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Constitution of the γ-Alumina Phase in Chemically Produced Mullite Precursors

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Abstract

The temperature development of type II mullite precursor powders have been studied in the temperature range of 150°C (as-received) and 1150°C. X-ray diffraction (XRD) measurements, infrared (IR) and ^{29}Si and ^{27}Al nuclear magnetic resonance (NMR) spectroscopy and analytical transmission electron microscopy (ATEM) have been performed on the heat-treated precursors. The investigations had the aim of contributing to the frequently discussed question, whether Si is incorporated into the γ-alumina spinel being formed as a transient phase in type II mullite precursors.

The as-received precursors consist of relatively large sperical particles (≤ 0·5 μm) of non-crystalline SiO_2 and of much finer-grained agglomerates of pseudo-boehmite crystals (γ-AlO(OH), ≈20 nm), which are embedded in a SiO_2 matrix. Above ≈350°C, pseudo-boehmite transforms to spinel type alumina (γ-Al_2O_3). During this transformation, all Si existing in the SiO_2 matrix of the pseudo-boehmite agglomerates is incorporated into γ-Al_2O_3 corresponding to a SiO_2 content of ≈12 mole% at 500°C. Up to 750°C, the SiO_2 content of the γ-alumina remains constant but above this temperature it gradually rises and reaches a maximum amount of ≈18 mole% at 1150°C. A marginal decomposition of the spherical non-crystalline SiO_2 particles may be the sources to provide diffusion of Si species into the γ-alumina during a temperature increase above 750°C. It is most likely that Si species diffuse into the γ-alumina crystals along the crystallite boundaries. The diffusion process and Si incorporation are facilitated with the temperature increase.

Die temperaturabhängige Phasenentwicklung von Typ II Mullit-Precursorpulvern wurde im Temperaturbereich zwischen 150°C (as-received) und 1150°C untersucht. Röntgenbeugungsuntersuchungen (XRD), Infrarotspektroskopie (IR), ^{29}Si und ^{27}Al Kernspinresonanzmessungen (NMR) und analytische Transmissionselektronenmikroskopie (ATEM) wurden an den wärmebehandelten Precursoren durchgeführt. Ziel der Untersuchungen war es, zu der häufig diskutierten Frage beizutragen, ob Si in den γ-Aluminiumoxid-Spinell eingebaut wird, der sich als Übergangsphase in Typ II Mullit-Precursoren bildet.

Die ungetemperten Precursoren enthalten relativ große kugelförmige Partikel (≤ 0·5 μm) aus nichtkristallinem SiO_2 und wesentlich feinkörnigere Agglomerate von Pseudoböhmit-Kristallen (γ-AlO(OH), ≈20 nm), die in eine SiO_2-Matrix eingebettet sind. Oberhalb ≈350°C wandelt sich der Pseudoböhmit um in ein Aluminiumoxid vom Spinelltyp (γ-Al_2O_3). Während dieser Umwandlung wird alles Si, das in der SiO_2-Matrix der Pseudoböhmit-Agglomerate vorhanden ist, in das γ-Al_2O_3 eingebaut, entsprechend einem SiO_2-Gehalt von ≈ 12 Mol% bei 500°C. Bis 750°C bleibt der SiO_2-Gehalt des γ-Aluminiumoxids konstant, aber oberhalb dieser Temperatur nimmt er graduell zu und erreicht einen Maximalwert von ≈ 18 Mol% bei 1150°C. Eine geringfügige Zersetzung der kugelförmigen nichtkristallinen SiO_2-Partikel könnte eine mögliche Quelle sein für die Diffusion von Si-Spezies in das γ-Aluminiumoxid während des Temperaturanstiegs oberhalb 750°C. Es ist sehr wahrscheinlich, daß die Si-Spezies entlang der Kristallitgrenzen in die γ-Aluminiumoxid-Kristalle

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hineindiffundieren. Diffusionsprozeß und Si-Einbau finden mit steigender Temperatur begünstigt statt.

L'évolution avec la température de précurseurs de la mullite du type II a été étudiée dans un domaine de température s'étalant de 150°C (poudre non traitée telle que reçue du fournisseur) à 1150°C. Des mesures par diffraction RX, spectroscopie infrarouge, spectroscopie par résonance magnétique nucléaire du ^{29}Si et ^{27}Al et microscopie électronique äl transmission analytique ont été réalisées sur les précurseurs ayant subi un traitement thermique. Ces études ont pour but d'essayer d'apporter une réponse à la question fréquemment discutée selon laquelle le silicium est incorporé dans l'alumine à structure spinelle formée en tant que phase transitoire dans les précurseurs de la mullite du type II.

Les précurseurs reçus tels quels consistent en des particules sphériques, relativement larges ($\leq 0{\cdot}5$ μm) de SiO_2 non cristallin et d'agglomérats de grains plus fins de pseudo-boehmite (γ-$AlO(OH)$, ≈20 nm) inclus dans une matrice de SiO_2. Au-dessus de ≈350°C, la pseudo-boehmite se transforme en alumine du type spinelle (γ-Al_2O_3). Durant cette transformation tout le silicium, issu de la matrice de SiO_2 comprenant les agglomérats de pseudo-boehmite, est incorporé au sein de l'alumine γ et il en résulte à une teneur en SiO_2 d'environ 12% molaire à 500°C. Jusqu'àl 750°C, la teneur en SiO_2 de l'alumine γ reste constante mais au-dessus de cette température elle augmente graduellement et atteint un maximum d'environ 18% molaire à 1150°C. Une décomposition marginale des particules sphériques de SiO_2 non cristallin pourrait constituer la source des espèces Si et permettre ainsi leur diffusion au sein de l'alumine γ durant l'augmentation de température au-dessus de 750°C. Il est plus que probable que les espèces Si diffusent dans les cristaux d'alumine γ le long des surfaces des cristallites. Le processus de diffusion et l'incorporation de Si sont alors facilités avec l'augmentation de température.

1 Introduction

The mullite formation process has been the subject of many studies over 30 years, beginning with the research on solid-state reactions and mechanisms that take place on heating kaolinite.[1-3] Kaolinite transforms to metakaolin at about 550°C, the latter decomposes near 950°C to a spinel-type structure, free silica and some minor amount of mullite. The composition of the transient spinel-type phase is still a subject of controversy: it is assumed to be pure γ-Al_2O_3[4-6] as well as a Si-rich Al_2O_3-spinel.[3,7]

Recently considerable research efforts have been concentrated on the description of the chemical composition of spinel-type alumina formed as transient phases in chemically produced mullite precursors. Among many studies investigating various routes of mullite precursor synthesis, one can summarize that there are three main types of mullite precursor,[8-10] independent of the starting materials and the synthesis method. Mullite forms as the first and only crystalline phase by an exothermic reaction at about 980°C from an initially amorphous precursor (type I); or γ-alumina forms as the first and only crystalline phase by an exothermic reaction at about 980°C from an initially amorphous phase (type III); or spinel forms between about 350° and 500°C from pseudo-boehmite which was initially present in the as-received precursor (type II).[8] Mullite crystallizes at about 1250°C from the spinel phase by an exothermic reaction.

Despite many studies, the controversy about the composition of the spinel-type-phase formed in the chemically derived mullite precursors still continues. In mullite precursors with an extreme phase segregation into alumina and silica rich regions, the presence of SiO_2 in the spinel phase has been rejected.[11-13] Therefore it was believed that mullitization at ≈1250°C should be the result of a reaction between pure γ-Al_2O_3 and SiO_2 phases in the diphasic (type II) gels.[11-13] Similarly Komarneni and Roy[14] deduced that the spinel-phase was essentially aluminium oxide, based on the apparent absence of the respective signals in the ^{29}Si MAS NMR spectrum for the diphasic mullite gels heat-treated at 1000°C. Okada and Otsuka[15] carried out research for characterization of the spinel phase on the various compositions of SiO_2 and Al_2O_3 ranging between $20Al_2O_3/80SiO_2$ and $100Al_2O_3$ (mole%) and in three different types of mullite precursors (SH = type I+III, RH = type III, NM = type II). Evaluation of the lattice parameters of the spinel phase with temperature showed that the *a*-lattice constant of spinel in the RH precursors decreases significantly between 900° and 1000°C. Because the lattice parameters of the spinel phase vary with the chemical composition as well as with the synthesis and heat-treatment conditions, it could not be decided whether this effect was caused by incorporation of silicon into the spinel phase. Further investigations on the same precursors with analytical transmission electron microscopy (ATEM) analysis demonstrated that the transition γ-alumina contains SiO_2 over a compositional range of 8–18 wt. %. Okada and Otsuka[15] also compared the infrared (IR) spectra of pure γ-Al_2O_3 and the spinel phases in the NM-type II and RH-type III precursors at

≈900°C and found that the IR spectra of the precursors contain two additional absorption bands which do not appear in the spectrum of γ-Al_2O_3. Wei and Halloran[16] investigated the mullite formation in diphasic gels and reported that the transition alumina with a nearly cubic spinel structure was to be virtually pure alumina and no evidence for a silicon incorporation was found by ATEM microanalysis. Low and McPherson[17] compared the Si-O-Si stretching modes of the leached aluminosilicate gels in the IR spectra with that of pure γ-Al_2O_3 and suggested that the spinel phase contains silicon and that the aluminium silicon spinel has nearly the same composition as 2/1-mullite, i.e. $SiAl_4O_8$ or more specifically is $\square_4Al_{12}{}^{VI}[Al_4Si_4]^{IV}O_{32}$ ($\square$ = vacancy). Low and McPherson[17] supposed the exothermic effect observed at ≈980°C to be due to the enthalpy release, caused by liberation of amorphous SiO_2 during the spinel formation with the 2/1-mullite composition. Recently Srikrishna *et al.*[18] confirmed that spinel is an aluminium silicon phase and possesses a chemical composition close to that of 3/2-mullite ($Si_3Al_6O_{13} = 3Al_2O_3 . 2SiO_2$).

The aim of this study is to contribute in the understanding of the constitution of the γ-alumina spinel phase resulting from type II mullite precursors, by using the evidence obtained from XRD, IR, MAS NMR and ATEM observations.

2 Sample synthesis

The mullite precursors investigated were prepared by admixing alcoholic solutions of tetraethoxysilane (TEOS) and aluminium *sec*-butylate (AlOBu) in proportions corresponding to stoichiometric mullite ($3Al_2O_3.2SiO_2$). In order to achieve phase segregation, TEOS was prehydrolysed by the addition of deionized water under strongly basic conditions (pH = 13). The molar ratio H_2O/TEOS has been kept as 26/1. After allowing a short time (10 min) for condensation and polymerization, the silica sol was put into the AlOBu solution which was prepared by only diluting with isopropanol alcohol. Upon mixing, the sol mixture gelled immediately and the derived gel was dried at 150°C, yielding a free-flowing powder. The DTA pattern of the as-received powder exhibits only a broad peak of low intensity at about 1250°C. According to the classification schemes used by Okada and Otsuka[15] and by Schneider *et al.*[8] the precursor is of type NM or II, respectively. The as-received powder was calcined individually at 350°, 500°, 600°, 750°, 900°, 1100°, 1150°, 1200° and 1300°C for 15 h and at 1650°C for 2 h. For leaching of the amorphous SiO_2-rich phase, the pre-calcined powders were treated in cold or boiling 1 N NaOH solution for 20 min. Subsequently they were filtered and washed with distilled water prior to drying.

3 Characterization techniques

X-ray powder diffraction studies were carried out with a computer-controlled Siemens D5000 powder diffractometer using Ni-filtered $Cu_{K\alpha}$-radiation. Diffraction patterns were recorded in the 10– 80°, 2θ-range, in step scan mode (3 s/ 0·02°, 2θ).

All ^{27}Al and ^{29}Si MAS NMR spectra were obtained on a Bruker MSL 300 NMR spectrometer at 78·2 MHz (^{27}Al) and at 59·6 MHz (^{29}Si), respectively. Also 4 mm (^{27}Al) and 7 mm (^{29}Si) o.d. ZrO_2-rotors were used, the spinning frequencies were 7–9 kHz (^{27}Al) and 4 kHz (^{29}Si). Chemical shifts are given with respect to external TMS (^{29}Si) and dilute aqueous $AlCl_3$, the latter ^{27}Al chemical shifts are uncorrected for second order shifts. Pulse widths of $\pi/12$(^{27}Al) and $\pi/4$ (^{29}Si) were used; in the case ^{29}Si recycle delays of 30 s were necessary.

Transmission electron microscopy (TEM) and microanalyses were performed with a Philips EM 430 analytical microscope (300 kV accelerating voltage, LaB_6 filament) equipped with a TRACOR system for energy dispersive X-ray spectroscopy. TEM sample preparation was performed by deposition of the suspended powders on a carbon film.

Infrared (IR) spectra were recorded with a Beckman photospectrometer 4220 in the wavenumber range of 4000–200 cm^{-1}. About 2 mg of the sample was finely powdered together with 200 mg RbI. The powder mixture was pressed into tablets 13 mm in diameter and about 1 mm thick at a pressure of 10 kbar. RbI was chosen because of its extended transmission range as compared to KBr or KI.

4 Results

4.1 X-ray diffractometry

Selected X-ray diffraction (XRD) patterns of heat-treated mullite precursors (Table 1) are shown in Fig. 1. The as-received samples display weak and broad diffraction peaks of pseudo-boehmite (γ-AlO(OH)). The mullite precursor, heat-treated at 350°C contains pseudo-boehmite and some low amounts of transition alumina (γ-Al_2O_3). Higher annealing temperatures up to 1150°C yield XRD peaks of γ-alumina spinel (γ-Al_2O_3) only. With increasing temperature, the XRD peaks of γ-Al_2O_3 become sharper and more intense. Simultaneously X-ray reflections have the tendency to split. (The

Table 1. Investigations carried out on mullite precursors heat-treated at different temperatures

Annealing temperature (°C)	*XRD*		*IR*		*NMR*				*TEM*			
					^{29}Si		*^{27}Al*		*Micro-structural observation*		*EDX*	
	NL	*L*	*NL*	*L*	*NL*	*L*	*NL*	*L*	*NL*	*L*	*NL*	*L*
As-received	×	—	—	—	—	—	—	—	×	—	—	—
350	×	—	—	—	×	—	—	—	×	—	×	×
500	×	—	—	—	—	—	—	—	×	×	×	×
600	×	—	—	—	—	—	—	—	×	—	×	—
750	×	—	—	—	—	—	—	—	×	—	×	—
900	×	—	×	×	×	×	—	—	×	—	×	—
1 000	×	—	×	×	×	×	—	—	×	—	×	×
1 100	×	—	×	×	×	×	×	×	×	—	×	×
1 150	×	—	—	—	—	—	—	—	×	—	×	×

XRD, X-ray diffractometry; IR, infrared spectroscopy; NMR, solid state nuclear magnetic resonance; TEM, transmission electron microscopy; NL, not-leached; L, NaOH-leached.

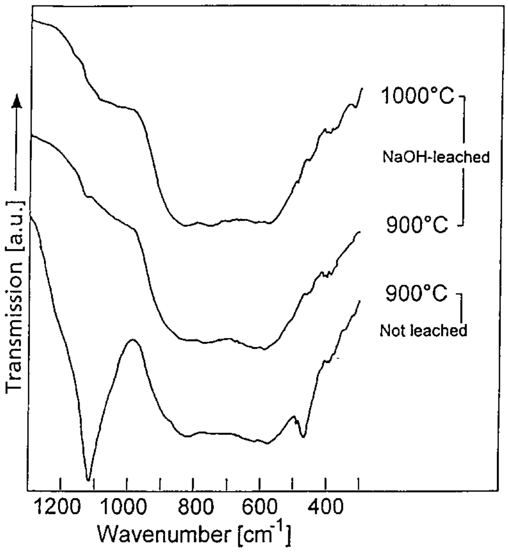

Fig. 2. Infrared (IR) absorption spectra of precursors, heat treated at 900° and 1000°C, not-leached and NaOH-leached.

transition alumina phase with the spinel structure has been designated as the γ-phase throughout the text, though, especially at higher temperatures, X-ray reflection splitting indicates that the phase is not cubic (γ-phase) but rather tetragonal or orthorhombic (δ-phase).) The XRD patterns exhibit an extremely broad diffraction maximum near 4 Å which is typical for non-crystalline SiO_2.

4.2 Infrared spectroscopy

Infrared (IR) absorption spectra have been recorded for precursors, heat-treated at 900°, 1000° and 1100°C, not-leached and NaOH leached (Table 1). The IR spectra of the not-leached samples exhibit strong and relatively sharp bands at ≈ 1100 cm^{-1} and ≈ 470 cm^{-1}, and a broad absorption area between ≈ 820 cm^{-1} and ≈ 580 cm^{-1}, displaying a very low fine structure (Fig. 2). The sharp and intense peaks at ≈ 1100 and ≈ 470 cm^{-1} are attributed to Si-O-Si stretching and O-Si-O bending vibrations in non-crystalline SiO_2.[15,19] The absorption region between ≈ 820 and ≈ 580 cm^{-1} is largely that of pure γ-Al_2O_3.[4] The IR-spectra imply that the precursors studied consist of an admixture of γ-alumina spinel-phase plus SiO_2 glass. The IR spectra of the NaOH-leached precursors differ strongly from those of the not-leached materials. The sharp and intense bands at ≈ 1100 and ≈ 470 cm^{-1} disappear completely, whereas the absorption region between ≈ 820 and ≈ 580 cm^{-1} does not change significantly. Simultaneously a broad but very weak absorption appears between ≈ 1080 and ≈ 980 cm^{-1} which can not be distinguished in not-leached precursors, certainly because of overlapping with the strong 1100 cm^{-1} band. The indicated absorption area between ≈ 1080 and ≈ 980 cm^{-1} which becomes slightly more intensive at higher annealing temperatures (Fig. 2) corresponds to Si-O-Si stretching modes in silicate matrices.[19] This may be interpreted by the incorporation of some Si in the γ-alumina spinel.

4.3 Nuclear magnetic resonance (NMR) spectroscopy

4.3.1 ^{29}Si NMR

Mullite precursors heat-treated at 350°C display weak ^{29}Si NMR signals at ≈ -80 ppm and stronger

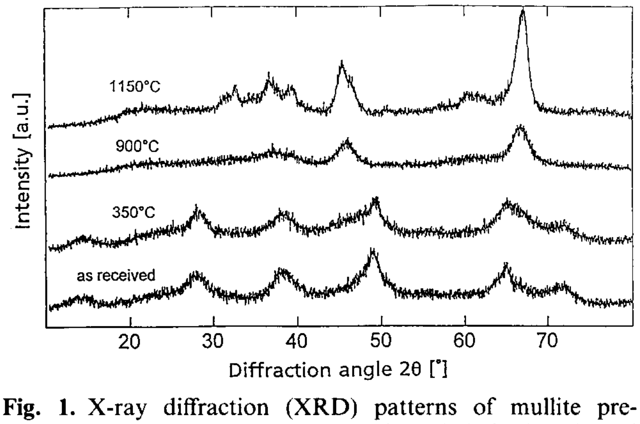

Fig. 1. X-ray diffraction (XRD) patterns of mullite precursors as-received and heat-treated at 350°C, 900°C and 1150°C.

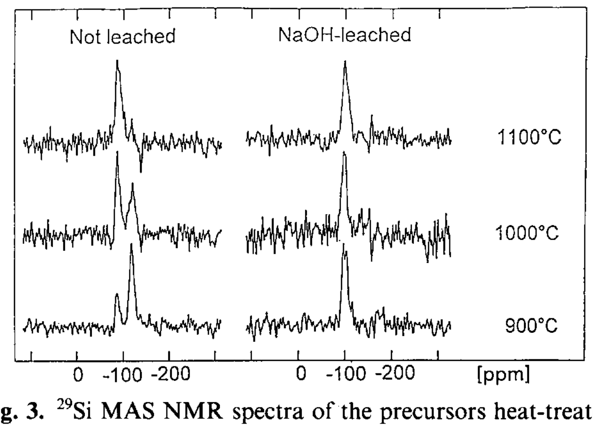

Fig. 3. ^{29}Si MAS NMR spectra of the precursors heat-treated at 900°C, 1000°C and 1100°C not-leached and NaOH-leached, respectively.

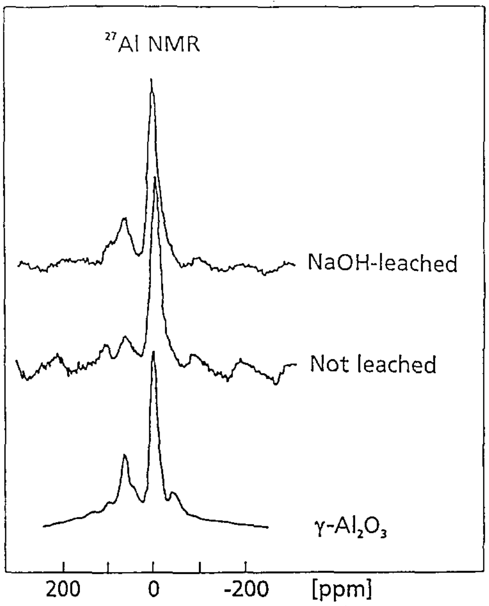

Fig. 4. ^{27}Al MAS NMR spectra of precursors heat-treated at 1100°C, not-leached and NaOH-leached, and of γ-Al_2O_3.

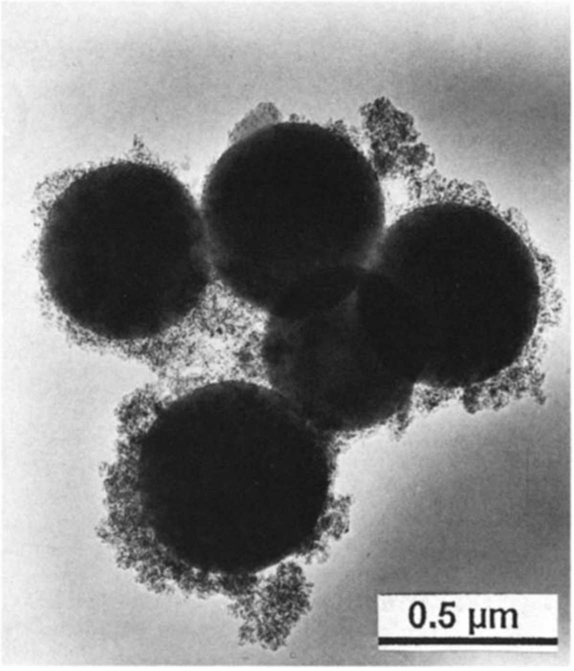

Fig. 5. Transmission electron micrograph (TEM) of the as-received mullite precursor. Note the occurrence of relatively large spherical SiO_2 particles and of fine-grained aggregates which according to ATEM consist of pseudo-boehmite plus SiO_2 matrix.

signals at ≈ −110 ppm. With increasing annealing temperatures, there is a slight shift of the −80 ppm signal position towards more negative values. Simultaneously the −80 ppm signal intensities increase significantly (Fig. 3). Within the same temperature sequence the −110 ppm peaks display decreasing intensities. Both ^{29}Si NMR peaks are relatively broad throughout the whole temperature range. The signals centring at ≈−110 ppm are assigned to (nearly) pure $SiO_2(Q^4)$, whereas those near −80 ppm are due to the Si atoms having four next nearest Al neighbours (Q^0).[20]

Mullite precursors heat-treated at 900°, 1000° and 1100°C and subsequently NaOH-leached exhibit ^{29}Si NMR signals, centring at about −80 ppm similar to those of the not-leached samples, but no signals at about −110 ppm (Fig. 3). This means that the SiO_2 (Q^4) compound disappeared by the leaching process, whereas the aluminium rich compound containing silicon in an aluminium rich environment is not affected by the NaOH treatment.

4.3.2 ^{27}Al NMR

Spectra of ^{27}Al NMR were taken from both not-leached and NaOH-leached mullite precursors heat-treated at 1100°C (Fig. 4). In both cases ^{27}Al NMR spectra exhibit an intense peak at ≈5 ppm and a weaker peak at ≈60 ppm, which are attributed to octahedrally and tetrahedrally bound aluminium, respectively. A signal at ≈30 ppm typical for non-crystalline mullite precursors[21] and for aluminium rich glasses is not observed.[22,23] The conclusion is that all or at least the main part of aluminium is bound in the γ-alumina spinel phase. This conclusion is supported by the fact that the

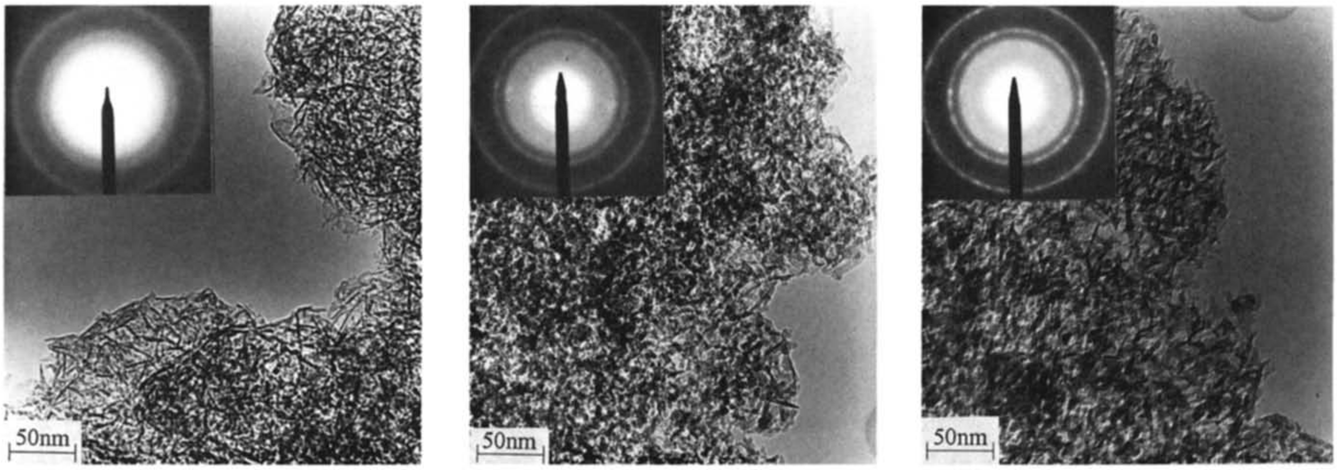

Fig. 6. Transmission electron micrographs of γ-alumina aggregates heat-treated at (a) 500°C, (b) 900°C, (c) 1100°C. The diffraction patterns show that the crystallinity of the phase increases with temperature.

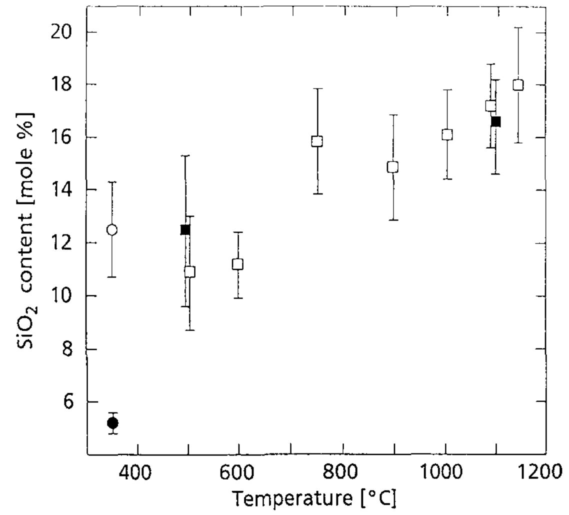

Fig. 7. SiO_2 content of pseudo-boehmite (350°C) and of γ-alumina spinel agglomerates (500–1150°C). Open symbols refer to not-leached samples, filled symbols to NaOH-leached samples. The SiO_2 content has been determined by EDX.

^{27}Al NMR spectra of the precursors are very similar to that of pure γ-Al_2O_3[24] (see Fig. 4).

4.4 Transmission electron microscopy (TEM)

As-received mullite precursors prepared from TEOS and AlOBu contain extremely fine-grained pseudo-boehmite aggregates and rather large spherical particles which are rich in SiO_2 (Fig. 5). After heat-treatment at temperatures between 500°C and 1150°C the powder morphology does not change significantly: SiO_2-rich spheres coexist with nanocrystalline agglomerates consisting of γ-alumina spinel. Figure 6(a)–6(c) show the microstructures of agglomerates and corresponding diffraction patterns (SAD) after treatments at different temperatures. Temperature increase leads to slight crystal growth and to a change in the crystal shape from rod-like to more isometric. Figure 7 gives the SiO_2 contents of the nano-crystalline spinel phases at different temperatures determined by EDX analysis. The bulk SiO_2 composition of the not-leached mullite-precursor phase at 350°C is ≈ 12 mole %. It is strongly reduced by leaching with NaOH. The SiO_2 content of the spinel phase is ≈ 12 mole% at 500°C and increases up to 18 mole % at 1150°C. In the latter samples no difference occurs in the chemical composition of the spinel phase in not-leached and NaOH-leached specimens.

5 Discussion

While previous X-ray diffraction (XRD), transmission electron microscopy (TEM) and infrared (IR) absorption studies indicate that the mullite precursors above ≈ 350°C contain γ-alumina and a non-crystalline SiO_2 compound, the nature and distribution of the γ-phase were not clear, and the question, whether an additional non-crystalline phase does occur, has not been answered. The present ^{29}Si NMR spectra obtained from precursors heat-treated at temperatures ≥ 350°C exhibit signals at ≈ -80 and ≈ -110 ppm, indicating two chemically different environments of silicon. According to the correlation of Engelhardt and Michel,[20] the -110 ppm signal is attributed to (nearly) pure SiO_2, whereas the -80 ppm peak is due to silicon in a matrix with four next nearest Al atoms. The latter can be explained with silicon in an additional Al_2O_3-rich non-crystalline compound, or with the incorporation of silicon into γ-Al_2O_3, respectively. An additional Al_2O_3-rich non-crystalline precursor phase should yield ^{27}Al NMR spectra with peaks near 5, 30 and 60 ppm, due to the presence of fourfold, fivefold and sixfold coordinated aluminium.[21–23] Furthermore, such a phase should be soluble in NaOH. The ^{27}Al NMR spectra of both not-leached and NaOH-leached samples following heat treatment at 1100°C are nearly identical, displaying strong peaks near 5 ppm and much weaker ones near 60 ppm. They are also very similar to the ^{27}Al NMR spectrum of pure γ-Al_2O_3 (Fig. 4, see also Ref. 24). These findings together with the observation that the ^{29}Si NMR signal at ≈ -80 ppm is not affected by the NaOH-leaching leads to the conclusion that the spinel phase is the only Al_2O_3-rich compound in the precursors. The assumption that no additional non-crystalline aluminium silicate compound does exist is also supported by IR spectroscopic measurements. The presence of an additional aluminium silicate compound should have been observed by the occurrence of a strong IR absorption band in the 1100–900 cm^{-1} wavenumber range. Observations show that this is not the actual case. The conclusion derived from the NMR, IR, XRD and TEM studies is that the mullite precursors above about 350°C are diphasic, consisting of spherical non-crystalline SiO_2 particles and of a γ-alumina transition phase, incorporating silicon at tetrahedral positions. The amount and temperature dependence of the incorporation of silicon into the spinel phase and the formation mechanisms of silicon-containing γ-Al_2O_3 are discussed below.

The maximum SiO_2 incorporation into γ-Al_2O_3 was achieved with the sample heat-treated at 1150°C and was 18 mole % (11·5 wt %). The degree of silicon incorporation into γ-Al_2O_3 is at a much lower level than the composition reported in some previous papers,[2,3,7,17,18,24] investigating the temperature dependent development of aluminium silicate gels and the thermal decomposition of kaolinite and related sheet silicates. On the other hand, the amount of silicon incorporation determined in this study is significantly higher than those reported by Percival *et al.*,[4] Leonhard,[5] Bulens *et al.*,[25] Hyatt and Bansal[11] and Lee and Yu[12] who quoted that the spinel phase was completely or nearly free of silicon. The present values of silicon incorporation into the γ-alumina phase fit well with data published by Okada and Otsuka[15] and Sonuparlak *et al.*[26] However, contrary to these previous studies, we are now able to provide strong, straight-forward and reproducible evidence for the existing important question whether and how much silicon is incorporated into transition γ-alumina, using independent spectroscopical (IR, NMR), microscopical (TEM) and diffraction (XRD, ATEM) methods. XRD and TEM studies showed that mullite precursors prepared from tetraethoxysilane (TEOS) and aluminium-*sec*-butylate (AlOBu) by rapid hydrolysis with excess H_2O in a very basic environment (pH > 10, designated as type II precursors[8]), and heat-treated up to ≈350°C contain extremely fine-grained pseudo-boehmite (γ-AlO(OH)) aggregates and rather large spherical particles (≥ 100 nm) (Fig. 5) being very rich in SiO_2. The pseudo-boehmite aggregates are intimately embedded in a nearly pure, non-crystalline SiO_2 compound. Although it was not possible to resolve the pseudo-boehmite and SiO_2 compounds by means of TEM facilities, our leaching experiments coupled with ATEM investigations proved that the SiO_2 phase is leached by NaOH-treatment and that the boehmite crystals themselves are (nearly) free of silicon. Above 350°C the SiO_2-content of the recently formed γ-alumina, before and after leaching is ≈11·5 mole % and this value is exactly the same as the amount of SiO_2 previously coexisting as a non-crystalline compound (below 350°C) with pseudo-boehmite. The conclusion is that in NaOH-leached samples above 350°C there exists no 'free' SiO_2 compound anymore and that all silicon was incorporated into γ-Al_2O_3. The silicon incorporation is feasible, because the reaction takes place at a nanometer scale at an activated state of the system during the transformation of pseudo-boehmite to the γ-alumina spinel phase.

As the temperature increases up to 600°C, the SiO_2 content of the γ-alumina phase remains constant (≈ 11 mole %) in both not-leached and NaOH-leached samples. This result is plausible since any further silicon supply for incorporation into the spinel requires extended diffusion distances of silicon species from the large spherical SiO_2 particles to the γ-alumina crystallites. Above 600°C, the SiO_2 content of the γ-alumina phase increases and reaches a final amount of 18 mole % at 1150°C. We believe that a marginal decay of the spherical non-crystalline SiO_2 particles at > 600°C enables a gradually increased incorporation of additional silicon into the agglomerates of γ-alumina spinel. Because of the smallness of this effect, shrinkage of SiO_2 spheres cannot be observed directly by TEM. A calculation based on chemical bulk composition and on the composition of the present phases yields a decrease in the SiO_2 phase content from ≈33 vol. % at 500°C to ≈30 vol. % at 1100°C. Diffusion of silicon species at the surfaces of the γ-alumina crystallites is facilitated by the temperature increase and therefore the silicon content of γ-alumina spinel gradually becomes higher with increasing temperatures (Fig. 7).

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