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Characterization and Surface Chemistry of Uncoated and Coated Silicon Nitride Powders

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Abstract

Various Si_3N_4 powders, produced by different procedures, were characterized by imaging (TEM) and analytical methods (EDS, FT-IR, XPS) in the as-received state as well as after doping with a metal oxide (MgO). For the doping, an alternative procedure to the usual methods, was applied, which is based on soluble organometallic compounds. Analytical transmission electron microscopy combined with lateral resolution element analysis and XPS measurements was used for morphological, structural and analytical characterization. The distribution of the dopant was deduced from measurements of XPS sputter depth profiles. These investigations were supplemented by FT-IR measurements in order to determine qualitatively and semi-quantitatively the reactive groups on the particle surfaces of the as-received powders.

For comparison, measurements were performed with Si_3N_4 powders which were doped by the above chemical procedure and by mechanical mixing. The results of the various characterization methods are interpreted in the form of a model display for surface reactions of organometallic doping reagents on the surfaces of ceramic particles. The results show that Si_3N_4 powders with high concentration of OH groups on their particle surface reveal very good distribution of the fluxing element (layer-like coating).

1 Introduction

It is well known that the improvement of homogeneity, reproducibility and sinter activity is an essential objective in the development of structural ceramics. In that context the surface chemistry and structure of sintering powders, which have been developed with even smaller particle sizes and in higher purity degrees, play an important role. Moreover, the distribution of sintering additives in the matrix material has to be improved, which can make it possible to reduce the additive concentration and to enhance the high-temperature properties. Consequently, investigations are necessary to improve the doping techniques, the characterization of the highly sinter active powders, and the homogeneity of (powder + sintering additive)-mixtures.[1] Up to now several techniques, such as mixing/milling processing, the sol-gel method, the precursor route and doping with inorganic metal compounds, have been used in order to introduce inorganic sintering additives (metal oxides).

In the mixing/milling processing frequently used, the raw materials are ground (homogenized) with the sintering additive (mostly metal oxides) in a milling device. Using this technique, the homogeneity of the additive distribution is limited by the particle size distribution (μm-range) of the starting powder and of the dopant. This method is not suited for the doping of silicon nitride powders with small amounts of sintering additives. Additionally, the mixture may be contaminated by abrasion materials.

The sol-gel method is based on the hydrolysis of multivalent metal alkoxides. The gel is subjected to a drying process in order to obtain the material in the powder state.[2,3] Another technique, which is also based on the use of chemical pre-products, is the liquid precursor route. Non-oxide powders have been produced by reaction pyrolysis of inorganic polymers.[4–6] However, both techniques are very expensive.

The disadvantages of inorganic metal compounds is the possibility of forming crystalline phases[7] and the contamination of the powder particles by additional elements from the counterions (N from nitrates, Cl, Br, I from halogenides, P from phosphates, S from sulfates etc.) which may have a detrimental effect particularly on high-temperature properties.[8] Therefore, these elements have to be removed during heating (formation of nitric oxide, sulfur dioxide, halogenic acids etc.).

In the present investigation another method is used to dope the mostly commercially available powders through soluble organometallic compounds based on Mg as model substance. This method provides several advantages compared to the procedures mentioned above.[9,10] By using Mg-methoxide as the organometallic compound, for example, which can act as the dopant compound, only those elements (in small amounts) are introduced in the matrix powder, which are anyhow incorporated into the raw material through organic additives (carbon, hydrogen and oxygen). This method allows a homogeneous introduction of doping elements even at low concentrations. The development of a chemical bonding between particle surface and organometallic compound suppresses the formation of a separate phase of the dopant metal.

2 Experimental Procedure

Organometallic chemistry was carried out in non-aqueous and water-free solvents; whereby magnesium methoxide as organometallic compound was used. During the mixing process of this solution with a suspension of the raw material in the same liquid, (alcohol), the surface groups of the Si_3N_4 powders act as polar reagent to which the metal alkoxide can be directly bonded generating an alcohol molecule ($Si{-}OH + (CH_3O)_2Mg \rightarrow Si{-}O{-}Mg{-}O{-}CH_3 + CH_3OH$). As a result, an excellent distribution of the sintering aids (in solution) may be assumed, which will subsequently be transferred to the particle surfaces in accordance with the distribution and density of the OH-groups. Thus, these are decisive parameters for the homogeneous distribution of the inorganic additives.

The infrared spectroscopy is an ideal method to achieve information about functional groups of molecules[11] through the vibrational excitation. To detect the functional surface groups, powder analysis was performed in the so called Barnes cell (Spectra Tech. Inc.) of an FT-infrared-spectrometer (Digilab FTS 15/80) in the reflection mode, wave numbers ranging from 4000 to 600 cm^{-1}. In the range of 4000–3000 cm^{-1} the stretching vibrations of the surface-OH-groups, which are important for the chemical dopant used here, can be determined. In the range of about 1000 cm^{-1}, the backbone vibrations of the lattices were observed.[12,13]

The silicon nitride powders investigated — either commercially available or special grades from industry — were produced by different procedures (Table 1). These powders were analyzed in the as-received state and after doping with magnesium methoxide with various concentrations between 0·5 and 2 wt% of Mg related to Si_3N_4. Analysis of the dopant reaction concerning the homogeneity of the element distribution was performed by transmission electron microscopy (Philips EM 430; accelerating voltage 300 kV; lateral resolution about 0·2 nm, equipped with EDS, Tracor) and X-ray-photoelectron-spectroscopy (Perkin Elmer PHI 5600). For comparison purposes, a powder mixture (Si_3N_4 grade UBE SN-E10 + 2 wt% MgO grade p.a. Merck) was produced by mixing the powders in a non-aqueous liquid.

Table 1. Oxygen content and specific surface area of the silicon nitride powders most investigated. Additionally, FT-IR measurements were performed with the following powders: HCST S1, Denka SN-9S, HCST LC10-S, HCST LC10-N, Bayer DF0014, HCST LC12-SX, HCST 3918 LC12 (special grade with 3 wt% oxygen), HCST GP, TOSOH TS10.

Product	*UBE SN-E10*	*Starck M11*	*Denka SN-9FW*
Synthesis method	Diimide precipitation	Nitridation	Nitridation
0 (wt%)	1·32	1·78	0·82
Spec. surface (m^2/g) area	11·9	13·5	11·7

3 Results and Discussion

3.1 FT-infrared spectroscopy

The infrared spectrum analysis of the silicon nitride powders investigated provides information about the surface bonded molecules. The height of

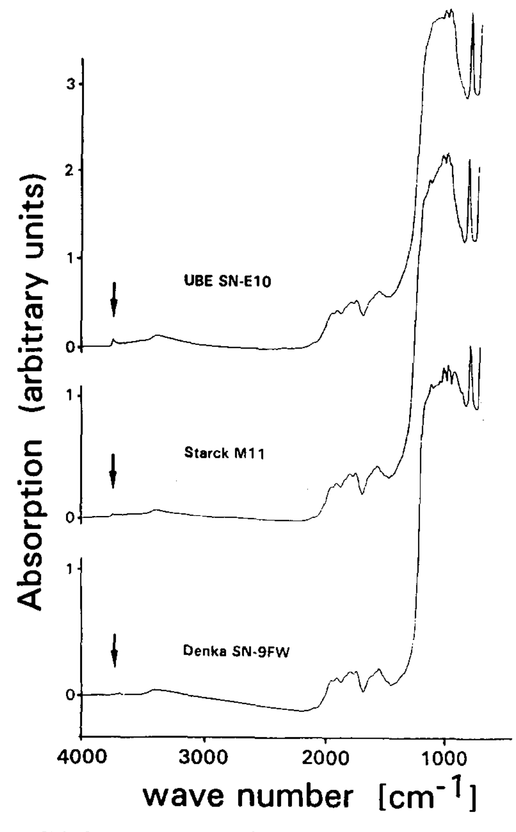


Fig. 1. FT-infrared spectra of various silicon nitride powders investigated (UBE SN-E10, Starck M11, Denka SN-9FW).

the absorption peak of the OH-stretching vibration at 3750 cm^{-1} indicates the amount of the OH-surface groups (Fig. 1). An increasing peak height was found spectroscopically in the sequence of the silicon nitride powders Denka SN-9FW, Starck M11, UBE SN-E10 (see arrows in Fig. 1); in other silicon nitride powders investigated, the intensity of the OH-vibration band increases in the following sequence: HCST Sl (low), Denka SN-9S, HCST LC10-S, HCST LC10-N, Bayer DF0014, HCST LC12-SX, HCST 3918 LC12 (special grade with 3 wt% oxygen), HCST GP, TOSOH TS10 (high). In the range of about 1000 cm^{-1} the backbone vibrations (Si–N–Si, Si–O–Si) of the lattices can be observed (a detailed association of each maximum of the overlapping vibration bands in this so-called 'fingerprint' region is not discussed in connection with the dopant reaction used here).

The silanol groups are used as reactive surface groups for the organometallic compounds. Measuring the extent of the OH-stretching vibrations at 3750 cm^{-1} allows an estimation of the surface occupation of these groups which is not strongly correlated to the total oxygen content of silicon nitride powders (compare Fig. 1 with the total oxygen content in Table 1). Thus, the variation in the intensities of the OH-vibrations gives an indication of suitability and potential for the chemical dopant reaction of each powder.

3.2 Photo-electron spectroscopy

Photo-electron spectroscopy (XPS) is an important analytical technique for surface and thin film characterization of solid materials. It provides qualitative and quantitative information relating to the outermost atom or molecule layers. The depth of information or the thickness of the analyzed surface layer ranges from 1 to 3 nm. This mainly depends on the kinetic energy of the photoelectrons. Sputter depth profiling is applied if concentration variations within a thick surface layer are of interest. The XPS spectra are commonly initiated by Mg K_α or Al K_α radiation. The resulting photo-electron lines can be correlated with the binding energy of the core level states of the atoms. That energy can respond sensitively to a charge transfer between neighbouring atoms. It provides a direct insight into chemical bonding

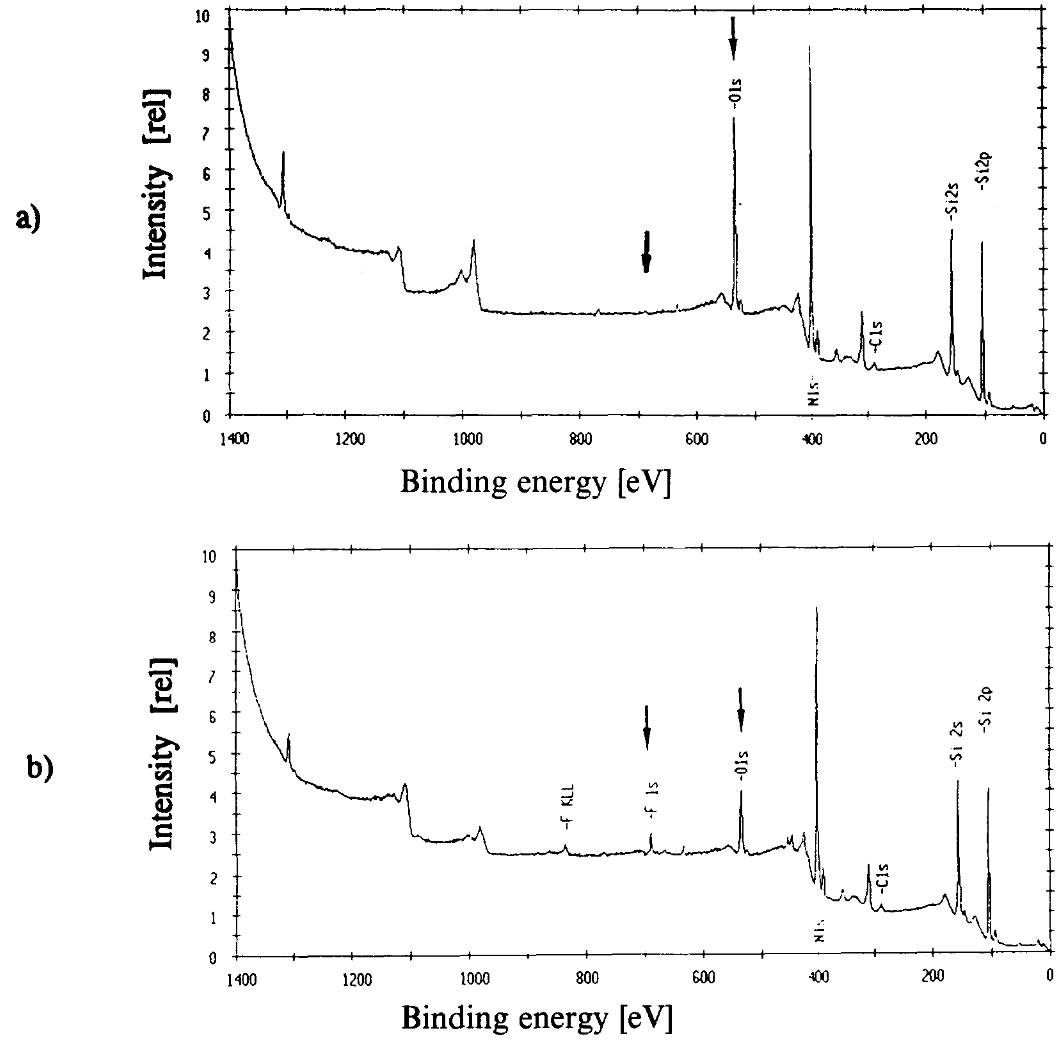
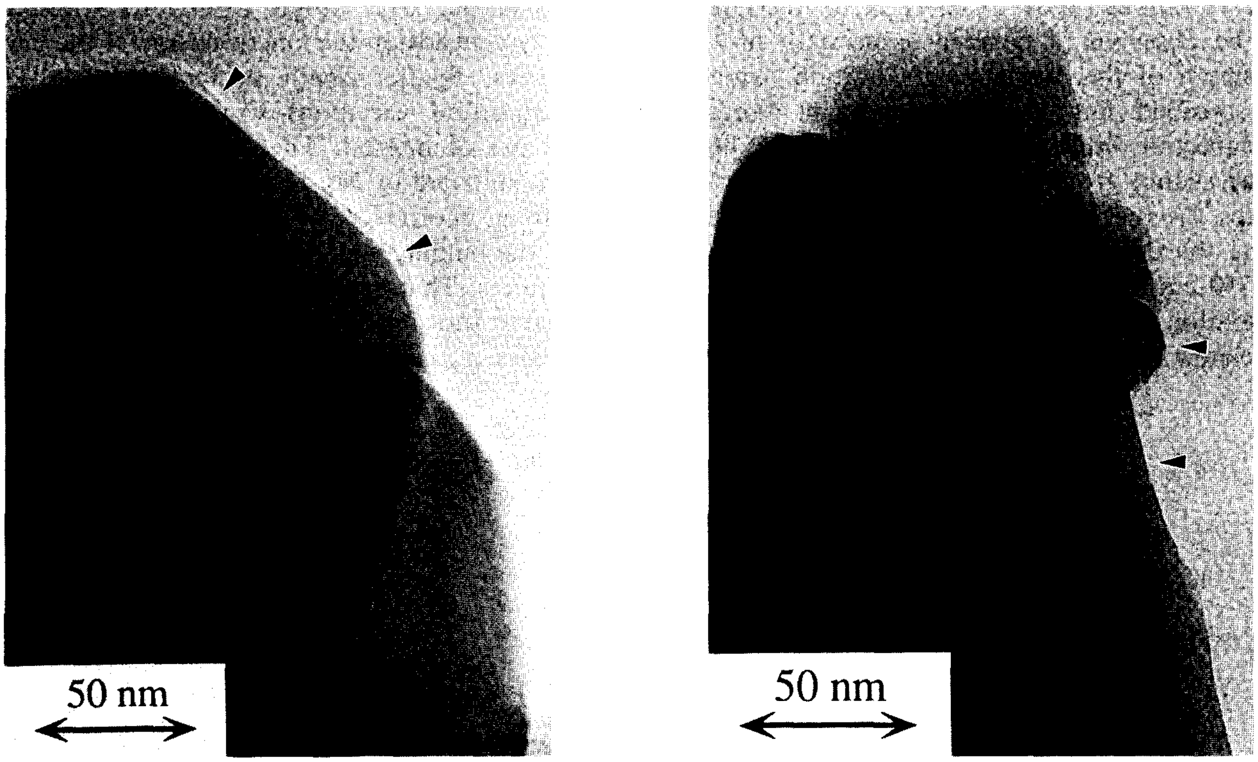


Fig. 2. XPS spectra of two silicon nitride powders with (a) high (UBE SN-E10) and (b) low (Denka SN-9FW) oxygen content.

parameters (chemical shift). XPS is therefore a powerful tool for the identification of chemical compounds and the modification of the electronic structure. A limitation, however, is the overlapping of several bonding states of different compounds.

In the case of the Si_3N_4 powders, a correlation between the XPS data and the TEM studies was found (Figs 2 and 3). The Denka powder SN-9FW reveals a lower oxygen concentration at the surface compared to the powder UBE SN-E10. The low oxygen content connected with the detection of fluorine is obviously caused by HF treatment of the powder. The result coincides with the thickness of the amorphous oxide layer in Fig. 3. The evaluation of the silicon peak in Fig. 4 shows the amount of oxidized Si (SiO_2 at 104·4 eV) in reference to the nitrogen bonded Si (Si_3N_4 at 102·8 eV). This proves that the Si_3N_4 powder synthesized by diimide precipitation has a higher amount of an oxidized phase on the particle surface compared to the Si_3N_4 powder synthesized by direct nitridation (followed by HF treatment). The essential point is that (because of the reaction of HF with the silanol groups) high fluorine contents cause a reduction in the number of OH groups.



(a) (b)

Fig. 3. TEM micrographs of Si_3N_4 particles with (a) a relatively thick and (b) a thin amorphous surface layer. The Si_3N_4 powders are synthesized by (a) diimide precipitation and by (b) direct nitridation.

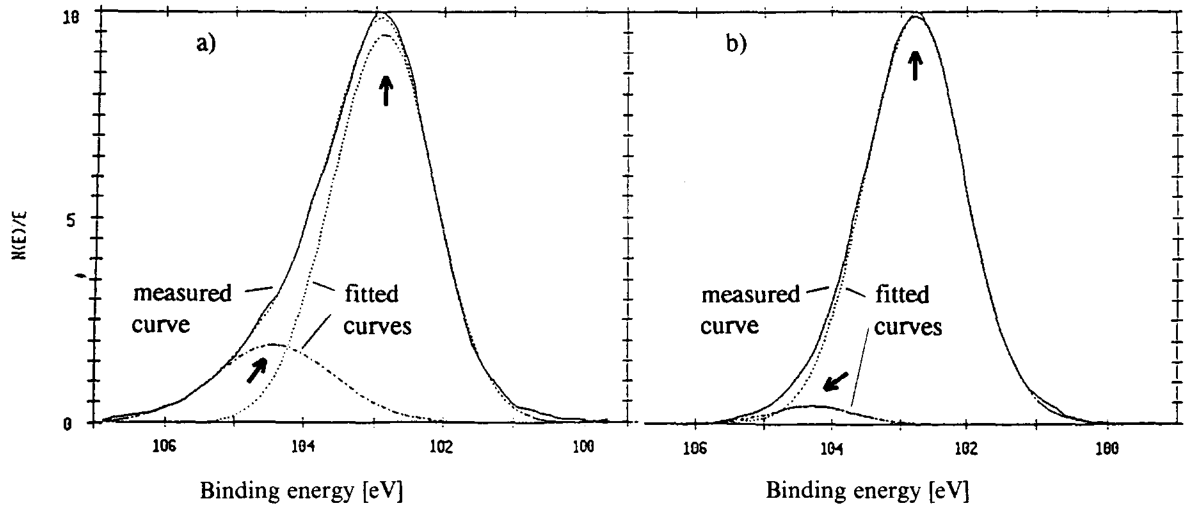


Fig. 4. Deconvolution of the measured peaks and fitted curves of the Si 2p lines (oxidized Si: 104·4 eV; nitrogen bonded Si: 102·8 eV) of XPS spectra of silicon nitride powders with (a) a relatively thick and (b) a thin amorphous surface layer. The Si_3N_4 powders are synthesized by (a) diimide precipitation and by (b) direct nitridation.

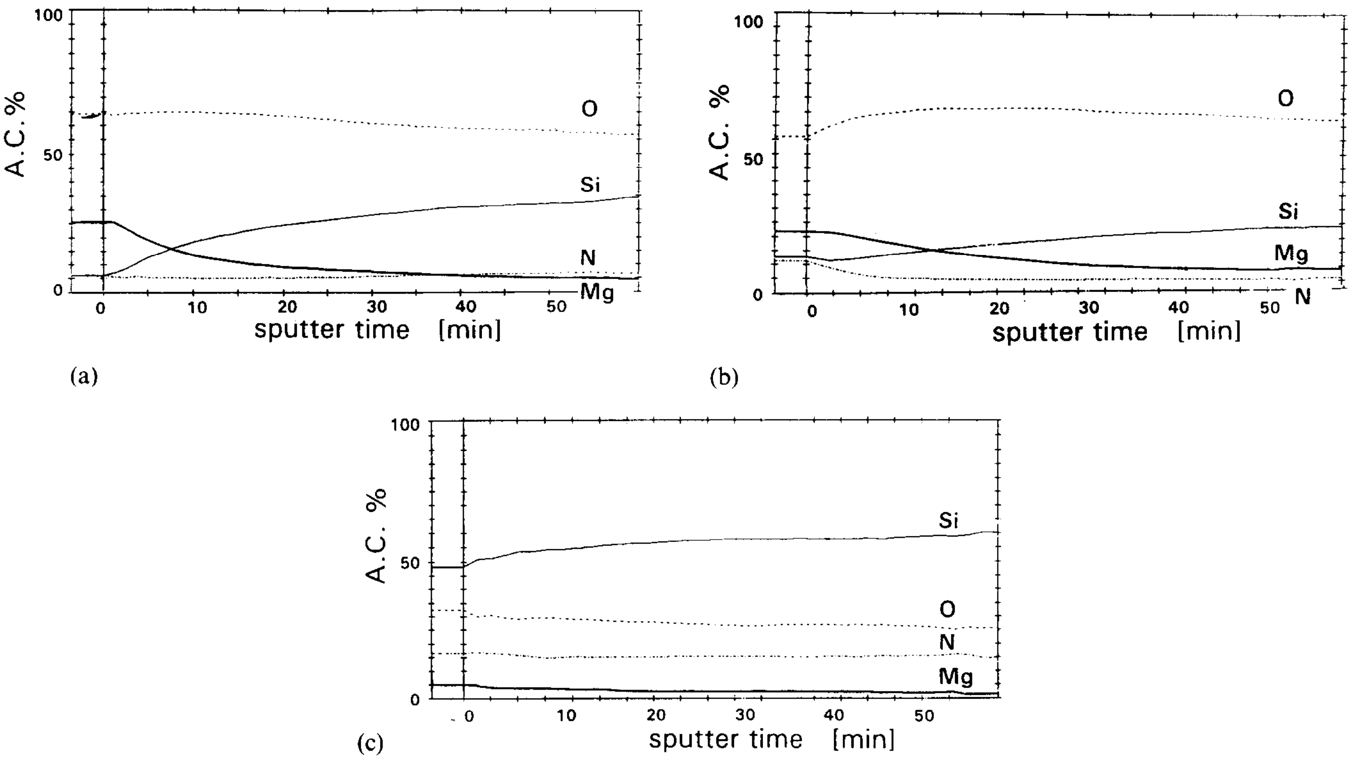


Fig. 5. XPS sputter depth profile measurements (concentration of Si, O, N and Mg as a function of sputter time) of Si_3N_4 powders doped with 2 wt% Mg: (a) chemically doped UBE SN-E10 (high number of OH groups); (b) chemically doped Denka SN-9FW (low number of OH groups); (c) mechanically doped UBE SN-E10.

In Fig. 5, the results of the XPS sputter depth profile measurements of silicon nitride powders, which are chemically and mechanically doped, are presented indicating the Mg-, Si-, O- and N-concentrations. The variation of the element concentration versus sputter time is different for the three

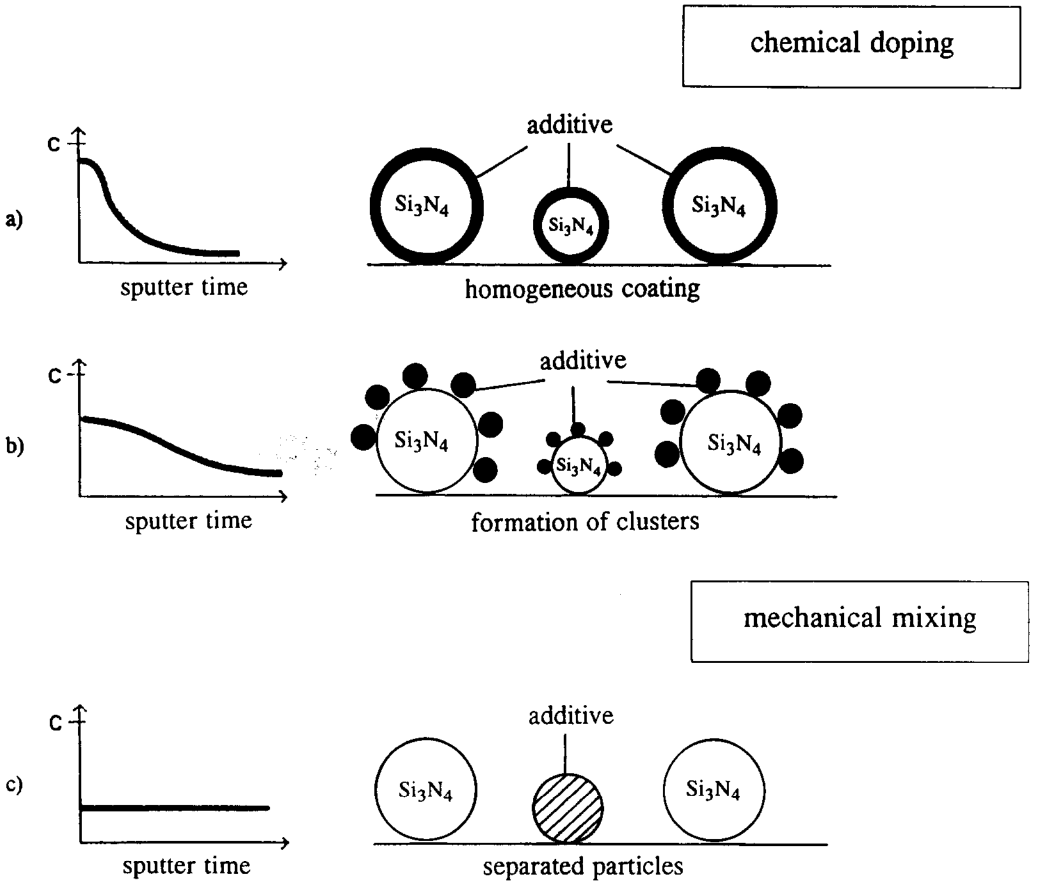


Fig. 6. Model of (a) layer-distribution (additive-coated Si_3N_4 particles), UBE SN-E10; (b) cluster-distribution (additive clusters on Si_3N_4 powder surface), Denka SN-9FW; (c) particle-distribution (additive-particle and Si_3N_4 particles), based on the sputter depth profiles of the dopant element (here schematic; experimental results see Fig. 5).

powder mixtures. From these results, information about the additive distribution in the three systems may be deduced (Fig. 6): a layer distribution (Fig. 6(a)), a particle–particle distribution (Fig. 6(c)) or, as a transition stage between these two, a cluster-like distribution of the dopant element at the powder surfaces (Fig. 6 (b)). For the mechanical doping of raw materials with metal oxide particles, the element concentrations remain mainly unchanged during sputter depth profile measurements because of the simply mixed particles. Powders doped with magnesium methoxide show in the surface-near region a higher magnesium content compared with the added total concentration.

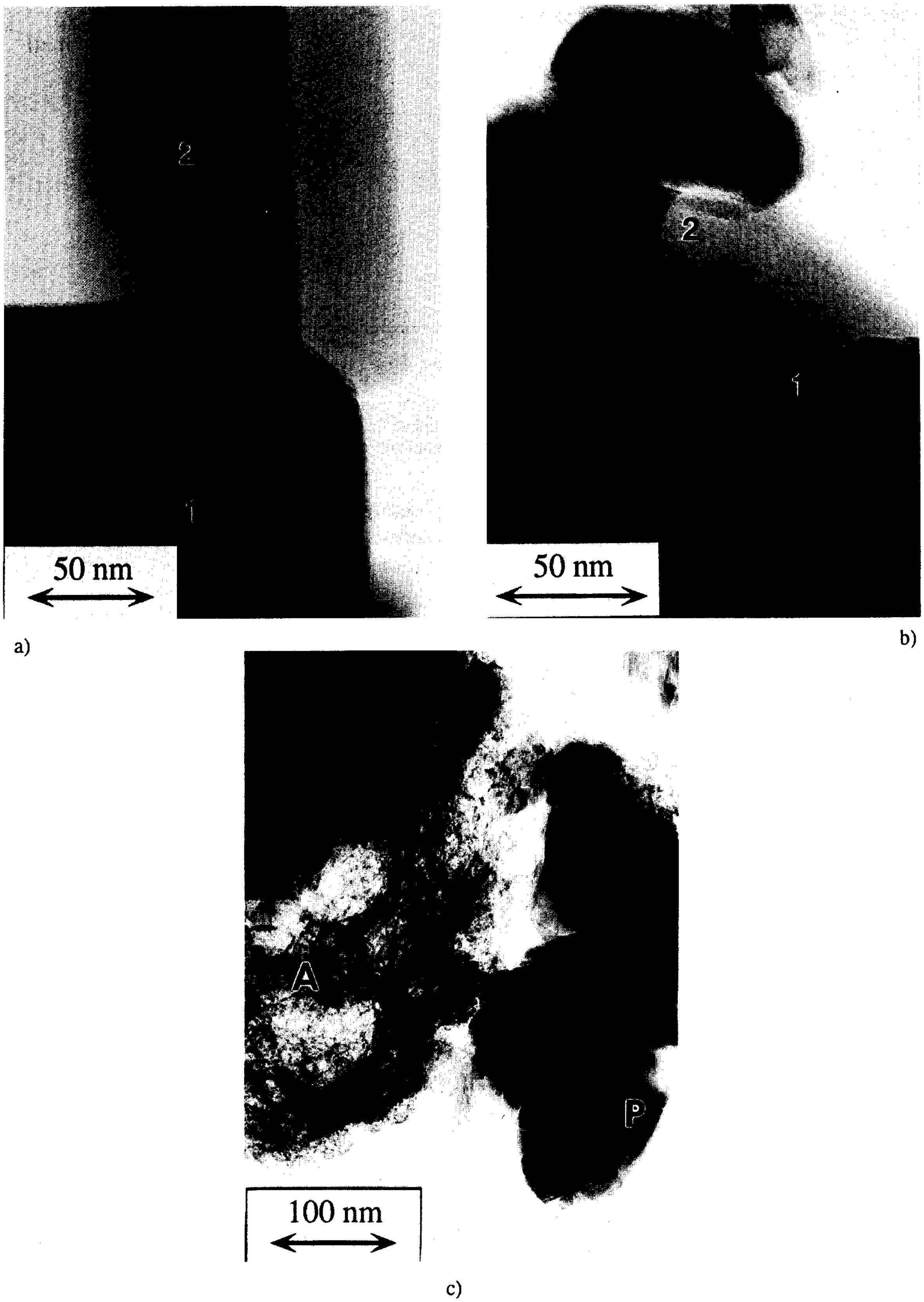


Fig. 7. TEM micrographs of various silicon nitride powders doped with 2 wt% Mg: (a) Si_3N_4 UBE SN-E10, particles 1 and 2; (b) Si_3N_4 HCST M 11, particles 1 and 2; (c) Si_3N_4 Denka SN-9FW, amorphous region A and particle P.

The magnesium concentration decreases with increasing sputtering time. This behaviour may be interpreted in terms of a layered coating or cluster-like doping of the single powder particles with the dopant metal. The higher the slope of the curve Mg = f (sputter time) the more the doping is approaching the layer-like coating.

The results show that the powder UBE SN-E10 with a higher amount of surface-OH-groups reveals a stronger decrease of the magnesium intensity compared to the powder Denka SN-9FW with a lower fraction of surface-OH-groups (see Figs 1 and 5), indicating the desired layer-like doping of each particle.

3.3 Analytical transmission electron microscopy

High resolution and analytical transmission electron microscopy (TEM) offers with extreme lateral resolution the unique possibility for structural, morphological and analytical characterization of powders.[14,15] By using TEM and EDS the local amount of magnesium in the powders was analyzed. Figure 7 shows TEM-micrographs of various silicon nitride powders doped with 2 wt% magnesium; Fig. 8 gives the results of EDS measurements. In the case of the Denka SN-9FW powder doped with 2 wt% Mg, a much higher content of magnesium was found in the amorphous regions (precipitated Mg compound) compared to the Si_3N_4 powder particles (see Figs 7(c) and 8(c)). In contrast to the Denka powder no amorphous region between the particles was observed in the powder mixtures of Si_3N_4-Starck M11 and Si_3N_4-UBE SN-E10 doped with 2 wt% Mg (see Figs 7(a) and 7(b) as well as Figs 8(a) and 8(b)). In these cases, particularly for UBE SN-E10,

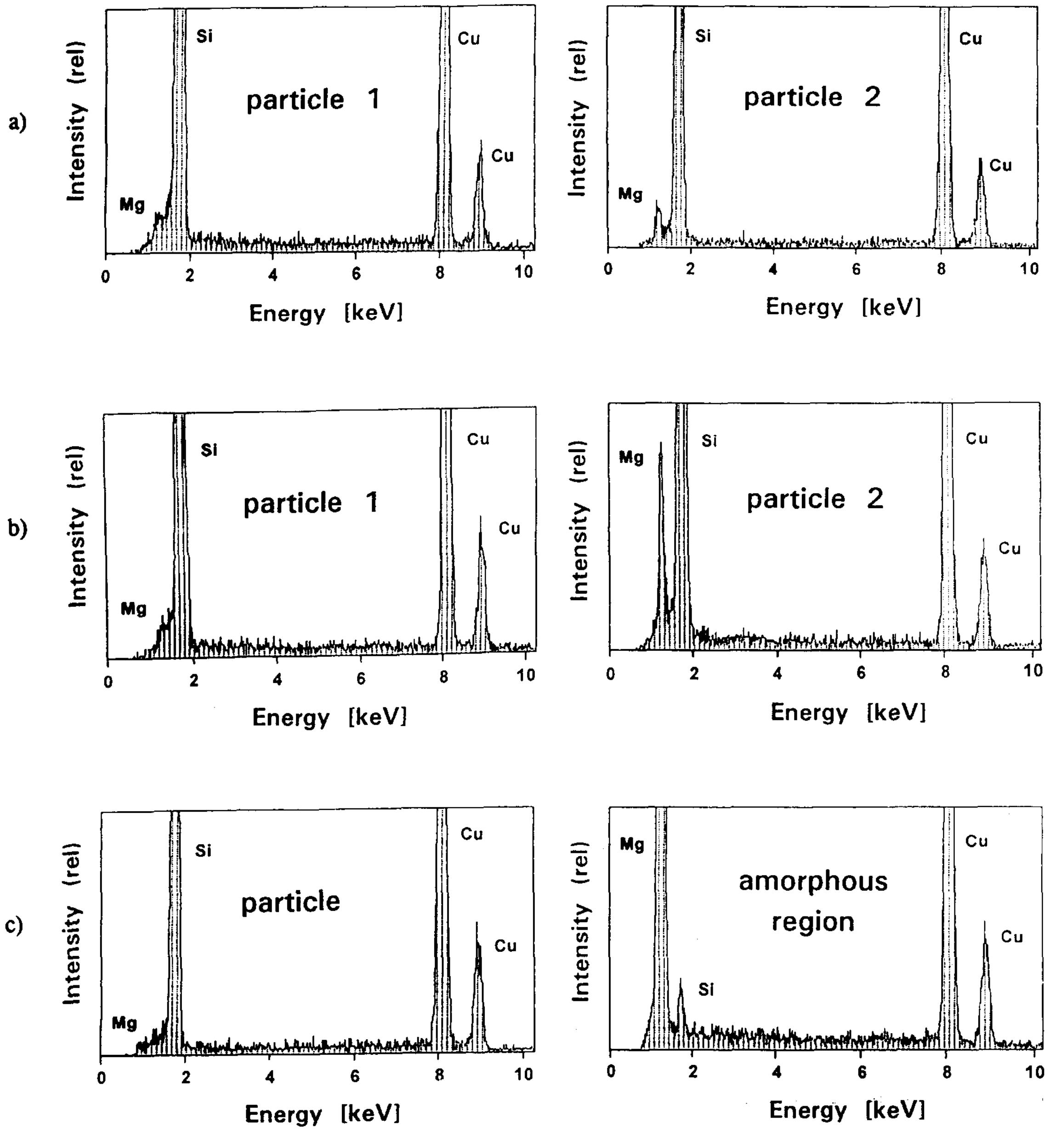


Fig. 8. EDS spectra on local sites of silicon nitride particles doped with 2 wt% Mg (Cu from copper grid): (a) Si_3N_4 UBE SN-E10; (b) Si_3N_4 Starck M 11; (c) Si_3N_4 Denka SN-9FW.

a more homogeneous distribution of the sintering aid was obtained. The reason is the relative high number of silanol groups on the surface as indicated in the FT-infrared spectra (see Fig. 1).

4 Conclusions

The dopant-technique involving organometallic compounds (strong alkaline reagents) provides a more homogeneous distribution of additives like magnesium. The use of analytical transmission electron microscopy, photoelectron spectroscopy and infrared spectroscopy allows an improved characterization of ultra-fine and doped sintering powders. The correlation of the results of the different analytical methods permits an interpretation about the quality of the distribution of sintering aids in ceramic raw materials. From the variation of the element concentration versus sputter time the distribution of the additives in the powder mixtures can be deduced, e.g. layer-like distribution, particle–particle distribution or a transition stage between these two cases, a cluster-like distribution of the additive on the powder surface.

The degree of homogeneity that can be achieved with the aim of eventually producing continuous thin coatings is strongly dependent on the number of OH groups (silanol groups, adsorbed water) on the powder particle surface which are controlled by the type of the Si_3N_4 powder and the pre-treatment as well as the amount of sintering additives. The number of silanol groups cannot be strongly correlated to the total oxygen content in the powders. However, a large specific surface area of the powders and a relatively high amount of oxygen at the particle surface is in general an advantage. In this connection it is important to note that fluorine (because of the reaction of HF with the silanol groups) results in a reduced number of silanol groups.

Based on the character of element distribution as a function of the number of surface groups, the dopant content and the test parameters, three idealized basic models may be deduced:

- a high number of OH-surface groups and low dopant content for dry powders and water-free suspension media result in a layer-like distribution of the sintering additive which is desirable;
- a low number of OH-surface groups and high dopant content for dry powders and water-free suspension media lead to amorphous precipitation of the dopant;
- a number of OH-surface groups nearly equal to the dopant content results in a domain structure of the additives.

In this scope it should be mentioned that in the case of a low number of OH groups relative to the amount of the dopant compound, and small amounts of water in the suspensions (powders with adsorbed water and/or water-containing suspension media) a domain structure of additives is enhanced.

The methodology is not restricted to the described powders, but also appreciable for other oxidic and non-oxidic raw materials. Moreover, it is suited for doping with more than one metal component, especially for low concentrations.

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