Journal of the European Ceramic Society 22 (2002) 955–961

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Organometallic precursors, an alternative route for the doping of silicon nitride powders?

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Received 14 December 2000; received in revised form 27 June 2001; accepted 9 July 2001

Abstract

Two silicon nitride powders prepared by diimide precipitation and direct nitridation were doped with 5 vol.% yttria using (i) a commercial Y_2O_3 powder and (ii) a soluble Y-organometallic compound as additive. The aim of this work was a direct comparison between those two doping methods. Homogeneity of additive distribution was characterized by Fourier transform infra-red spectroscopy (FT-IR), photo electron spectroscopy (XPS) and transmission electron microscopy (TEM). Depending on the doping technique used, no major difference in sintering behavior and microstructure evolution were monitored. However, chemical doping results in (i) an enhanced densification rate in the early stage of sintering, (ii) a slight shift of the densification rate maximum (ds/dt) to higher temperatures, and (iii) in a slightly finer final microstructure. Note that doping via organometallic precursors can only be successfully applied, when the powder particle surface reveals the presence of silanol groups, as in case of diimide starting powders. Electron microscopy, Organometallic dopants, Sintering, Si_3N_4 © 2002 Published by Elsevier Science Ltd.

Keywords: Dopants; Electron microscopy; Organometallic-precursors; Sintering; Si_3N_4

1. Introduction

Dense silicon nitride ceramics reveal an excellent combination of thermo-mechanical properties, which favor this group of materials for a wide range of technical applications.[1–6] However, it is well established that improved homogeneity, reproducibility as well as sinterability are essential requirements to develop high-grade structural ceramics. Since the Si–N chemical bond is of covalent character and Si_3N_4 decomposes incongruently at temperatures exceeding 1800 °C,[7,8] densification commonly necessitates both the addition of external sintering aids and a N_2 overpressure to counteract decomposition. To initiate the liquid-phase sintering mechanism at elevated temperatures, sintering additives should be finely dispersed within the powder compact, in order to lower affective diffusion distances. Several techniques to introduce those sintering aids have been reported in literature[9–18] such as (i) mixing with metal oxides via ball milling, (ii) the precursor route, (iii) the sol-gel approach and (iv) using metal salts as starting compounds to form the respective oxides.

The optimization and adjustment of the amount and composition of sintering additives required for densification as well as their effect on the high-temperature performance of Si_3N_4 ceramics are of wide interest.[5] During mixing/milling, which is commonly used in technical processes, metal oxide powders are ground with the Si_3N_4 starting powder for several hours. This technique does not allow a fine dispersion of the metal oxide and can introduce impurities due to wear of milling media. Moreover, it is difficult to homogeneously disperse a small amount of additives. A method which is also of interest for homogeneous doping of ceramic powders, in particular, when a small amount of sintering aid is required, is the use of soluble organometallic compounds.[19] Soluble organometallic precursors as well as commercial metal oxide powders were employed in this study to incorporate the sintering aid. This direct comparison of doping routes should enable us to answer the question whether organometallic precursors are indeed favorable for Si_3N_4 doping and if this technique is in general applicable, i.e. being independent from the Si_3N_4 starting powder. Therefore, an improved characterization of the Si_3N_4 powders, exceeding the methods generally used,[20–33] was

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0955-2219/02/$ - see front matter © 2002 Published by Elsevier Science Ltd.
PII: S0955-2219(01)00397-1

performed here, to fully exploit/understand the potential of this chemical doping method. In this context, surface sensitive techniques [Fourier transform infra-red spectroscopy (FT-IR), photo electron spectroscopy (XPS)] and imaging systems [scanning electron microscopy (SEM), and transmission electron microscopy (TEM)] were used to characterize the chemistry and morphology of Si_3N_4 powder particles.

2. Experimental procedures

For the present investigation two silicon nitride powders Tosoh TS-10 (synthesized by diimide precipitation) and Denka SN-9FW (processed by direct nitridation) were utilized.[34,35] Special characterization of the starting Si_3N_4 particle-surface properties was performed by FT-IR, XPS, and TEM. These analysis techniques are different in lateral and depth resolution. FT-IR was used to analyze surface OH groups while XPS and respective sputter profile measurements monitor the oxygen distribution in a surface-near region. The lateral resolution of these two techniques is typically lower than the particle diameter. The characterization of ceramic powders by TEM yields additional information about the local chemical composition.[36]

Y_2O_3 was introduced as sintering additive by (i) solid metal oxide powder (H.C. Starck, Goslar) during ball-milling for 4 h (Si_3N_4 milling media) and (ii) via an Y-organometallic compound (Y-methoxyethoxide in methoxyethanol) followed by calcination. The chemical doping reaction was performed in a water-free suspension by adding a solution of the reactive organometallic compound under vigorous stirring. A covalent Si–O–Y unit is formed by reaction of the strong alkaline precursor with surface OH groups.[37] The total additive content (calculated as metal oxide) was varied between 1.0 and 10.5 wt.% (the latter being above the limit of homogeneous chemical doping). The two powders were dried, sieved (mesh size 0.250 mm) and wobbled in an eccentric tumble mixer to form granules. Powder compaction was performed by die pressing (6.5 MPa) and subsequent cold-isostatic pressing (National Forge NF-E) at 170 MPa. Hydrocarbon residues of the organometallic compound were removed by calcination at 800 °C (Nabertherm furnace N60/HR), which fully converts the organometallic precursor to Y_2O_3, as verified in a control experiment with pure substances.

Thermal densification was performed by gas-pressure sintering (5 MPa N_2 pressure for 1 h at 1875 °C as maximum temperature) combined with in-situ dilatometry measurements (KCE-system FPW). Identical sintering cycles were employed for both doping techniques, in order to allow a direct comparison. FT-IR spectra were obtained by a Digilab FTS 15/80 spectrometer in the range of 4000–600 wavenumbers in reflection mode. XPS spectra were monitored by a Leybold AS spectrometer (Mg-K_α and Al-K_α radiation).

The Y_2O_3 distribution in the Si_3N_4 powder compacts was characterized by SEM equipped with an energy-dispersive X-ray spectrometer (EDX; Tracor, Noran) in conjunction with TEM equipped with an EELS system. SEM measurements were carried out using a Jeol JSM 6400, while TEM investigations were performed on a Philips CM20FEG (field emission gun) instrument, operating at 200 kV (point resolution = 0.24 nm). The TEM microscope was fitted with an EELS-spectrometer (parallel detection, Gatan, Model 666).

3. Results

The Si_3N_4 powders Tosoh TS-10 and Denka SN-9FWS used in this investigation are quite different regarding their synthesis method (diimide precipitation vs. direct nitridation with additional HF-cleaning of the oxidized surface). Analytical data, given by the manufacturers, are summarized in Table 1.

The Denka powder (direct nitridation) reveals a lower total oxygen content, as compared to the Tosoh powder. The XPS spectrum shows only a minor oxygen O1s peak intensity, but an additional fluorine peak with noticeable intensity and nearly no OH vibration band in the FT-IR spectrum, as given in Fig. 1. The fluorine content is a consequence of the subsequent HF-treatment, also eliminating silanol surface groups. Skeletal vibrations near 1000 cm^{-1} [38–42] show a minor intensity for Si–O–Si compared to Si–N–Si groups. The oxygen concentration does not strongly decrease during ion sputtering, which indicates a homogeneous distribution within the Si_3N_4 lattice. For this powder a lack of surface bonded oxygen and the absence of reactive surface groups is noted, although the total oxygen content of the powder is similar to the diimide powder (1.1 vs. 1.5 wt.%, compare also Table 1). The particle morphology is globular with a rather wide particle size distribution ranging from 10 to 1000 nm.[33] The Denka powder, and in general powders from direct nitridation, reveal a high amount of oxygen within the α-Si_3N_4 crystal lattice up to 1.0 wt.%.[43–46]

For the Tosoh TS-10 powder (diimide precipitation) a relatively high number of OH groups and a localization

Table 1
Powder characteristics of the two Si_3N_4 starting powders

Powder	Tosoh TS-10	Denka SN9FW
Synthesis method	Diimide precipitation	Direct nitridation
Oxygen content (wt.%)	1.5	1.1
Surface area (m^2/g)	14.3	12.5
Metallic impurities (wt.%)	<0.03	<0.4
$\alpha(\alpha+\beta)$ (%)	96	92

of oxygen at the particle surfaces was found by FT-IR, XPS and TEM investigations. FT-IR spectra reveal an pronounced vibration band due to the stretching mode of O–H bonds at 3750 cm^{-1} [see Fig. 1(a)]. XPS spectra show a relatively high intensity of the O1s peak, which decreases rapidly with continuous sputtering time (depth profile measurements), as compared to the nitrogen N1s peak.

The spectroscopic data clearly show that in the case of the Tosoh powder (and in general for diimide powders[37]) a higher volume fraction of oxygen is bonded to Si_3N_4 in a near-surface region (outer shell). This oxidized surface layer (with a relatively high SiO_2 concentration) is advantageous for thermal densification, because a higher number of reactive silanol groups are present, which yield homogeneous doping with the organometallic precursors. In contrast, the addition of Y_2O_3 powder results in a localized concentration of the sintering aid (compare Fig. 2).

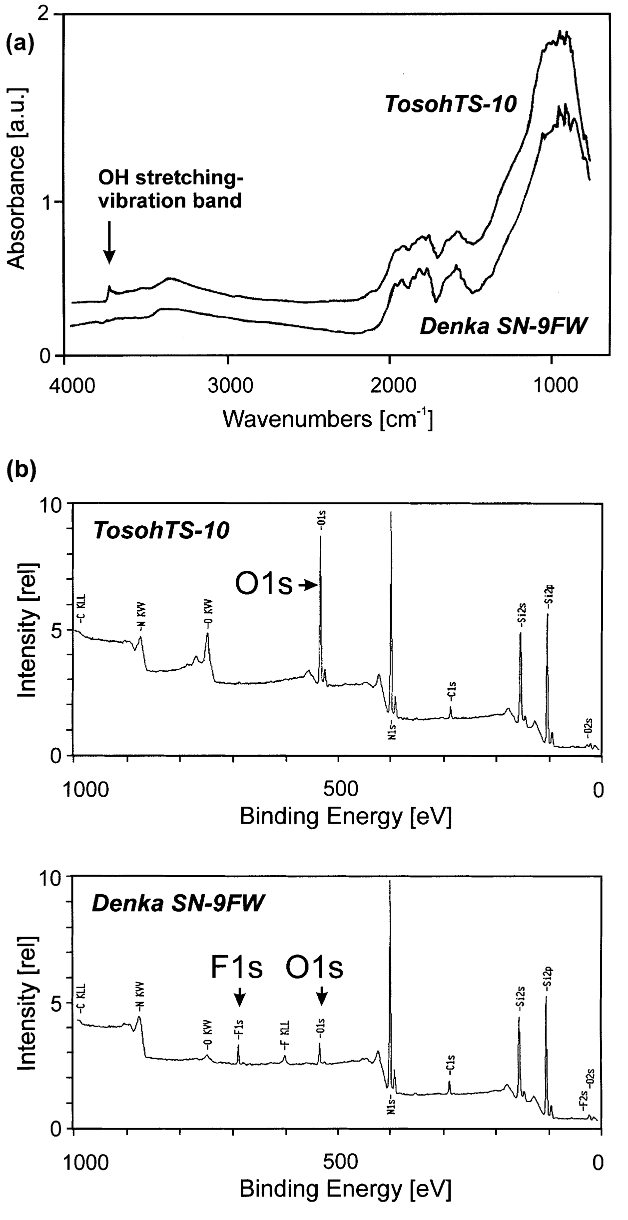

Fig. 1. (a) FT-IR and (b) XPS spectra of the two as-received Si_3N_4 powders Tosoh TS-10 (diimide precipitation) and Denka SN-9FW (direct nitridation) studied. Note that fluorine was only observed in the Denka powder (HF-leaching).

Gas-pressure sintering combined with in-situ dilatometry was performed to investigate the thermal densification behavior. Diimide powders stand out for their high potential for chemical doping, due to their higher number of silanol surface groups. Therefore, the analysis of the sintering behavior shown here concentrates only on the Tosoh powder samples doped with 7.7 wt.% Y_2O_3. It should be noted that when adding 2.5 or 4.0 wt.% yttria, no difference in densification behavior as well as final microstructure was monitored (compare also Table 2). Therefore, we here focus only on those samples doped with 5 vol.% additive (equivalent to 7.7 wt.%), which however are representative for the general trend observed.

The values of total densification are about the same for the two doping methods (compare Table 2, final density). As given in Fig. 3, the first densification maximum is slightly shifted to higher temperatures, when Y-methoxyethoxide is used as additive, as compared to the same concentration of metal oxide powder. The diagram also shows a slightly enhanced densification rate at lower temperatures for samples with organometallic doping (faster initial densification rate at ≈1550 °C). This enhanced densification rate in the early stage of sintering (shift of the sintering onset to a lower temperature) is due to the homogeneous distribution of the sintering aid, which consequently lowers the affective diffusion distance. When the eutectic temperature of the Si_3N_4–SiO_2–Y_2O_3 system is reached, capillary forces favor a fast (and homogeneous) distribution of the sintering aid throughout the ceramic body. As a consequence,

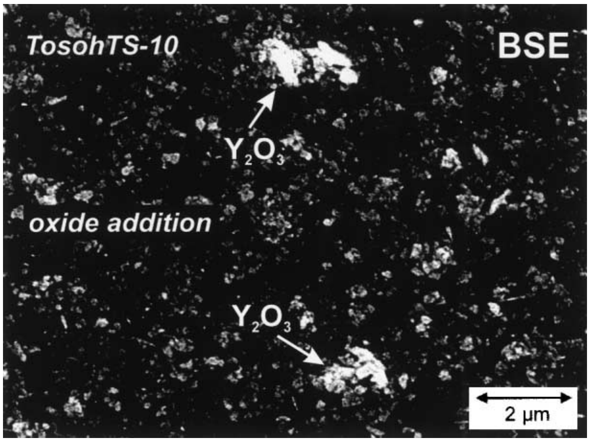

Fig. 2. SEM micrograh of the powder compact (Tosoh TS-10) with 7.7 wt.% Y_2O_3 powder addition. Since back scattered electrons (BSE) were monitored, the local inhomogeneous distribution of the sintering aid becomes obvious.

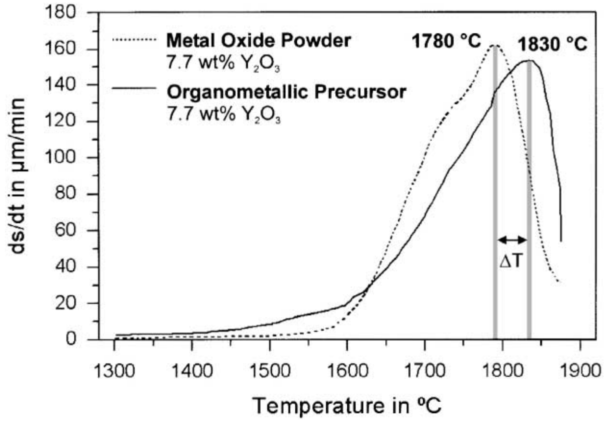

Fig. 3. In-situ dilatometry data (ds/dt vs. temperature) of the Si_3N_4 powder Tosoh TS-10 doped with 7.7 wt.% Y_2O_3. Employing organometallic doping, two distinct differences are seen compared to metal oxide addition: (i) shift of the onset of sintering to lower temperature (≈1550 °C) and (ii) shift of the first densification maximum to a higher temperature (1780 vs. 1830 °C).

local rearrangement and densification is promoted at a relatively low temperature.

Upon densification, the resulting microstructure was characterized by SEM. Fig. 4 shows the polished and plasma-etched surface of both Y-doped Si_3N_4 materials. Employing organometallic doping yields a slightly finer microstructure, as compared to metal oxide powder addition. However, the overall microstructure evolution of the two materials is rather similar, so that no marked variations in corresponding mechanical properties are expected.

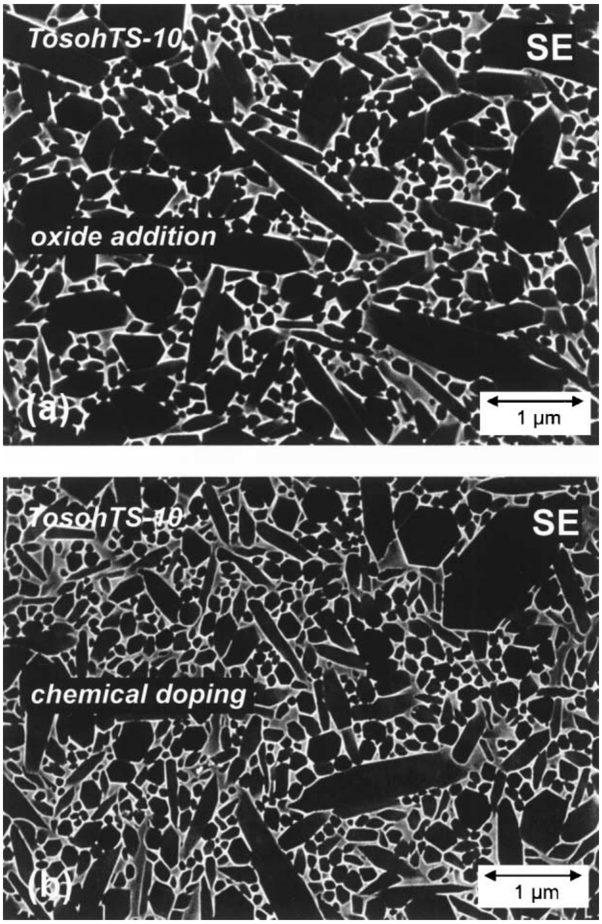

Fig. 4. SEM images of polished and plasma-etched surfaces of the dense Si_3N_4 ceramics sintered at 1830 °C, 1 h, 5 MPa N_2 pressure and doped via (a) metal oxide (Y_2O_3) addition and (b) organometallic presursor (Y-methoxyethoxide).

4. Discussion

Si_3N_4 powders synthesized by direct nitridation have in principal good properties for thermal densification such as a wide particle-size distribution and a favorable particle morphology. However, in the case of the Denka powder, a removal of the surface oxygen (HF-treatment) hinders thermal densification even under supplement of sintering aids.[27] Hence, oxygen distribution within the Si_3N_4 particle (crystal lattice vs. surface coating) dominates densification. In nitrided powders, up to 1.0 wt.% of oxygen is commonly dissolved within the Si_3N_4 crystal lattice,[44–46] but no oxidized surface layer was observed. As a consequence, although the total amount of oxygen would be sufficient for rapid densification, such a powder cannot be densified even when employing a higher volume fraction of sintering aid. Therefore, organometallic doping showed in general no advantage as compared to metal oxide addition; the samples simply revealed a high amount of residual porosity.

Silicon nitride powders synthesized by diimide precipitation reveal a higher potential for chemical doping, because of their relatively high number of reactive OH groups at the particle surface, in contrast to powders

Table 2
Comparison of density values and first sintering maximum of the two materials doped by metal oxide powder and organometallic precursor

Tosoh TS-10	Metal oxide powder			Organometallic precursor		
Wt.% Y_2O_3	Green density (g/cm^3)	Final density (% th.d.)	First max. (°C)	Green density (g/cm^3)	Final density (% th.d.)	First max. (°C)
1.0	1.65	83.8	1837	1.73	87.2	1835
2.5	1.64	98.6	1785	1.71	99.2	1808
4.0	1.71	98.7	1785	1.71	98.9	1834
7.7	1.72	98.5	1780	1.69	98.8	1830
10.5	1.70	87.5	1718	1.62	89.6	1714

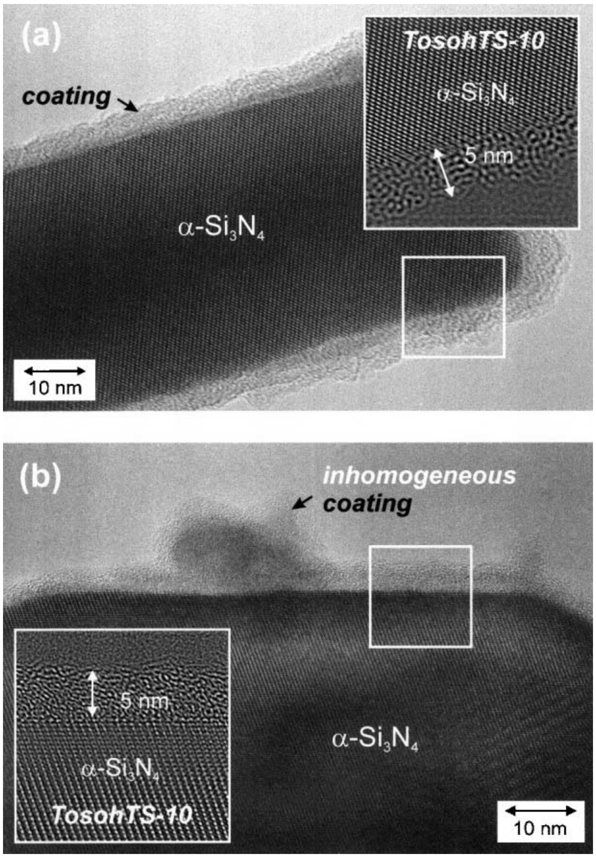

Fig. 5. TEM micrographs (high-resolution images) of doped Si_3N_4 powder particles (Tosoh TS-10) revealing a continuous thin coating (5 nm thickness) with the sintering aid on the particle surface: (a) Si_3N_4 powder particle doped with 7.7 wt.% Y_2O_3 and (b) with 10.5 wt.% Y_2O_3 addition (both organometallic doping). Note that when a high volume fraction of sintering aid is used, areas with local additive precipitation start to occur.

obtained by direct nitridation. The important parameter here, affecting the efficiency of chemical doping, is the surface density of the OH groups due to a high oxygen concentration at the particle surface. Doping with reactive organometallic compounds leads to a covalent chemical bond between Si–O– and metal oxide, which directly bonds the doping agent to the oxidized surface layer and forms a thin homogeneous surface coating, as depicted in Fig. 5. However, the addition of a higher volume fraction of organometallic precursor (e.g. 10.5 wt.%) leads to a local precipitation of amorphous metal oxide clusters on Si_3N_4 particles [see also Fig. 5(b)], because in this case there are not sufficient silanol groups at the near-surface region.

SEM imaging of the dense sampled revealed a slightly finer microstructure when utilizing organometallic doping. Since homogeneous distribution of the sintering aid (organometallic precursor) resulted in a higher densification rate at the early stage of sintering, one would expect just the opposite, a coarser final microstructure. However, since the first densification maximum was shifted to a higher temperature (1780 vs. 1830 °C, see also Fig. 3), the positive low-temperature effect is counterbalanced. It is assumed that residual carbon contamination as a residue from the organometallic precursor limits densification at high temperature and, therefore, results in both a retardation of the high-temperature sintering process and the evolution of a finer microstructure, as shown in Fig. 4. The latter observation is rationalized by the fact that the total affective time for grain growth at high temperature is reduced, due to this slightly retarded densification process.

5. Conclusions

After calcination at 800 °C, organometallic doping yields a yttria layer at the surface of the ceramic particle. XPS in conjunction with TEM revealed that each single powder particle is coated by a thin amorphous metal oxide film. Therefore, chemical doping of diimide powders, which reveal a sufficiently high number of silanol surface groups, leads to a homogeneous distribution of sintering aids (even of a small amount) within the powder compact, which cannot be achieved by adding metal oxide powders and subsequent ball-milling. This homogeneous additive distribution reduces the affective diffusion length in the early stage of sintering and enhances densification at a relatively low temperature ($\approx$1550 °C). Moreover, in-situ dilatometry studies during gas-pressure sintering showed that the sintering behavior (e.g. temperature of the first densification maximum and final density) is slightly enhanced by using Y-organometallic compounds, as compared to doping with metal oxide powder. In addition, a slightly finer microstructure was observed, when employing organometallic precursors, which was rationalized by the presence of residual carbon retarding both densification and grain growth. It should be emphasized that, since this doping technique is very sensitive to the Si_3N_4 particle surface (i.e. the amount of silanol surface groups), it is not directly applicable to any kind of Si_3N_4 powder. For example, when using nitrided Si_3N_4 powders, a pre-oxidation treatment is required prior to organometallic doping, because such powders typically do not show a high oxygen concentration at the particle surface and therefore no silanol groups.

It has to be concluded that organometallic doping only represents an alternative doping method (i) when suitable Si_3N_4 powders are utilized and (ii) when the amount of sintering aid is above a threshold value of 2.0 wt.%, which allows to complete the surface reaction.

Acknowledgements

The authors would like to thank the AiF (applied industrial research agency) for financial support throughout the work.

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