 7a and b. As one can see, these products are small particles, the size of which being less than <50 nm. Some of them are gathered in agglomerates. At the same time, new formations with porous structure and of about 2–3 μm sizes are present. The presence of Ge, Si and Fe at least in products derived after mechanical treatment of polymer was detected by EDS analysis (Fig. 8).

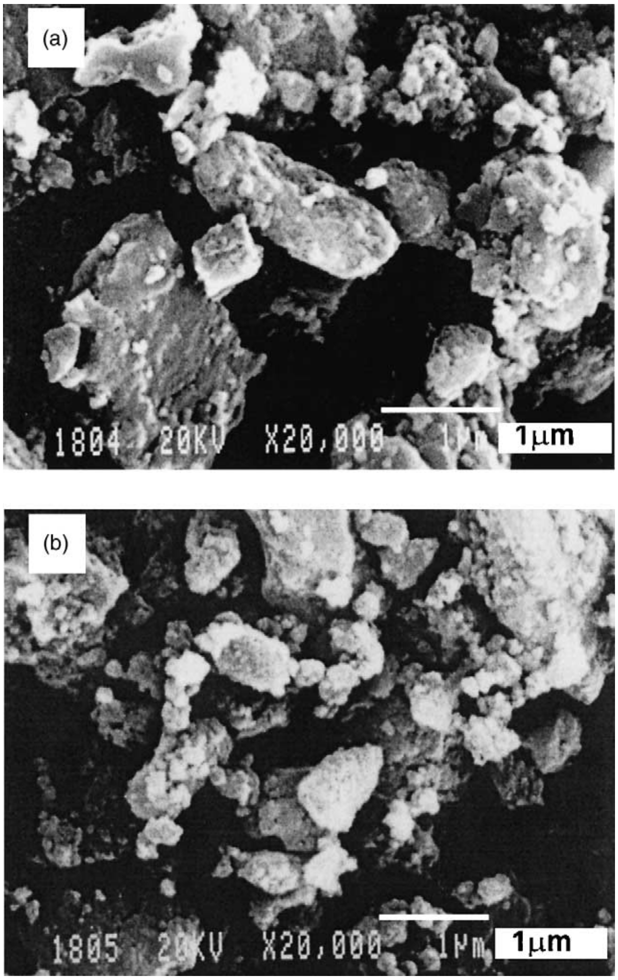

Fig. 7. SEM micrographs of polymer treated products: (a) 20 min and (b) 30 min.

4. Discussion

The different types of processes which take place during mechanical treatment of organic substances probably can be divided into two groups.[10] One of these groups comprises the processes of conformational transformation, disordering and amorphization of crystalline structure which are generated by split of intermolecular bonds. Another group presents mechanochemical reactions initiated by deformation of valence angles and bonds. Under mechanical stress, primarily the intermolecular bonds split resulting in disorder of substance structures. At the same time, the deformation of angles and bonds of molecules occurs giving rises the splitting of covalent bonds in molecules. Amount of produced radicals depends on kind of mechanical action, power input, and substance structures.[10] The possibility of the formation of new covalent bonds between molecules appears and as result the cross-linking process of polymer occurs.

Experimental data confirm the fact that under high-energy ball milling during the first 10 min the cross-linking of PGSE with the formation of rigid network structure occurs. The formation of bridging –CH_2– and conjugated groups in conjunction with decreasing of intensities of vibrations of the CH_3– groups in IR spectra, and the absence of any characteristic bands in Raman spectrum allows us to account that a high-energy ball milling of polymer leads to considerable

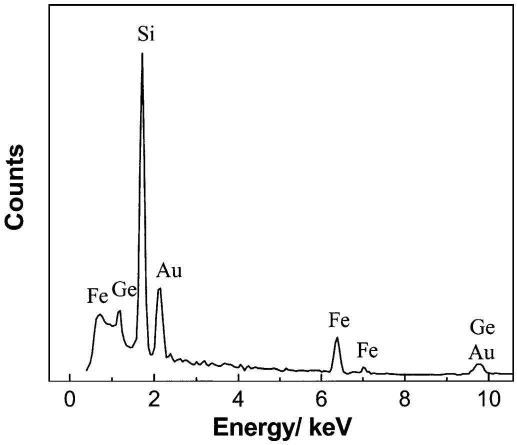

Fig. 8. EDS spectrum of the 30 min treated polymer.

and irreversible transformations. This conclusion is also confirmed by DTA data. No exotherm in the 220–280 °C region of DTA curve is observed for the preliminary 10 min treated polymer of unlike the initial polymer (Fig. 1). As was mentioned above, this exotherm was a result of cross-linking process of initial polymer. It should also be noted that after mechanical treatment for 10 min polymer becomes practically insoluble in chloroform. It can be an evidence that cross-linking of polymer at the first stages of mechanical treatment occurs. However, together with cross-linking process the decomposition of polymer at the 10 min stage of treatment cannot be excluded. The solid-state[13] ^{13}C NMR studies of thermolyzed unsaturated organosilicon polymers carried out by Baklanova et al.[5] demonstrate that at about 400 °C not only cross-linking process but the formation of strongly distorted carbon structure with changed bond lengths and angles was observed.

During the first time of treatment of PGSE, the sharp increase in specific surface area (∼100 times) takes place. It can be conditioned by strong disordered rigid network structure and possible by the formation of strongly disordered free carbon phase.

During subsequent mechanical treatment (20 min) the further evolution of formed rigid network system proceeds. The evolution includes two processes that proceed simultaneously. On the one hand, cross-linking proceeds. It is confirmed by the increase in intensities of groups that are formed as a result of cross-linking and decrease in intensities of vibrations of CH$_3$– groups in comparison with those of product derived from the 10 min mechanical treated. IR-spectroscopy data are indicative of increasing amount of molecules involved in formation of three-dimensional rigid amorphous covalent network. On the other hand, the transformation of rigid network occurs together with cross-linking. As was above mentioned, we observed the decrease of mass loss in the 400–700 °C for polymer preliminary mechanically treated for 20 min in comparison of the 10 min treated polymer. This is an evidence that the part of polymer is decomposed during of mechanical treatment. The product formed at this stage represents SiC-based phase and posseses a high hardness. Therefore, some iron-containing phase as contamination arising from attrition is revealed in products of the 20 min mechanical treated polymer (Fig. 6).

With increasing time of mechanical treatment until 30 min, the process of conversion of polymer into ceramics is completed. A set of experimental data demonstrates the formation of inorganic phases. In IR spectrum of product the only broad band attributed to Si–C stretching vibration in SiC$_4$ tetrahedral species (∼820 cm^{-1}) is observed. Raman spectra prove that free carbon phase is present in the mineralization product. However, we suggest that not only conversion of polymer into ceramics is reason of appearance of free carbon phase. It can be possible the interaction between SiC-based structure and ball mill material. It was well stated that SiC can be chemically unstable in the presence of transition metals.[18] The negative free-energy change may provide the driving force for interaction of Fe with SiC to form silicides instead of carbides and leave free carbon. Low-temperature liquid formation through eutectic reaction may offer kinetic convenience to the SiC–Fe reaction. As was found by Pan and Baptista,[18] carbon and iron silicides, preferentially Fe$_3$Si, were formed in the system SiC–Fe in the 850–1600 °C temperature range. However, interaction between iron and strong reactive intermediates that are formed during polymer decomposition cannot be excluded on stages that precede a formation of silicon carbide. Special experiments on mechanical treatment of mixture of germanium and polysilethyne[4,6] (PCS) (atomic ratio Si:Ge is 8:1) for different periods of time were carried out by us. The XRD patterns of products on different stages are presented in Fig. 9. One can see that FeSi is formed after the 20 min treatment, whereas SiC features are observed after the 40 min mechanical treatment. However, it should be noted that no reflections of iron silicides are observed in XRD patterns of treated PGSE. Nevertheless, the presence of silicon in forming Fe-containing phase cannot be excluded.

The behavior of germanium during transformation of polymer under mechanochemical treatment is more complicated. Early it was shown by Baklanova et al.[7] that as a result of thermolysis of organosilicon polymer with Ge atom in main chain the formation of germanium as separate phase at temperature above than 600 °C could be detected by X-ray analysis. Germanium was revealed as drops in SEM images of products derived from polymer thermolyzed at temperatures about 800–1000 °C. The release of germanium as separate phase can be explained by instability of germanium carbide unlike silicon carbide.[19] No germanium as drops in SEM images or features of germanium phase in the X-ray diffraction patterns of products derived from mechanical treated polymer were detected. It suggests that germanium released during mechanical treatment of polymer can react with iron resulting in the

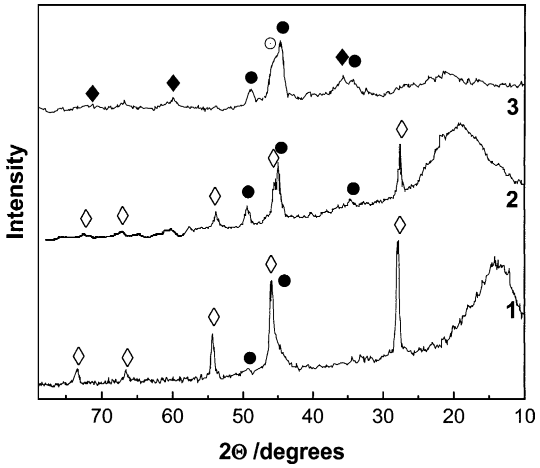

Fig. 9. XRD patterns for the 20 min (1), 30 min (2), and 40 min (3) mechanical treated mixture (PCS + Ge). Reflections of (◆) SiC, (◇) Ge, (●) FeSi, (○) "FeGe."

formation of different Fe–Ge intermetallic phases. According to XRD patterns of products of treated mixture of Ge and polysilethyne (PCS) the intensities of the Ge peaks are diminished with increasing of time of mechanochemical treatment. No peaks belonging to germanium were detected after 40 min of treatment. At the same time the XRD peak that can be assignable to Fe–Ge containing phase is appeared. It is difficult to determine phase composition of the FeGe-containing products because they exhibit one wide reflection in XRD patterns as presented in Figs. 6 and 9.

According to Kwon et al.[20] a single peak in the XRD pattern of product derived after milling of iron and germanium mixture is present. This peak was assigned to phases based on bcc lattice. Several phases in the Fe–Ge phase diagram have the bcc structure and are distinguished from each other by weak superlattice reflections. Besides, Fe–Si–Ge solid solutions up to about 11 at.%. Ge and Si with bcc structure (α-phase), β-phase and hexagonal Fe_3Ge phase have the strongest XRD reflection in the same region.[20,21] Due to difficulty in the determination of the exact position because of a very wide width single peak and a high noise of XRD pattern of product derived during milling it is impossible to assign exactly the XRD peak at about $2\theta = 45^\circ$. So it is impossible to determine the composition of the Fe–Ge-containing phase(s) obtained during mechanical treatment of polymer we denoted it as “FeGe” one.

Thus, mechanical treatment gives rise to transformations in polymer under investigation. Under mechanical stress on PGSE, the disruption of intermolecular bonds and the distortion in angles and length of intramolecular bonds occur resulting in split of covalent bonds in molecules. Cross-linking process including the formation of new covalent bonds between molecules and three-dimensional rigid covalent network occurs. Simultaneously, the conversion of network system to nano- and microsized inorganic phases, such as silicon carbide, carbon and germanium takes place. By-products of interaction of these phases with ball mill material are formed under long mechanical treatment.

5. Conclusion

The mechanical treatment of polygermasilethyne for different period of time was carried out. According to infrared and Raman spectroscopy, thermal analysis, X-ray analysis, as well as scanning electron microscopy analysis unsaturated Ge-containing organosilicon polymer undergoes irreversible transformations. During mechanical treatment two different processes occur. Firstly, the cross-linking process of polymer including the formation of new covalent bonds between molecules and rigid three-dimensional network occur. At the same time, the amorphous solid network is converted to nano- and microsized inorganic phases: silicon carbide, carbon and germanium. By-products of interaction of these phases with ball mill material are formed. The results of this work allow us to consider high-energy ball milling as a promising root of conversion of organosilicon polymers to ceramic products.

Acknowledgements

The authors are thankful to Professor Kwon Young-Soon (ReMM University of Ulsan, Korea) for SEM and EDS analysis and Professor Logvinenko V.A. (Institute of Inorganic Chemistry SB RAS, Novosibirsk) for DTA-TG analysis. This work was supported by Integral grant #17 of Siberian Branch RAS.

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