Formation and stability of β-Si₃N₄ and Si₂N₂O phases in composite materials during mechanochemical treatment of powder mixtures including silicon, Taunite-M and nitrogen-containing components

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ABSTRACT
Scientific research and exploratory work on the creation of new technologies are continuing, the purpose of which is to increase the level of mechanical and high temperature properties of materials. A multicomponent carbon composite material (MCCM) containing silicon nitride and oxynitride was synthesized by the method of sequential stepwise high-energy mechanochemical treatment (MCT) and isothermal annealing at 1100 °C of powder mixtures of Taunite-M, silicon, g-C_3N_4 phase and melamine. Using X-ray diffraction analysis, IR spectroscopy and Raman spectroscopy, it was proved that β-Si_3N_4 and Si_2N_2O phases are present in the MCCM. Their crystallographic characteristics and crystal lattice parameters were determined. A crystal chemical explanation of the formation and stability of these phases in the realized synthesis is proposed. The synthesized MCCM is a promising material for high-temperature heat-resistant ceramics.
KEYWORDS
subcritical growth multicomponent carbon composite material • IR spectroscopy • Raman spectroscopy X-ray diffractometry • silicon nitride • silicon oxynitride

Introduction

Formation of silicon nitride and oxynitride phases in a carbon matrix significantly changes the properties of carbon composite materials. This is due to their high hardness, shape morphology and distribution pattern in the composite. With standard technologies [1], the formation of these phases is achieved through prolonged high-temperature treatment and/or at elevated pressure. We implemented a different approach in our research. The technology of mechanochemical treatment (MCT) of multicomponent polyphase powder mixtures is used [2]. The elemental, phase and fractional compositions of the components of the initial powder mixture and the gas composition of the technological atmosphere undergo changes in the process of sample preparation and the initial stage of MCT. This is necessary for the subsequent mechanochemical alloying of the components in a high-energy planetary mill, the formation of nonequilibrium structural-phase states. The presence of fine single-crystalline silicon particles in the processed powder mixture promotes the synthesis on such a substrate with its random favorable crystallographic orientation in the carbon matrix and the real technological atmosphere of the desired

phases: silicon nitride and oxynitride. The resulting state was stabilized by isothermal annealing. Varying the parameters and conditions of the MCT technological process provides the necessary set of types of impact action (of the balls on the powder mixture), their energy and kinetic patterns. This includes the duration and nature of the interaction, the gas composition of the technological environment in which local impact processes and various physical and chemical processes occur during subsequent mixing of the powder in the working volume [3]. Alternating the above technological parameters makes it possible to form micro- and nano-particles of powder material of various shapes. The use of subsequent isothermal annealing makes it possible to detect the formation of silicon nitride and oxynitride phases and ensures the formation of the required phase composition in the synthesized multicomponent carbon composite material (MCCM). Since the formation and distribution of phases in the volume of the synthesized MCCM is significantly influenced by the form factor of the initial carbon material, we used Taunite-M type nanostructured carbon material in the work. When using high-energy ball mills for synthesis, it is necessary to create a protective or reducing environment. At the level of micro- and nano-processes, the composition of the technological atmosphere in the local volume of direct impact interaction comes to the fore. For these purposes, a component (melamine) was added to the processed powder mixture, which, upon decomposition during the synthesis process, released nitrogen-containing gas components (including ammonia), forming a reducing or protective environment, both in the local interaction volume and in the entire working volume [4]. In addition, at all subsequent repeating stages of MCT and stepwise heat treatment (SHT), the factor of the reducing atmosphere of nitrogen-containing compounds formed at the first stage of synthesis is continuously enhanced by the active (atomic) carbon of working environment in the local volume of impact interaction, which primarily binds technological oxygen residues to form carbon monoxide.

Therefore, the purpose of the performed work was to use diffraction and spectral research methods to prove the synthesized MCCM contains such phase components as silicon nitride (Si_3N_4) and silicon oxynitride (Si_2N_2O).

Methods

The considered multicomponent carbon composite material (MCCM) was obtained by synthesis using mechanochemical treatment (MCT) in a PM-100 planetary ball mill (Retsch Technology, Hamburg, Germany) and subsequent stepwise isothermal annealing in a vacuum furnace at a temperature not exceeding 1100 °C and vacuum of $1 \cdot 10^{-3}$ mbar for at least three hours.

To obtain MCCM, we used carbon nanostructured material Taunite-M as a basis: quasi-one-dimensional, nano-sized, thread-like formations of polycrystalline graphite, predominantly cylindrical in shape with an internal channel compliant with TU 2166-001-77074291-2012 produced by LLC NanoTechCenter (Tambov, Russia).

In order to accelerate the process of phase formation, powder material obtained using the technology described in [4] was added to the mixture together with Taunite-M. This technology involves the thermal decomposition of carbamide (in our case, melamine) to graphite-like carbon nitride. The presence of the g-C_3N_4 phase in the processed mixture

Formation and stability of β-Si3N4 and Si2N2O phases in composite materials during mechanochemical treatment
of powder mixtures including silicon, Taunite-M and nitrogen-containing components

58

is a necessary condition for the formation of β-Si_3N_4 during synthesis. The weight proportionality of the charge components of powder mixtures corresponds to the requirement of substance balance during synthesis.

The mixture included four components of optimal proportional weight composition and homogeneous fractional composition: Taunite-M; g-C_3N_4; silicon (KR0 GOST 2169-69); melamine (GOST 7579-76). The total mass of the powder mixture did not exceed 4 g and was controlled at all stages of the synthesis with an accuracy of $\pm$ 0.002 g. All components used were fractions of $\leqslant$ 56 μm composition.

At the first stage, mechanochemical synthesis was carried out in a PM-100 planetary mill at 600 rpm in an agate jar with agate balls in ethanol. The processing time was 10 hours, while the mode included stopping the process every 2 hours for 0.5 hours. This mode maximizes phase formation in the processed carbon material. The ratio of the mass of the balls to the mass of the load was 18:1.

Next, the resulting material was dried at a temperature of (60 $\pm$ 2) °C for 4 hours and pressed into tablets with a diameter of 6 mm at a pressure of 1.5 tons (hydraulic press with a maximum force of 10 tons). The mass of the samples was (0.060 $\pm$ 0.001) g. At the third stage, multi-stage annealing was carried out in vacuum: at 360 $\pm$ 5 °C for 1 hour; at 450 $\pm$ 5 °C for 1 hour; at 1100 $\pm$ 5°C for 3 hours.

The first two stages of heat treatment are carried out to decompose the melamine and thereby create a protective atmosphere.

The phase composition of the resulting MCCM was studied by X-ray diffractometry using a DRON-3M diffractometer and Co Kα filtered radiation. The shooting was carried out according to the Bragg–Brentano setup (ϑ–2ϑ) in the angle range of 2ϑ = (10 $\div$ 90) angular degrees with a scanning step of 0.05° and exposure at a point of 3 s. At least three samples synthesized under the same conditions were analyzed. The ratio of the min-max total set of pulses at a point provided a statistical error of 0.05/0.005.

IR spectroscopy was performed on a Shimadzu IRPrestige-21 infrared spectrometer with Fourier transform, standard measurement parameters, spectral range of 7800–350 cm^{-1}, ceramic radiation source, KBr beamsplitter, DLATGS detector.

Raman spectra were taken on a Centaur scientific research complex, including a Renishaw Virsa spectrometer with excitation wavelength of 785 nm, 5 s exposure time, without radiation attenuation.

Results and Discussion

The X-ray studies had increased accuracy: we increased the number of samples examined (up to three per analysis); used analytical slits of reduced sizes and Soller slits to limit the axial deflection of the X-ray beam; increased shooting time per point by 3 times; reduced the scanning step; installed an iron β-filter for Co-radiation. Figure 1 shows the results of X-ray diffraction studies of the synthesized MCCM. The analysis proves, with a high degree of reliability, the presence of β-Si_3N_4 and Si_2N_2O phases in the synthesized material. When decoding the identified diffraction maxima, we used the data from our previous studies [5]. The fundamental factor in the studies performed is the fact of the existence of diffraction maxima that belong exclusively to the β-Si_3N_4 and Si_2N_2O phases

(see Fig. 1). Thus, X-ray studies indeed indicate that the proposed hybrid technology of MCCM synthesis produces silicon nitride and oxynitride.
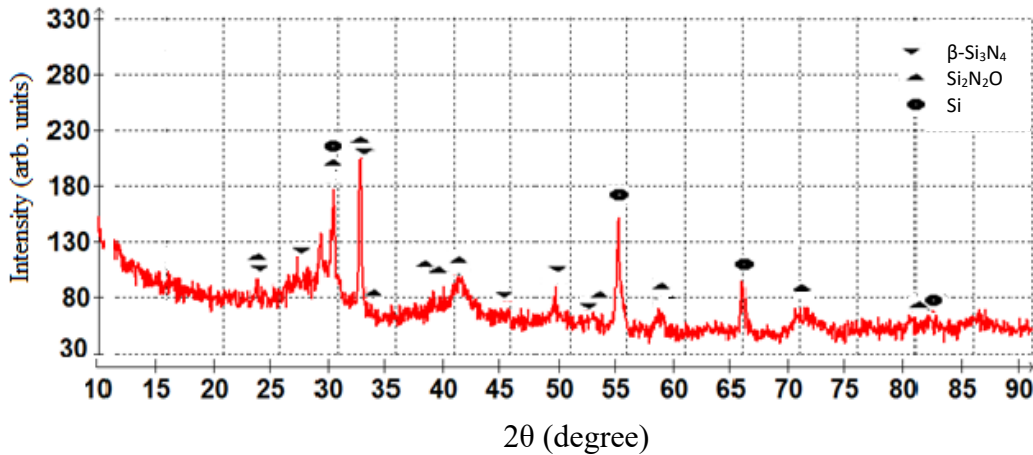

Fig. 1. X-ray diffraction pattern of MCCM obtained using the hybrid technology

However, since the synthesized MCCM has a multiphase state (four phases), as a consequence all diffraction patterns obtained from X-ray analysis are complex: many diffraction peaks belonging to different phases, often closely spaced and often overlapping with each other [5]. In such cases, the results of phase analysis require clarification by other methods. For this purpose, in order to confirm that β-Si_3N_4 and Si_2N_2O phases formed during synthesis, we performed spectral studies of the MCCM samples using infrared spectroscopy (IR) and Raman spectroscopy (RS). This choice of spectral analysis methods is due to their increased sensitivity to the type of interatomic (intermolecular) interaction. The research results are shown in Figs. 2 and 3 and in Tables 1 and 2.
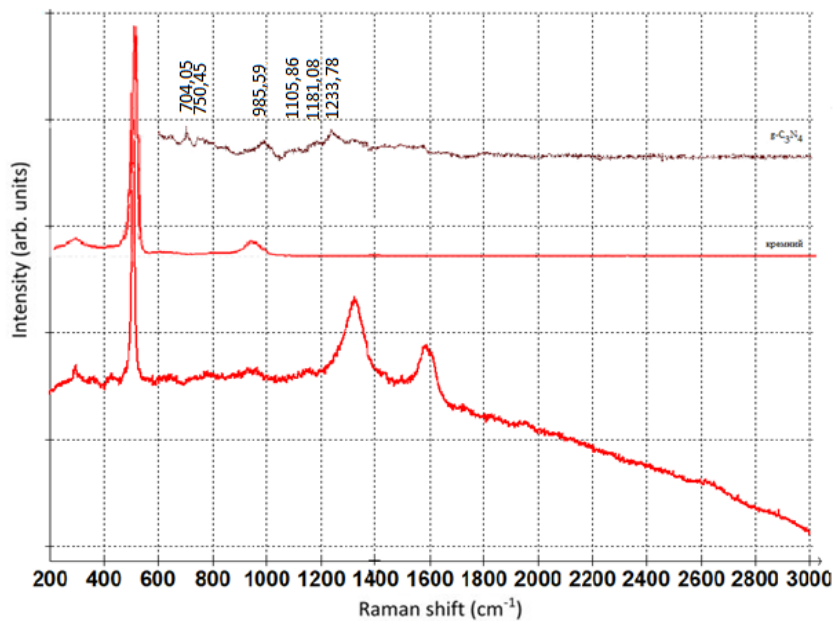

Fig. 2. Results of Raman scattering by samples of the synthesized MCCM (lower graph) and mixture components used for synthesis (Si and g-C_3N_4)

Formation and stability of β-Si3N4 and Si2N2O phases in composite materials during mechanochemical treatment of powder mixtures including silicon, Taunite-M and nitrogen-containing components
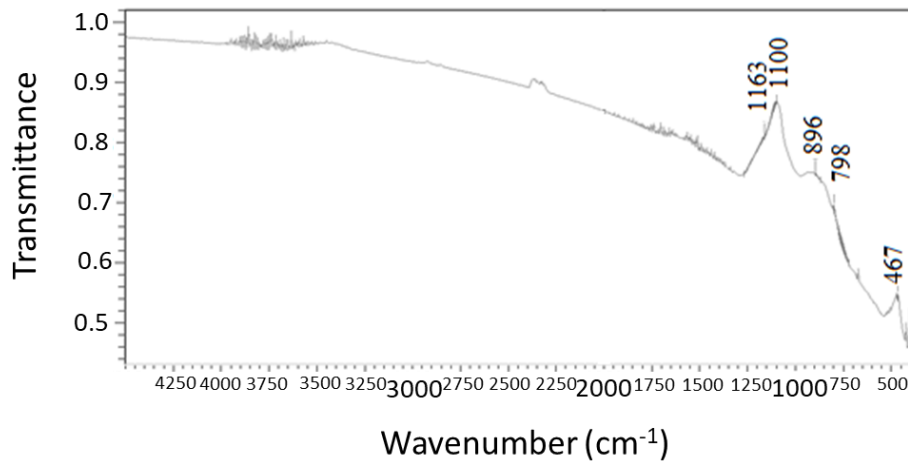
60

Fig. 3. Results of IR spectroscopy of the synthesized MCCM samples

Table 1. Interpretation of Raman scattering data for the synthesized MCCM samples (Raman spectroscopy)

Experimentally obtained peaks, cm^{-1}	Literature data	Phases
296.53	259; 365 α-Si$_3$N$_4$ [8] 303.24 Si experiment	α-Si$_3$N$_4$
411.75	400 Si-N [9]	Si-N
440.55	480 Crystalline Si [10]	Crystalline Si
505.23	515 α-Si$_3$N$_4$ [8] 520 amorphous Si [10] 518.08 Si experiment	α-Si$_3$N$_4$ amorphous Si
656.24	668 α-Si$_3$N$_4$ [8]	α-Si$_3$N$_4$
704.05	g-C$_3$N$_4$ experiment	g-C$_3$N$_4$
750.45	g-C$_3$N$_4$ experiment	g-C$_3$N$_4$
800.44	804 heptazine rings [11] 800 Si-C [10] 800 Si-N [12]	heptazine rings Si-C Si-N
809.84	810 [13] melamine degradation	melon
849.01	~860 Si-N [14]	Si-N
925.76	915 α-Si$_3$N$_4$ [8] 946,81 Si experiment	α-Si$_3$N$_4$
962.19	975 α-Si$_3$N$_4$ [6]	α-Si$_3$N$_4$
1034	1034 α-Si$_3$N$_4$ [6]	α-Si$_3$N$_4$
1100-1700	1.3.5-s-triazine rings [12]	1.3.5-s- triazine
1105.86	g-C$_3$N$_4$ experiment	g-C$_3$N$_4$
1181.08	g-C$_3$N$_4$ experiment	g-C$_3$N$_4$
1350		D-graphite
1582		G-graphite
1620		D'-graphite
2100-2300	~2200 Si-H [11]	Si-H
2700		2D-graphite
~3250	~3300 N-H [11]	N-H

Figure 2 shows the results of Raman scattering studies for the synthesized MCCM samples. Note the shift of the silicon peak towards lower values. The authors of [6,7] proved that a shift of the silicon peak to lower values occurs upon heating due to a change

in the thermal conductivity of silicon, which is covered with an oxide film. In our studies, a bond between silicon and nitrogen is formed, which can also change the thermal conductivity of the sample material and cause a change in the position of the Raman peak and its half-width.

Table 1 shows the interpretation of the Raman spectra indicating the sources that served as justification for the adoption of the phases. For silicon and g-C_3N_4, experimental data were taken, obtained by recording the initial components of the mixture. The results presented in the table clearly confirm the fact of the formation of silicon nitride.

However, note that although the silicon peak shifted, there are no peaks characteristic of the Si-O bond. In this case, the well-known peaks of amorphous disordered graphite are present. This result somewhat contradicts the known fact of graphitization at 700 °C. In our opinion, this is due to the formation of open and closed pores in the material. Closed pores presumably prevent graphitization at higher temperatures.

As the graph demonstrates, there are three areas of low-intensity bands (noise), which can be attributed to the result of the melamine degradation and the formation of the g- C_3N_4 phase, the formation of CO_2 and thin graphene films. Table 2 shows the interpretation of the IR spectra indicating the sources that confirmed the presence of specific bonds between atoms in the phases existing in the synthesized MCCM samples.

Table 2. Interpretation of IR spectroscopy data for the synthesized MCCM samples

Experimental data, cm^{-1}	Literature data	Bonds
467	470 Si-N [16,19] 480 Si-Si [9,10] 457 Si-O rocking bands [10]	Si-N
798	814 Si-O bending bands [10]	Si-O
896	875 Si-N stretching bonds [15] 865 Si-N [10] >850 Si-N [16]	Si-N
1100	1100 HN-H [17] 1080 Si-O [15] 1069↑t 1080 Si-O [10]	HN-H, Si-O
1163	1170 N-H [16] 1175 N-H [10]	N-H
1300-1700 ('noise')	Low-intensity absorption bands with maxima at wavenumbers from 1554 to 1234 cm^{-1} correspond to bending and stretching vibrations of the C-N bonds of the heptazine ring [11]	C-N heptazine rings
2300-2400 ('noise')	2260-2300 CO_2[11]	CO_2
2350	2200 Si-H [9]	Si-H
2851	Graphene [18]	
2924	Graphene [18]	
3350	3340 Si-N [16,19]	Si-N

As can be seen from the table, the samples contain a Si-O bond. However, X-ray studies do not confirm the formation of silicon oxide [20]. Therefore, the Si-O and Si-N bond can be rightfully attributed to the silicon oxynitride phase.

Conclusion

The non-equilibrium of the processes and the structural-phase states during mechanochemical treatment, the degradation of metastable phases and structural formations when the technological process is interrupted, and the use of stepwise heat treatment, form multicomponent carbon composite materials with a very complex phase composition, both in the type (set) of phases, and in their chemical composition and structural (defective) condition. The phase composition of a composite primarily determines its physical and chemical properties and the range of possible applications. The production of carbon composites (MCCM) containing phases of silicon nitride and oxynitride by mechanochemical treatment and stepwise heat treatment opens up new prospects for their use as a functional material, including for microelectronics.

Based on the results of X-ray and spectral studies, it can be stated that the proposed hybrid technology of MCCM synthesis induces β-Si_3N_4 and Si_2N_2O phases. Their formation and stability are determined by the weight proportions and composition (set of components) of the mixture and the physicochemical laws of the processes in the system during hybrid synthesis by high-energy mechanochemical treatment and subsequent isothermal vacuum annealing at a temperature of 1100 °C.

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