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Mechanism of Si_3N_4 nucleation during carbothermal reduction of silica

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The process of carbothermal reduction of SiO_2 in a nitrogen flow at temperatures of 1673–1723 K was investigated. It was established that mixtures obtained by the sol–gel technique are not microhomogeneous and consist of silica and carbon aggregates, inside which the processes of structure and phase ordering occur during heat treatment. The contact region of these aggregates is the place where SiO_2 reduction occurs. In this region the following transformation takes place: partial SiO_2 reduction, appearance of a film of melt of the composition SiO_x, where $x < 2$, enveloping of the carbon particles by this melt, destruction–activation of the carbon particles, implantation of nitrogen in the highly oxygen-defective melt, formation of silicon oxynitride and, subsequently, silicon nitride. α-Si_3N_4 forms in the presence of a large carbon nucleus, β-Si_3N_4 forms in its absence (or on two-dimensional particles).

1. Introduction

In the opinion of many investigators, the silica carbothermal reduction process with simultaneous nitridation is an advanced method of silicon nitride synthesis, because it uses non-scarce low-cost raw materials. It provides the possibility of producing powders with controlled particle size, morphology and crystalline structure.

In spite of the large number of works which deal with nitride formation in the temperature range between 1573 and 1823 K, there is no single version of the Si_3N_4 particle nucleation mechanism. This apparently can be connected with the fact that the reaction $3SiO_2 + 6C + 2N_2 \rightarrow Si_3N_4 + 6CO$ is the sum total and consists of a series of simultaneous and sequential chemical reactions. According to various authors [1–7] the following reactions occur

$$SiO_{2(s)} + C_{(s)} \rightarrow SiO_{(g)} + CO_{(g)} \quad (1)$$

$$2SiO_{2(s)} + C_{(s)} \rightarrow 2SiO_{(g)} + CO_{2(g)} \quad (2)$$

$$CO_{2(g)} + C_{(s)} \rightarrow 2CO_{(g)} \quad (3)$$

$$3SiO_{(g)} + 3C_{(s)} + 2N_{2(g)} \rightarrow Si_3N_{4(s)} + 3CO \quad (4)$$

$$3SiO_{(g)} + 3CO_{(g)} + 2N_{2(g)} \rightarrow Si_3N_{4(s)} + 3CO_2 \quad (5)$$

The appearance of silicon carbide, observed by a number of authors [6, 7], in the early stages of silica and carbon nitridation, allowed us to conclude that the following reactions of nitride formation are also possible

$$SiO_2 + 3C \rightarrow SiC + 2CO \quad (6)$$

$$SiC + 2SiO_2 \rightarrow 3SiO + CO \quad (7)$$

Silicon oxinitride appears to be the stable equilibrium phase if O_2 ($p > 7.2 \times 10^{-15}$ Pa) is present in the atmosphere [1]

$$2SiO_2 + N_2 + 3C \rightarrow Si_2N_2 + 3CO \quad (8)$$

Silicon carbide becomes the stable phase, if the CO partial pressure exceeds 3.5 Pa [1].

The variety of the silica carbothermal products in a nitrogen atmosphere indicates that to obtain "pure" silicon nitride with the crystalline structure desired (α or β) in substantial degrees, depends on the type of raw materials used and such technological factors as synthesis temperature, reactant ratio and dispersion of the components and atmospheric composition [1].

Until now the silicon nitride nucleation mechanism has been the least studied. It follows from the presented reactions, that SiO partial pressure determines nucleation and growth of silicon nitride particles [2]. In this work an attempt was made to analyse the mechanism of Si_3N_4 nucleation on carbon and SiO_2 interfaces.

2. Experimental procedure

Silicic acid (H_2SiO_3) and saccharose ($C_{12}H_{22}O_{11}$) were used as raw materials. The mixture was prepared by using H_2SiO_3 gel with $C_{12}H_{22}O_{11}$ water solution and further drying at 393 K. The C/SiO_2 ratio was changed from 2 to 3. Together with binary mixtures, ternary mixtures were also prepared, the third components in the latter were NH_4OH or NH_4Cl or CH_3COOH. Their content did not exceed 25 wt %. The mixtures obtained were subjected to heat treatment in a nitrogen flow in the temperature range

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473–1723 K. The exposure time at the required temperature was chosen from 30–300 min. For some samples, a two-stage heating was used, first at 672 or 873 K for 60 min and then at 1723 K for 60–300 min. The mixtures were reacted in molybdenum crucibles, filled to a depth of 5 mm. Nitrogen purity was 98% and the main impurity was oxygen ($\sim$2 wt %).

Heat-treatment product investigations were carried out using different methods. X-ray analysis was conducted using DRON-0.5 diffractometer with CuK_α-radiation. Brass was chosen as a standard. The phase content was determined by the areas of diffraction lines which were not overlapped and correspond to the phases investigated. Infrared absorption spectra were obtained using a “Specord M-80” spectrometer. Electron paramagnetic resonance spectra were recorded by a SE/x 2547 radiospectrometer on 3 cm band in air and in a vacuum ($p \sim 0.1$ Pa). To perform the quantitative measurements MgO tablet was used as a special standard; it was prepared from MgO powder with additives of Mn^{2+} ions and was fixed on the bottom of a measurement ampoule. The accuracy of measurement of the electron paramagnetic resonance (EPR) line amplitude (A) was $\pm$ 10%. Amplitude width, ΔB, was $\pm$ 30%. The relative content of paramagnetic centres was evaluated by the formula: $A = A_{sig}/(A_{st}P)$, where A_{st} is the amplitude of the hyperfine (fourth) line of the central transition of Mn^{2+} ions into MgO; A_{sig} is the amplitude of the line of a spectrum investigated; P is the sample mass. To reveal the carbon signal with $\Delta B \sim (1\text{–}3) \times 10^{-4}$ T corresponding to the formation of the aromatic regions of polyconjugation of large size during saccharose thermodestruction, measurements should be carried out in vacuum. Paramagnetic centres mentioned above are sensitive to oxygen content, which changes the relaxation characteristics of the centres. When a sample is being evacuated, the EPR signal was first registered and then disappeared, as air was bled in. This phenomenon is called the “oxygen effect”. The nitrogen content in the samples was estimated according to K’eldal method.

3. Results

3.1. X-ray studies

a) The nitride formation process during the heat treatment of the H_2SiO_3–saccharose mixture, for which $C/SiO_2 = 2$, initiates from $T_{tr} \gtrsim 1573$ K. The powders were amorphous up to this temperature. On the X-ray diffraction patterns a halo with maximum at $\theta = 9\,°$ is observed, the intensity of which decreases with increasing crystalline phase content at T_{tr} up to 1723 K (Fig. 1a). The main phases identified are β- and α-Si_3N_4 and Si_2N_2O. The total nitrogen content in the samples increases with temperature (Fig. 1b).

Increasing the exposure time at $T_{tr} = 1723$ K up to 300 min leads to the growth of α- and β-phase contents and the disappearance of silicon oxynitride. The α-Si_3N_4 content became equal to β-Si_3N_4 (Fig. 2).

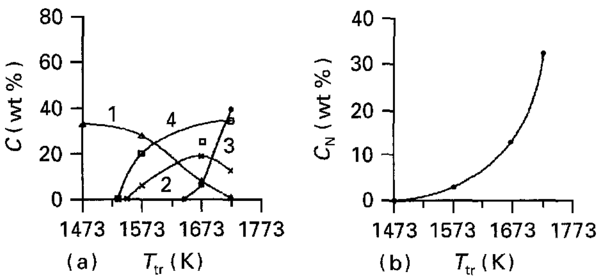

Figure 1 (a) Crystalline phase content and (b) total nitrogen content as functions of the treatment temperature of the H_2SiO_3–saccharose mixture ($C/SiO_2 = 2$) in nitrogen flow for a period of 60 min. (1) Halo, (2) Si_2N_2O, (3) β-Si_3N_4, (4) α-Si_3N_4.

The addition of acetic acid (CH_3COOH) to the H_2SiO_3–saccharose mixture did not lead to a substantial change in the α- and β-ratio. However, the dominant products are α-Si_3N_4 for the mixture with NH_4Cl additive and β-Si_3N_4 for the mixture with NH_4OH after heat treatment at 1723 K and $t_{tr} =$ 300 min (see Fig. 2). An increase of the heat-treatment time was accompanied by narrowing of the diffraction lines of the Si_3N_4 due to structure perfection and growth of the crystalline particles. It should be noted that in the temperature region of mixture treatment, there were no silica phases, according to X-ray analysis. Silicon carbide was identified only during the early stages of nitridation (around 60 min) at $T_{tr} = 1673$ K when CH_3COOH and NH_4Cl were added to the main mixture. The nitrogen content was found to be considerably more in these cases (see Figs 1b and 2e).

The use of preliminary low-temperature heat treatment did not change the ratio of α- and β-phase. From Fig. 3a it is seen that increasing preliminary heat-treatment temperature leads to a decrease in the quantity of nitride formed and an increase in the silicon oxynitride content. Carbon content in the mixtures, according to chemical analysis, changes with increasing preliminary treatment temperature from 27 wt % at $T_{pr\text{-}tr} = 673$ K to 22.9 wt % at $T_{pr\text{-}tr} = 873$ K. Thus the mixtures are characterized by different C/SiO_2 ratios, which are caused by a more intensive saccharose thermodestruction, with $T_{pr\text{-}tr}$ increasing and with the release of a greater quantity of gaseous carbon-bearing components.

b) In the samples with $C/SiO_2 = 3$, the α-phase formation was dominant (Fig. 4). At $T_{tr} = 1723$ K and $t_{tr} = 300$ min, the α-phase content was 96%. Increasing the preliminary heat-treatment temperature leads to a decrease in the quantity of β-Si_3N_4 and Si_2N_2O formed (Fig. 3b).

A comparison of α- and β-phase ratios in the mixtures with additives indicates that the use of the latter did not change the α-phase content substantially. At $T_{tr} = 1723$ K and $t_{tr} = 300$ min, the α-phase became dominant. Silicon carbide, as in the binary systems, was identified only in the early stages of the process, when NH_4Cl or CH_3COOH are added to the mixture. In this case, the α-Si_3N_4 content decreased to between 80% and 90%.

X-ray data shows that α- and β-Si_3N_4, oxynitride and silicon carbide appear practically simultaneously. When the silicon nitride content increases, oxynitride and silicon carbide contents decrease. Pure silicon nitride forms only during long heat-treatment exposures at 1723 K. Increasing the C/SiO_2 ratio is known

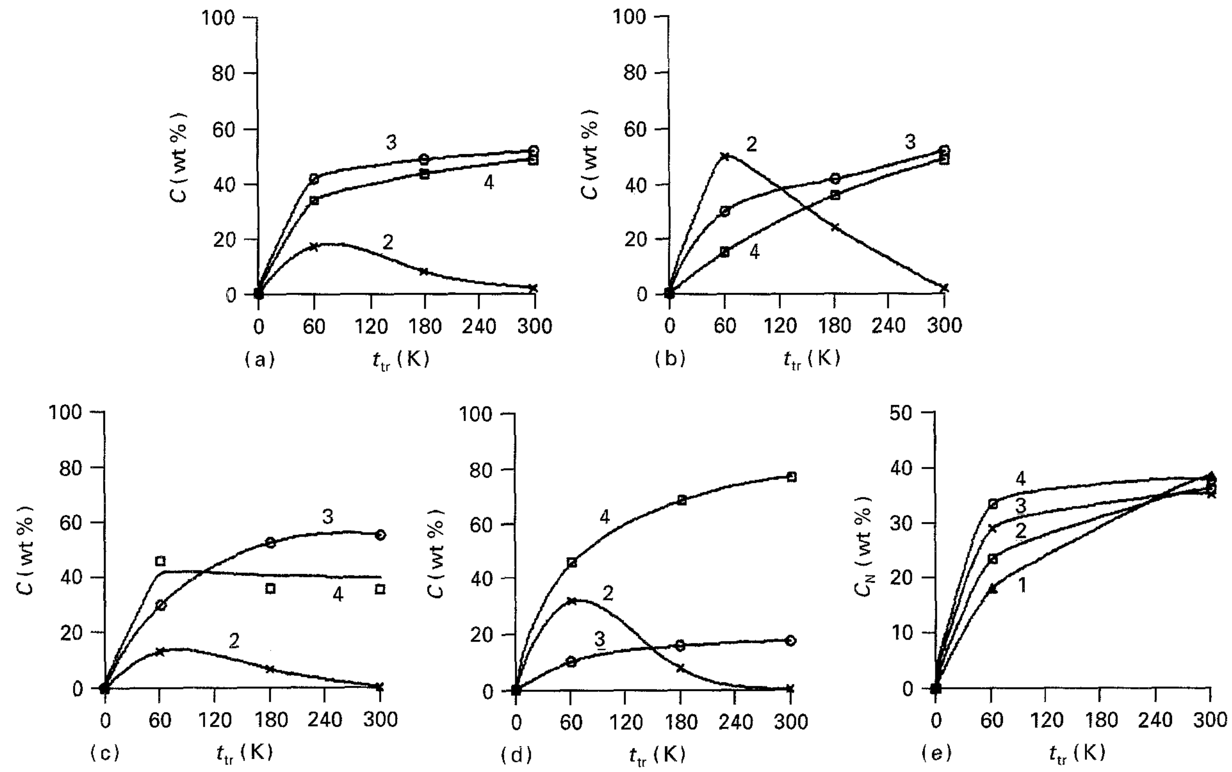

Figure 2 (a–d) Crystalline phase content and (e) total nitrogen content as functions of the nitridation time of (a) binary and (b–d) ternary mixtures in nitrogen flow at $T_{tr} = 1723$ K. Curve numbers are the same as in Fig. 1. $C/SiO_2 = 2$. (a) H_2SiO_3–saccharose, (b) H_2SiO_3–saccharose–CH_3COOH, (c) H_2SiO_3–saccharose–NH_4OH, (d) H_2SiO_3–saccharose–NH_4Cl. (e) (1) binary mixture, (2) with CH_3COOH, (3) with NH_4OH, (4) with NH_4Cl.

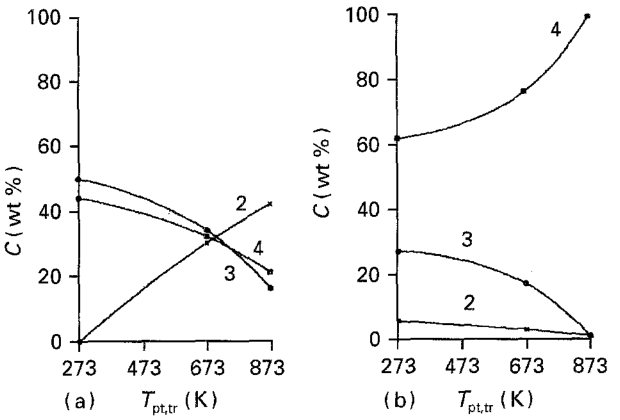

Figure 3 Crystalline phase content as function of the preliminary treatment temperature of the H_2SiO_3–saccharose mixture with (a) $C/SiO_2 = 2$ and (b) $C/SiO_2 = 3$. $T_{tr} = 1723$ K, $t_{tr} = 180$ min. Curve numbers are the same as in Fig. 1.

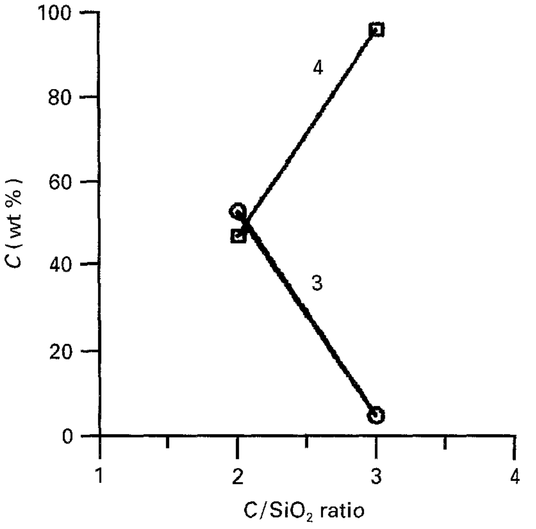

Figure 4 Crystalline phase content versus C/SiO_2 ratio in the binary system. $T_{tr} = 1723$ K, $t_{tr} = 180$ min. Curve numbers are the same as in Fig. 1.

to provide a more active silicon nitride formation [2]. Furthermore, the use of definite additives, for example NH_4Cl, for the mixtures with a small C/SiO_2 ratio was found to promote α-Si_3N_4 and Si_2N_2O formation. However, the role of such additives at a high C/SiO_2 ratio is negligible.

3.2. IR spectroscopy

a) IR absorption spectra for H_4SiO_3–saccharose mixture with a ratio $C/SiO_2 = 2$ within the region $T_{tr} = 473$–673 K (Fig. 5) indicates that vitreous silica occurs in the main phase, for which a strong band at $\nu \sim 1100\ \mathrm{cm}^{-1}$ corresponds to Si–O valence vibrations and the band at $\nu \sim 470\ \mathrm{cm}^{-1}$ corresponds to Si–O–Si deformation vibrations [8]. The appearance of duplicate indications show that a small part of silicon is present in the form of α-quartz. In all infrared spectra of the samples, exposed at temperatures below 1673 K, in the main band of Si–O–Si bonds, a shoulder is registered at $\nu \sim 960\ \mathrm{cm}^{-1}$ (Fig. 6). It can be supposed that this shoulder corresponds to the Si–O–C bonds, which formed in the early stages of carbon-component and SiO_2 production. As the temperature T_{tr} increases, the absorption lines of silica

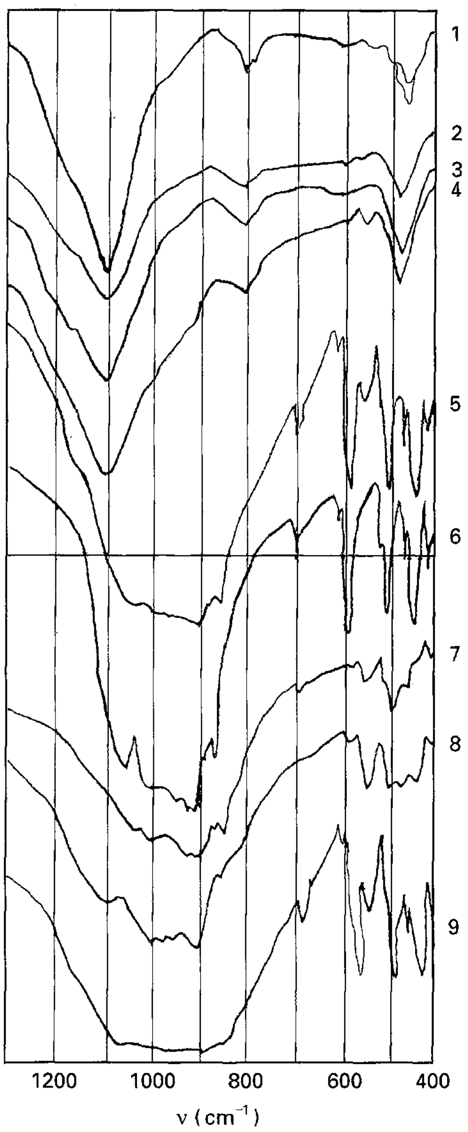

Figure 5 Infrared spectra of binary H_2SiO_3–saccharose mixtures subjected to heat treatment at (1) 473 K, (2) 873 K, (3) 1273 K, (4) 1673 K, (5) 1723 K for a period of 60 min, (6) 1723 K for a period of 300 min, and for ternary mixtures subjected to heat treatment at 1723 K for a period of 60 min, with different additives: (7) NH_4Cl, (8) CH_3COOH, (9) NH_4OH.

become wider and their intensity becomes weaker. Only in the samples obtained at 1273 K are the SiO_2 crystallization and α-quartz formation indications observed again. Furthermore, in the region of ν ~ 600 and 540 cm^{-1}, the bands, which are caused by Si–Si bonds, appear [9]. Therefore, silica regions enriched in silicon, appear.

Further widening of all SiO_2 absorption bands and an increase in shoulder intensity at ν ~ 960 cm^{-1}, which already corresponds to Si–O–N bonds (Figs 5 and 6), indicate oxynitride formation at $T_{tr} > 1473$ K. For silicon oxynitride of variable composition, the bands situated in the region from 1080–850 cm^{-1} [10, 11], are characteristic. According to these data, at $T_{tr} = 1673$ K simultaneous formation of the compounds, which can be written as $x\text{SiO}_2\ y\text{Si}_3\text{N}_4$, where $y = (88–73)\%$, occurred [10].

At $T_{tr} = 1723$ K during 60 min nitridation, the active formation of amorphous silicon nitride, α- and β-Si_3N_4, is registered (see Fig. 5, curve 5). There is no need to enumerate all the absorption bands, corresponding to the phases mentioned, in so far as they are known [12]. It should be noted, however, that formation of α- and β-phase is easy to register by using the bands with ν ~ 500 cm^{-1} and ν ~ 580 cm^{-1}, respectively. Amorphous phase availability can be judged from the width of the most intensive line, covering the range 800–1100 cm^{-1}. The phase line narrows and a number of lines appear on it with increasing exposure time. This is caused by the development of crystallization processes of nitrides (see Fig. 5, curve 6). The results obtained coincide with the X-ray data.

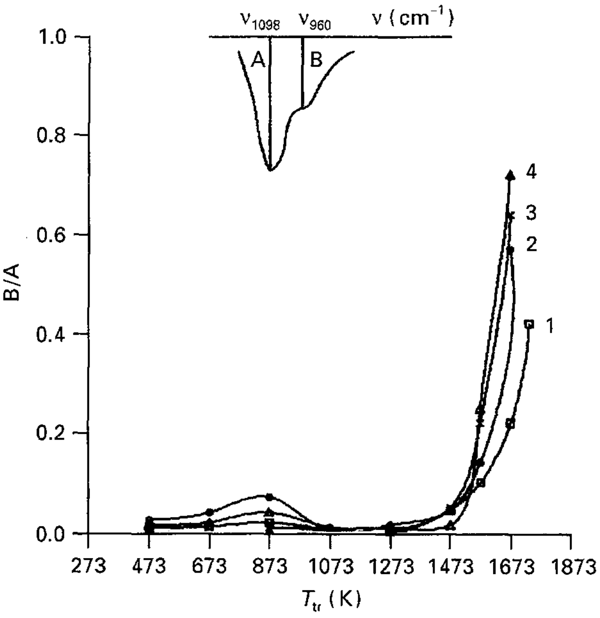

Figure 6 Ratio of IR absorption band intensity (*B*/*A*) of the samples versus treatment temperature of the mixtures (1) H_2SiO_3–saccharose, (2) H_2SiO_3–saccharose–CH_3COOH, (3) H_2SiO_3–saccharose–NH_4OH, (4) H_2SiO_3–saccharose–NH_4Cl. t_{tr}. = 60 min.

The use of additives during mixture preparation promotes the nitridation process at 1673 K (see Fig. 6). It should be noted that the silicon nitride formed at first is nearer to amorphous, as in the case of the binary system. However, when T_{tr} and t_{tr} increase, the crystalline phases are shown more clearly. All spectra of the samples obtained at 1723 K and $t_{tr} = 300$ min represent a superposition of α- and β-Si_3N_4 (Fig. 7a). The phase ratio is close to the values obtained from the data of X-ray analysis.

A characteristic feature of the spectra of all the samples, obtained up to 1573 K from ternary mixtures, is the increase in shoulder intensity at ~ 960 cm^{-1} in comparison with the value of the latter for the binary system. The formation of Si–O–C bonds is most active in the case of adding CH_3COOH or NH_4Cl (see Fig. 5). Silica is present in the vitreous condition. It should be noted that the high values of the *B*/*A* ratio at $T_{tr} = 1673$ K (Fig. 6, curves 3, 4) were also caused to some degree by the creation of Si–O–C bonds. The values of *A* and *B* correspond to the intensities of the absorption band at ν ~ 1098 cm^{-1} and to the shoulder at ν ~ 950–960 cm^{-1} (see Fig. 6).

Preliminary low-temperature heat treatment changes to some degree the ratio of α- and β-phases in the silicon nitride, but increases a part of the amorph-

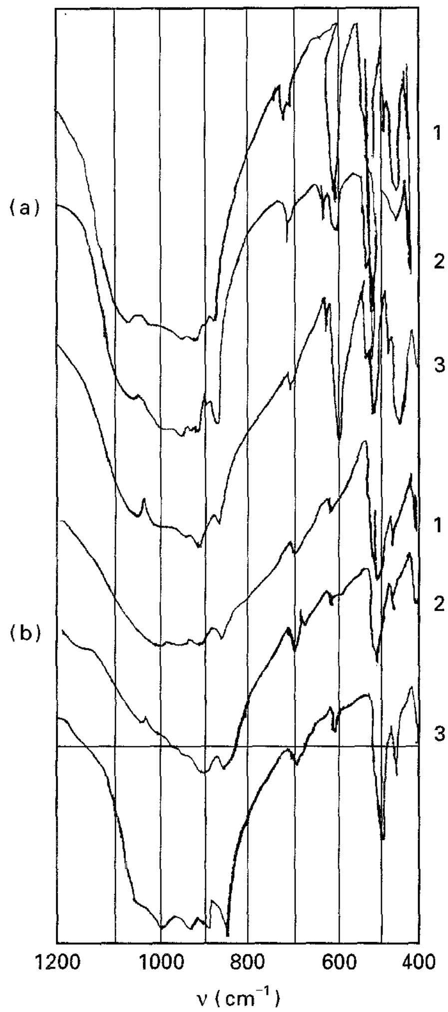

Figure 7 Infrared spectra of Si_3N_4 produced from H_2SiO_3–saccharose mixtures with ratio of (a) $C/SiO_2 = 2$ and (b) $C/SiO_2 = 3$, which contain (1) NH_4OH, (2) NH_4Cl, (3) CH_3COOH, $T_{tr.} = 1723$ K, $t_{tr} = 300$ min.

ous component. The latter is revealed by a widening of the main (fundamental) absorption line in the region 1100–800 cm^{-1} (Figs 5 and 8).

b) In the samples synthesized from mixtures with a ratio of $C/SiO_2 = 3$, an increase in the absorption lines, which correspond to the α-phase of Si_3N_4, is clearly observed. Preliminary low-temperature heat treatment acts in the same direction (Fig. 8, curves 4–6). Addition of NH_4Cl and NH_4OH to such a mixture increases the content of amorphous Si_3N_4 (Fig. 7b, curves 1, 2). However, for the mixtures with acetic acid, α-Si_3N_4 crystallization is observed.

Using IR spectroscopy data one can conclude that the nitride formation process includes a series of transformations: disordered $SiO_2 \rightarrow SiO_2$, defective in oxygen → silicon oxynitride → amorphous Si_3N_4 and then its crystallization. A substantial increase in the α-Si_3N_4 content can be achieved either by increasing the C/SiO_2 ratio, or by using additives in the mixtures with a low content of carbon. The first conclusion correlates with the data of Zhang and Cannon [2].

Noted features of silica crystallization indicate the existence of microregions in which the common transformation process of amorphous SiO_2 to α-quartz occurs, although at low temperatures.

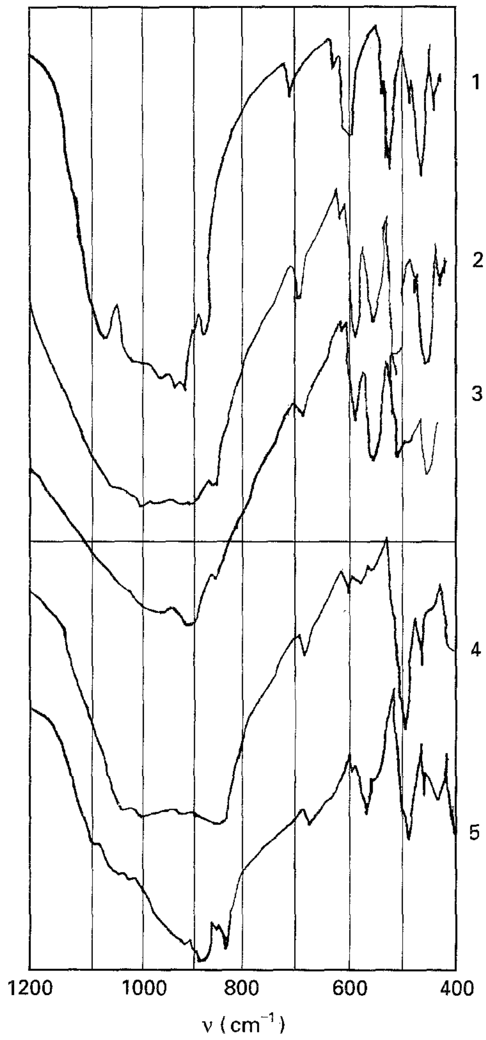

Figure 8 Infrared spectra of Si_3N_4 produced from the mixtures with ratio of (1–3) $C/SiO_2 = 2$ and (4, 5) $C/SiO_2 = 3$ at $T_{tr.} = 1723$ K, $t_{tr} = 300$ min and with different types of preliminary treatment: (1) without preliminary treatment: (2, 4) $T_{pr\cdot tr\cdot} = 673$ K; $T_{pr\cdot tr\cdot} = 873$ K.

X-ray analysis and infrared spectroscopy data allow us to suppose that the use of additives and preliminary low-temperature heat treatment change the properties of the carbon component which is formed during thermodestruction of saccharose [13].

3.3. EPR

To elucidate the features of the saccharose thermodestruction process and carbon formation, the EPR method was used. The usefulness of the EPR method lies in the fact that it enables one to follow the processes of nucleation, coarsening and ordering of two-dimensional carbon structures, that form and transform during destruction of an organic substance on the stage when the X-ray method does not give unambiguous information. The way in which carbon structure formation and crystallite nucleation occur may be judged on the basis of following indications: the magnitude of the spectroscopy splitting factor (the *g*-factor), the EPR line width (ΔB) and its intensity, and the proportional concentration of paramagnetic centres. It was revealed that during H_2SiO_3–saccharose heat treatment, aromatic regions of polyconjuga-

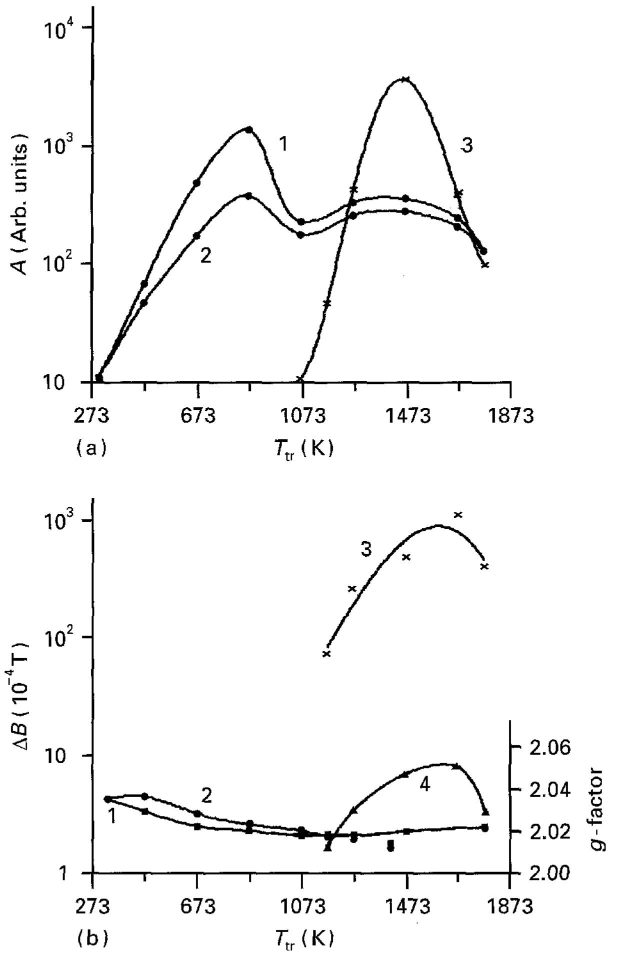

Figure 9 (a) Amplitude and (b) width of resonance signals versus treatment temperature of H_2SiO_3–saccharose treatment for measurement (1) in vacuum (0.1 Pa), (2) in air, (3) in a vacuum and in air, (4) g-factor value of signal (3).

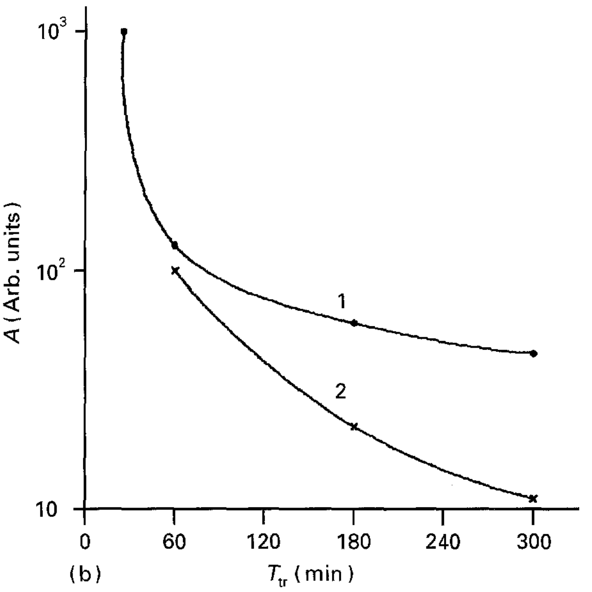

Figure 10 Amplitude of (1) narrow and (2) wide carbon resonance signals versus exposure time of the samples at 1723 K. Measurement was conducted in vacuum and in air.

tion (ARP) of small size were formed first, followed by their coarsening. This process has been studied and well described [14–17]. Saccharose thermodestruction is characterized by the appearance of "carbon" EPR signals, attributed to uncoupled π-electrons, delocalized from polyconjugation regions. The g-factor is close to value of 2.0025 ± 0.0002. For ARP of small size, the width of the resonance line (ΔB) is about $(9–6) \times 10^{-4}$ T, for an ARP of a larger size the latter is $(3–1.5) \times 10^{-4}$ T. The registering of the EPR lines only for the samples under vacuum, or "oxygen effect", is typical for the latter (Fig. 9). The "oxygen effect" enables one to follow the growth of ARP (growth of the size of two-dimensional carbon forms) and to separate ARP of large size from ARP of small size, which are still present in the carbon material. Thus, the EPR signal corresponds to an ARP of small size only during measurement in air. Intensity increment and growth of the EPR signal amplitude is proportional to the content of ARP of large size during registering in a vacuum. Beginning from $T_{tr} > 1073$ K, a third wide signal appeared in the spectrum. Its amplitude (A), g-factor and ΔB increase with increasing heat-treatment temperature up to 1473 K (see Fig. 9a, b, curves 3, 4). Such a picture is characteristic for the development of carbon structure with three-dimensional ordering: lamella formation and microcrystallite nucleation [18–20]. At the same time, the weakening of the resonance signal at $T_{tr} > 1473$ K with its simultaneous narrowing and shifting of the g-factor to small values, and also the constant presence of a narrow EPR signal, are attributed to the active development of the transformation process of the ordered carbon structural forms (microcrystallites) into two-dimensional structures (ARP of large size [20, 21]). The disappearance of the "oxygen effect" for such newly generated paramagnetic centres indicates that they are "screened" by the outer atmosphere. A similar picture was observed during SiC synthesis from SiO_2–C mixtures in an argon flow [19–21].

When the heat-treatment time increases above 60 min at 1723 K, the wide signal narrows and disappears and the narrow signal with $\Delta B \sim (3–9) \times 10^{-4}$ T decreases insignificantly (Fig. 10). Paramagnetic centres remain insensitive to the outer atmosphere, although such centres are characterized by the "oxygen effect". Firing of the powders in air at 1073 K for 60–120 min does not eliminate the carbon signal. If carbon is in the form of separate free inclusions, it should be oxidized at this temperature. On the basis of these factors, one can conclude that Si_3N_4 particles contain carbon, which is presented in the form of ARP of different size. It should be noted that widening of the narrow EPR signal from ARP of large size (for which ΔB changes not from 1 to 3×10^{-4} T, but from 3 to 9×10^{-4} T) with increasing T_{tr} (see Fig. 9, curve 2) can be explained by silicon atom implantation into the carbon structure and by variations in relaxation characteristic of carbon paramagnetic centres.

The use of additives during mixture preparation changes the reconstruction process of the carbon component. This is revealed by width changes in the EPR lines especially in the wide resonance signal (Fig. 11). In comparison with the binary system (see Fig. 9b, curve 3) ΔB of the wide line does not achieve high

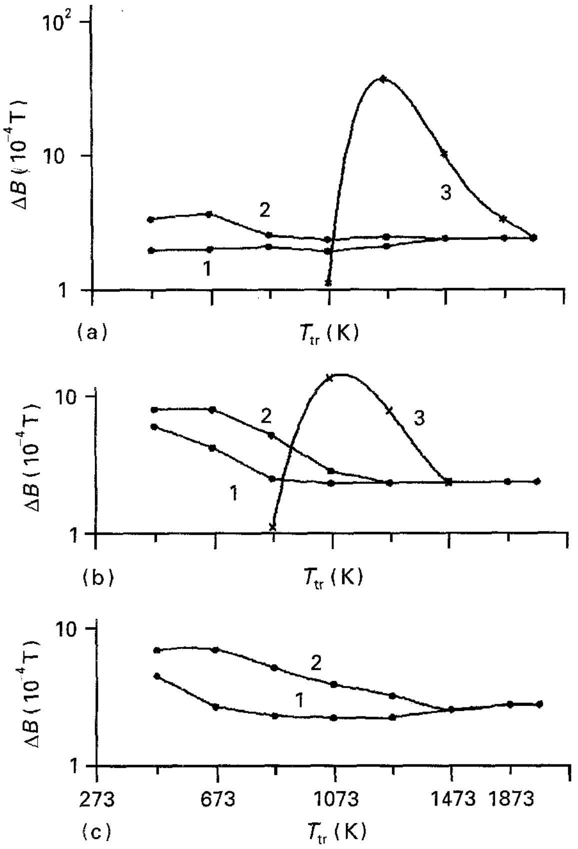

Figure 11 Resonance signal width versus treatment temperature of the H_2SiO_3–saccharose mixtures with additives: (1) NH_4OH, (2) CH_3COOH and (3) NH_4Cl. $t_{tr} = 60$ min at measurement (1) in vacuum, (2) in air, (3) in vacuum and in air.

values. Therefore, the process of three-dimensional ordering is prevented by the use of additives. The most disordered carbon structural forms are attributed to the use of NH_4Cl as an additive. The degree of ordering increases in the order $NH_4Cl \rightarrow CH_3COOH \rightarrow NH_4OH$. For Si_3N_4 particles, obtained at 1723 K and $t_{tr} = 300$ min, a signal is registered from ARP of different size. In the samples with ARP of larger size (the amplitude and width are greater), the α-Si_3N_4 content is higher (see Table I and Fig. 2).

An increase in the saccharose content of the mixture ($C/SiO_2 = 3$) does not, in principle, change the hypothesis about the formation and three-dimensional ordering, or about the destruction of the carbon component. As in the case of the mixtures with $C/SiO_2 = 2$, Si_3N_4 particles contain a carbon nucleus. However, it represents more ordered carbon structural forms, than ARP. Apparently, they consist of "fragments" of microcrystallites and carbon lamellae. Orientation effects in such structural forms lead to the appearance of a resonance line of complex form, which may be represented as a superposition of differently oriented lines (see Table I).

The use of additives during preparation of the H_2SiO_3–saccharose mixture with $C/SiO_2 = 3$ leads to some change of the carbon nucleus "condition" in the silicon nitride particles obtained at 1723 K, $t_{tr} = 300$ min. The α-Si_3N_4 content is higher when the "orientation effect" is observed more clearly. It seems that α-phase forms on the larger carbon structural forms more actively than on ARP of especially small size.

As it can be seen from Figs 9 and 11, low-temperature preliminary treatment at 673 and 873 K for any SiO_2–C mixture leads to the formation of carbon components, the properties of which differ to some degree. Further, this difference influences the efficiency of the silica carbothermal reduction.

It follows from EPR data that for the carbon component formed during saccharose thermodestruction, ARP consolidation and microcrystallite growth are characteristic. The addition of NH_4Cl, CH_3COOH and NH_4OH prevents this process and leads to an increase of the component contact area (SiO_2 and C). Such an effect is also achieved by increasing the C/SiO_2 ratio. The disappearance of the "oxygen effect" for ARP destruction of the carbon microcrystallites with simultaneous formation of new ARP of different sizes, together with infrared spectroscopy data, indicate that SiO_2 reduction initiates in the regions with carbon particles of high activity from the formation of Si–O–C bonds, gradual destructive "enveloping" of carbon microparticles by the product of partial SiO_2 reduction, and then formation of Si–O–N bonds. From a comparison of X-ray analysis and EPR data, it follows that α-Si_3N_4 forms when a large carbon nucleus is present on the Si_3N_4 particle. β-Si_3N_4 is obtained when a two-dimensional structural form or, especially, ARP of small size, is predominant.

4. Discussion

As mentioned above, the fundamental reactions of nitride formation are reactions of gas–gas and gas–solid, where SiO, CO and N_2 are the reagents of the interaction. The presence of Si_2N_2O and SiC

TABLE I EPR carbon signal parameters in Si_3N_4 particles, produced at 1723 K, $t = 300$ min

Additive	$C/SiO_2 = 2$		$C/SiO_2 = 3$		
	I (Arb. units)	ΔB (10^{-1} T)	I (Arb. units)	ΔB (10^{-1} T)	
Without additive	90	6	1000	binary line $\Delta B_1 = 14$	$\Delta B_2 = 8$
NH_4OH	100	7	240	14	6
CH_3COOH	340	9	220	12	5
NH_4Cl	binary line 620	$\Delta B_1 = 14$ $\Delta B_2 = 8$	960	16	9

in some samples, synthesized at 1673–1723 K and $t_{tr} \sim 60$ min, reveal the value of mixture gas permeability in nitrogen flow changes [1, 2]. The disappearance of silicon carbide with increasing heat-treatment time is attributed to the interaction of SiC with SiO_2. As far as the velocity of a given reaction depends on the CO partial pressure [7], it can be supposed that in mixtures with a lower pressure, SiC cannot reliably be identified by the X-ray technique, owing to the great velocity of the interaction of oxide with carbide and the small quantity of the latter. It seems that the absence of an absorption band of Si–C bonds in the infrared spectra and the registering of Si–O–C bonds, are caused by the fact that SiC is screened by the layer of reduced SiO_2.

The decrease in the Si_2N_2O content during prolonged heat treatment in a nitrogen flow at 1723 K can also be explained by interaction with silicon carbide, but the reaction $Si_2N_2O + SiC + N_2 \rightarrow Si_3N_4 + CO$ is formal.

Consider the mechanism of Si_3N_4 formation with the participation of the reactions solid–solid–N_2 gas. All the data obtained reduce further the picture of SiO_2 carbothermal reduction and Si_3N_4 nucleation.

The technique of mixture preparation by the mixing of H_2SiO_3 and $C_{12}H_{22}O_{11}$ in water, supposes a high degree of homogeneity of SiO–C in the mixture. However, indications revealing crystallization in the silica subsystem and three-dimensional ordering in the carbon subsystem, show that the SiO_2–C mixture is not microhomogeneous. It represents a mixture of silica and carbon aggregates, inside which the processes of ordering–crystallization occur during heat treatment. It should be noted that the hypothesis about interacting aggregates of SiO_2 and carbon with complex porous structure allows us to explain the inhomogeneity of the nitrogen flow, not only by the dependence upon the size of filling, but also by its different movement features inside the different layers.

SiO_2 reduction initiates in the contact region of silica and carbon aggregates in the microhomogeneous mixture during heat treatment in the region 1000–1473 K. This is why in the infrared spectra the intensity of the absorption band attributed to Si–O–C bonds increases and the Si–Si bonds band appears. The latter is attributed to the oxygen depletion of silica and the production of a highly defective layer, for instance SiO_x, where $x < 2$. The appearance of Si–O–C and Si–Si bonds is accompanied by the disappearance of the "oxygen effect". An insignificant increase in the amplitude of the EPR signal from ARP development of three-dimensional ordering in the carbon subsystem, allowed it to be concluded that silica reduction is prevented up to 1473 K, and that the carbon structure microforms which appear are not in contact with the outer atmosphere. The mechanism of such screening was observed elsewhere [19]. It supposes the "envelopment" of carbon particles by silica due to the breaking of Si–O–Si bonds and the formation of Si–O–C and Si–C bonds.

At $T_{tr} > 1473$ K the process of silica reduction becomes more active. In this case the activation–destruction of carbon-ordered microregions (microcrystallites) and aggregates occurs as a result of evolution of the gaseous products of the reaction of SiO_2 and carbon, namely SiO_2, CO and CO_2. Activation–destruction proceeds, as discussed elsewhere [19], according to the radical self-activation mechanism. The intensity of the Si–O–C and Si–Si bands, and subsequently Si–O–N bands, increases. At $T_{tr} = 1723$ K ($t_{tr} = 60$ min) the "oxygen effect" for carbon paramagnetic centres disappears entirely. The appearance of silicon oxynitride and silicon nitride, and some quantity of silicon carbide is observed on the infrared spectra and X-ray diffraction patterns. At a given temperature, part of the nitride, undoubtedly, can form due to participation of source gaseous products. However, the formation of Si–Si, Si–O–Si and subsequently Si–O–N bonds allows it to be supposed that nucleation of not only silicon carbide, but silicon oxynitride and silicon nitride as well, occurs in the region of silicon reduction. The formation of silicon carbide should be the most preferable in the SiO_2 and carbon contact region. In reality it takes place during mixture treatment in a vacuum, and at higher temperatures in an argon flow as well. However, SiC is found in powders investigated only after a small heat-treatment time at 1723 K.

Now consider the mechanism of Si_3N_4 formation in the components contact region and the factors preventing SiC formation. With this end in view, the SiO_2 and carbon contact region at 1723 K should be observed. It is enriched by silicon and transforms into SiO_x, where $x < 2$, as a result of component interaction. The temperature for such a state is the temperature of softening and melting [22]. It is clear that the "oxygen effect" disappears and the SiO_2 reduction process becomes very active. Nitrogen diffuses into a thin oxygen-defective layer (film) of the melt. As the process develops, silicon oxynitride and, subsequently, silicon nitride form. Depending on the content of nitride phases and melt quantity, the former will be either amorphous or crystalline. These centres of crystallization should be considered as nuclei of the nitride phase.

Taking into account that at 1723 K, simultaneously with nitridation, the destruction–activation of carbon particles, active gas volatilization and hence, intermixing of the components and an increase of mixture porosity occur, the contact area of the components (SiO_2 and carbon) and mixture gas permeability, continuously increase. This leads to the entire completion of the nitride formation reaction with increasing nitridation time.

"Second-step" carbon microparticles–fragments, as well as the initial aggregates, may be of different size. If they are large enough, the silicon nitride formed on them would be present as the α-phase. β-Si_3N_4 must form on the ARP of small size, or in the absence of carbon nucleus. The given conclusion is close to the observation of α-Si_3N_4 formation in the presence of silicon and impurities [23]. Undoubtedly, α- and β-Si_3N_4 can form according to other mechanisms.

Conclusions about interacting aggregates lead to an understanding of the action of a number of additives and the influence of preliminary low-temperature heat treatment of the mixtures. In essence, they change the size of the carbon aggregates and the component contact area. When additives promote an increase of the SiO_2 and carbon contact area, which is equivalent to increasing the C/SiO_2 ratio, for example by adding NH_4Cl, the α-Si_3N_4, silicon oxynitride and silicon carbide contents are higher after the first hour of nitridation, as compared with those obtained using NH_4OH, or without the use of additives at all.

5. Conclusion

The investigation of nitride formation during SiO_2 carbothermal reduction shows that the use of a solution technique for the preparation of SiO_2–C mixtures does not ensure their microhomogeneity. In reality, the initial system is a mixture of silica and carbon aggregates. Increasing the mixture microhomogeneity can be achieved by the use of additives or preliminary heat treatment, changing the character of saccharose thermodestruction and preventing the coarsening of the carbon particles. This is equivalent to a C/SiO_2 ratio increase. Furthermore, increasing the C/SiO_2 ratio promotes the growth of α-Si_3N_4 and Si_2N_2O contents. The region of SiO_2 reduction, in which a fusible layer of SiO_x type, where $x < 2$, forms, is localized at the places of silicon nitride nucleation. When it is incorporated in such a highly defective layer, β-Si_3N_4 forms on two-dimensional carbon particles, whilst α-Si_3N_4 forms on the larger ones (with elements of three-dimensional ordering).

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