The Determination of Oxygen in Si_3N_4 Powder

G. Kaiser & H. Schubert

Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaft, Pulvermetallurgisches Laboratorium, Heisenbergstrasse 5, 7000 Stuttgart 80, Germany

Abstract

The oxygen content of Si_3N_4 starting powders and the uptake of oxygen during processing affect the formation and composition of the glassy phase, and of a possible crystalline phase, and hence the densification and the properties of the material. The determination of oxygen, not only in raw and starting materials but also during processing, is therefore of the utmost importance. In the individual steps of powder processing, oxygen is taken up from various sources in different forms of binding.

The sintering process is mainly influenced by oxygen which is bound to the solid. Powder processed samples, however, also contain surface active compounds, i.e. deflocculants (aminoalkanols, polycarbonic acids), binders (polyvinyl alcohol, cellulose ester, polyvinylpyrrolidone), pressing aids (polyethylene glycol, glycerine), and residual water and alcohols. The uptake of oxygen and of water during processing is monitored by carrier gas hot extraction analysis using commercially available gas analysers, and interest is particularly focused on the determination of total oxygen contents, on systematic errors inherent in the determination and on the differentiation of the individual oxygen-containing species, i.e. weakly bound, oxidic and lattice oxygen.

Der Sauerstoffgehalt von Si_3N_4-Ausgangspulvern und die Sauerstoffaufnahme während der Pulververarbeitung beeinflußen die Bildung und die Zusammensetzung der Glasphase und einer möglichen kristallinen Phase und damit auch das Verdichtungsverhalten und die Eigenschaften des Werkstoffes. Die Bestimmung von Sauerstoff nicht nur in den Roh- und Ausgangsstoffen, sondern auch während der Verarbeitungsvorgänge, ist deshalb von äußerster Bedeutung. Während der einzelnen Schritte der Pulververarbeitung wird Sauerstoff ausgehend von verschiedenen Quellen und in verschiedenen Bindungsformen aufgenommen.

Der Sinterprozeß wird hauptsächlich durch aufgenommenen Sauerstoff, der an die festen Phasen gebunden ist, beeinflußt. Pulverproben hingegen enthalten aber oberfächlich aktive Verbindungen, wie Entflockungsmittel (Aminoalkanole, polykarbon säuren), Binder (Polyvinyl alkohol, cellulose-Ester) und Preßhilfen (Polyethylenglykol, Glyzerin), und Restwasser und -alkohol. Die Sauerstoff- und Wasseraufnahme während der Materialverarbeitung wird mittels Trägergas-Heiß-Extraktions-Analyse verfolgt, wobei handelsübliche Gasanalysatoren verwendet wurden. Besonderes Interesse wird auf die Bestimmung des Gesamtsauerstoffgehaltes, auf systematische Fehler, welche mit der Sauerstoffbestimmung einhergehen und auf die Unterscheidung der einzelnen Sauerstoff enthaltenden Spezies, d.h. schwach gebundenen, oxidischen und im Gitter gelösten Sauerstoff, gerichtet.

La teneur en oxygène initiale d'une poudre de Si_3N_4 et l'absorption de cet élément pendant le traitement affectent la formation et la composition de la phase vitreuse ainsi que celle d'une possible phase cristalline et donc aussi la densification et les propriétés du matériau. La détermination du taux d'oxygène, non seulement dans les matières premières mais aussi pendant le processus d'élaboration, est par conséquent d'une extrême importance. En effet, à chaque étape du traitement de la poudre, l'oxygène peut être incorporé dans la masse céramique à partir de diverses sources et résulte dans différents types de liaisons.

Le processus de frittage est surtout influencé par l'oxygène qui est lié au solide. Toutefois, les échantillons de poudre prélevés durant l'élaboration contiennent aussi des tensio-actifs, c'est-à-dire des défloculants (aminoalcools, acides polycarboxyliques), liants (alcool polyvinylique, ester cellulosique, polyvinylpyrrolidone), lubrifiants (polyethylène glycol, glycérine), et résidus d'eau et d'alcool. L'absorption d'oxygène et d'eau pendant le traitement a été analysée et contrôlée par une technique

d'extraction à chaud par un gaz porteur, en utilisant des analyseurs de gaz classiques commerciaux. Notre intérêt s'est concentré particulièrement sur la détermination de la teneur totale en oxygène, sur les erreurs systématiques inhérentes à la technique de mesure et sur la différenciation des espèces contenant de l'oxygène prises individuellement, c'est-à-dire celles liées faiblement, l'oxygène de réseau et celui présent suite à l'oxydation.

1 Introduction

1.1 Properties and sintering behaviour of Si_3N_4

Sintered Si_3N_4 ceramics requires the presence of oxidic sinter additives to form a binary or, more often, ternary eutectic melt.[1-3] These additives (Y_2O_3, Al_2O_3, MgO, Yb_2O_3) react with the intrinsic oxygen content which is present at the surface of any commercial Si_3N_4 powder.

The composition of the melt depends therefore both on the sinter additive weight and on the oxygen content of the Si_3N_4 powder. They also determine sinterability, phase composition and properties of the final material. Therefore a reliable method for the determination of oxygen, both in the powder and during processing, is mandatory.

The difficulty in the determination of oxygen is traced to the numerous sources in high surface area Si_3N_4 powders. Oxygen appears in various types of binding and originates from the Si_3N_4 powder, the sinter additives and from organic processing aids (binders, deflocculant), as well as from residual solvents (alcohol, water). This subject is discussed in the following sections.

1.2 Occurrence of oxygen in different forms

In the Si_3N_4 starting powder, oxygen occurs in various forms: on the surface as an oxide and weakly bound as e.g. silanol, siloxamine or oxynitride,[4] as
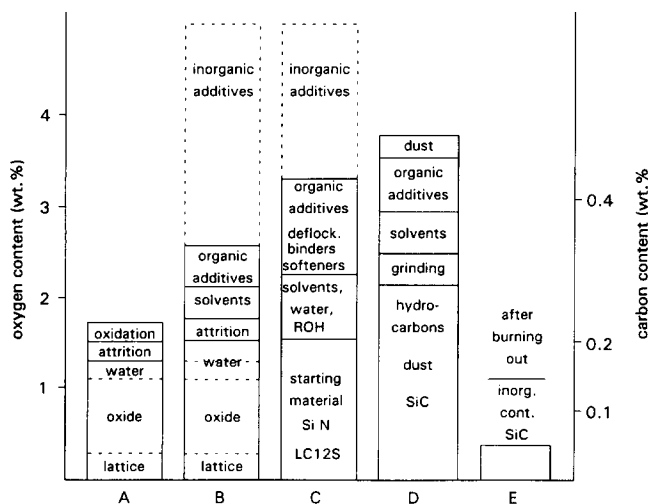

Fig. 1. Sources for the uptake of oxygen and carbon during processing of Si_3N_4.

lattice oxygen, as a component of sinter additives (Al_2O_3, MgO, Y_2O_3, Yb_2O_3, Nd_2O_3) and in the form of water. In processed powder, residues from solvents, e.g. alcohols and reaction products (esters),[5] from deflocculants, e.g. aminoalkanols and polycarbonic acid,[6] from binders, e.g. polyvinyl alcohols (PVA), polyvinylpyrrolidone (PVP), cellulose esters and polyvinyl butyral (PVB), and from pressing aids, e.g. polyethylene glycol (PEG) and glycerine, contribute to the total oxygen content. In column C of Fig. 1 the starting components are listed which affect the oxygen (columns A, B) and carbon (columns D, E) contents. On the ordinates the rough concentrations for oxygen (A, B) and carbon (C, D) are given for orientation.

1.3 Uptake of oxygen during processing

The starting powders are agglomerated in the as-received state. Thus, milling and grinding is applied to achieve complete deglomeration and a homogeneous dispersion of the sinter additives. During the milling and grinding processes, the surface of the powder increases owing to the deglomeration and to the grinding of the crystallites, as a result of which the oxygen content increases by hydrolysis and by adsorption of polar liquids and compounds already mentioned. While the weakly bound oxygen-containing adsorbates can be substantially removed in a burn-out step at 500°C, the hydrolysis products remain in the sample and affect the sinter behaviour and the properties of the material. When analysing the samples for oxygen in the course of the process, the differently bound oxygen-containing species have been taken note of in order to detect the effective oxygen content.

2 Experimental

2.1 Powders and reagents

2.1.1 Powders

The investigation of the effect of water, alcohol and water/deflocculant mixtures on the determination of oxygen were carried out with Si_3N_4 type LC12S Lot No. 102/90 (H. C. Starck, Goslar, Germany). Various powders from different manufacturers were used (Table 1) to compare the individual oxygen contents. Doubly distilled water and 2-propanol were used as solvents, an aminoalkanol type KV 5088 (Zschimmer & Schwarz, Lahnstein, Germany) as a deflocculant, and fine-grained alumina type AKP30 (Sumitomo Chemical, Japan) and Y_2O_3 fine grade (H. C. Starck, Goslar, Germany) were used as sinter additives.

2.1.2 Reagents

All reagents were of analytical grade (E. Merck, Darmstadt, Germany) and all gases were obtained

Table 1. Starting materials and treatment

Number	Type	Preparation route	Treatment
1	LC12S[a]	Direct nitridation	Raw material
2	LC12S	Direct nitridation	1 h tumbling in 2-propanol, drying in air at 70°C
3	LC12S	Direct nitridation	1 h tumbling in water, drying in air at 70°C
4	LC12S	Direct nitridation	1 h tumbling in water deflocculant[f] mixture, drying in air at 70°C
5	LC12S	Direct nitridation	No. 4, burned out at 500°C
6	LC12S	Direct nitridation	Oxidized at 1000°C/1 h, reacted at 1800°C/10 h/N₂
7	LC12S	Direct nitridation	Reacted at 1800°C/10 h/N₂
8	LC12SX[b]	Direct nitridation	Raw material
9	GP 1[c]	Gas phase reaction	Raw material
10	GP 2	Gas phase reaction	Surface oxygen reduced
11	ESP[d]	Di-imide	Raw material
12	E 10[e]	Di-imide	Raw material

Note: The specimen number will be henceforth referred as depicted in this table.
[a] H. C. Starck, Goslar, Germany, Lot 102/90 1-2.
[b] H. C. Starck, Goslar, Germany, Lot 151/90.
[c] Bayer AG, Ürdingen, Germany, Lot 14/9.
[d] UBE, Japan, Lot S91032.
[e] UBE, Japan, Lot A610252.
[f] Zschimmer & Schwarz, Lahnstein, Germany, KV 5088, 5 wt%.

from Messer Griesheim, Düsseldorf, Germany, if not stated otherwise. For the determination of C and H_2O, the oxygen and nitrogen were 99·995% pure, and for the determination of oxygen He 99·996% was used. The powder was weighed in a Ni or Sn capsule (Lüdi, Flawil, Switzerland) and, as additive for the differentiation of oxygen species, graphite powder (Part No. 501-073, Leco Instrumente, Kirchheim b. München, Germany) was used. As standard reference materials for the determination of water, $CaSO_4.2H_2O$ and $Li_2SO_4.H_2O$ were used. For the determination of oxygen, annealed ZrO_2 Art. No. 400300 (Johnson Matthey) and SiO_2 (rock crystal) Art. No. 530-225 (HRT Labortechnik, Kirchheim b. München, Germany) and steel pins Art. No. 501-553 (Leco Instrumente) were used.

2.2 Powder processing

Milling was performed in a continuously working attritor-type mill with a polyethylene rotor and Si_3N_4 stator (type RSK 05/15, Matter & Partner, Buchs, Switzerland) and Si_3N_4 milling balls (Tosoh, Japan). The slurries were spray dried in a parallel flow-type spray dryer (Nubilosa, Konstanz, Ger-

Fig. 2. Applied preparation route and sampling for the processing of Si_3N_4.

many), and isostatically pressed at 200 MPa (oil pressure) type KIP 500E (Weber, Remshalden, Grunbach, Germany). For burning-out of the green compact, a steel muffle furnace type LHT 04/14 (Nabertherm, Lilienthal, Germany) was used. For densification, a graphite heated and insulated gas pressure sintering furnace (type FPW 125/180-2200-100-KS/Sp, KCE Sondermaschinen, Roedenthal, Germany) was used. The process is described in detail elsewhere[7,8] and a flow diagram is given in Fig. 2.

2.3 Determination of water

For the determination of water, a gas analyser equipped with a quartz tube furnace (type CWA 5003, Rosemount Analytical, Hanau, Germany) was used. Sample introduction was done with Al_2O_3–SiO_2 (Pythagoras®, Steinzeugwerke Friedrichsfeld, Mannheim, Germany) and quartz boats. Water is released from ceramic materials by heating a powder sample in a quartz tube furnace to a temperature $\leq 1000°C$, which is unobjectionable to quartz, and detected in an IR absorption cell. The sensitivity of the method depends on the size of the cell. With the analyser available as little as 30 μg can be detected. In routine analysis, the limit of determination depends on the blank value of the boats. Even after a baking-out process at 1000°C, about 70 μg of water on average is taken up again. When using quartz boats, the blank value can be reduced to 10 μg after three heating cycles at about 900°C. Blank values have to be determined prior to each analysis if precision is required. The analyser is calibrated with $CaSO_4.2H_2O$ or $Li_2SO_4.H_2O$. A relative standard deviation of $\leq 1\%$ can be achieved at levels ≥ 1 mg.

The analysis can be run at a fixed temperature or with a temperature ramp which allows assignment

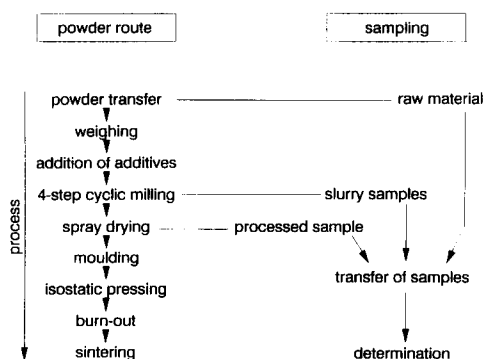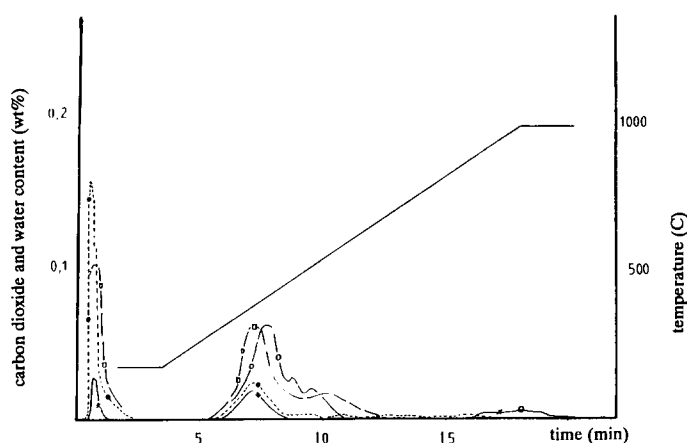**Fig. 3.** Evolution of H_2O (●) and CO_2 (★) with N_2 and with O_2 from Si_3N_4 after treatment with 2-propanol (LC12S, No. 2): □, H_2O; ○, CO_2.

of the evolution of water to a discrete temperature. Thus, conclusions can be drawn as to the origin of the measured water. In most cases physisorbed and chemisorbed water can be distinguished, as can be shown on a Si_3N_4 sample attrition milled in 2-propanol (Fig. 3). In complex systems (water, alcohols and organic remnants) the situation is more complicated as the individual peaks overlap. In some cases a Karl Fischer titrator (Metrohm, Filderstadt, Germany) for the determination of water was used for comparison.

In the analysis of Si_3N_4 the sample weights range from 0·1 to 0·2 g and the relative standard deviation was found to be ≤3% if the quantity of water to be determined is ≥0·3 mg.

2.4 Determination of oxygen
For the determination of oxygen, a gas analyser (type TC 436, Leco Instrumente) was used.

Today, carrier gas hot extraction is the most widely used procedure to determine oxygen in various kinds of matrices. A series of publications appeared on this subject, dealing mainly with the analysis of metallic materials.[9,10] Generally there are two techniques:

Bath technique—in order to remove the blank values the graphite crucible and the metallic additive are preheated and a melt (bath) is formed. The sample is given into this melt.
Flux technique—both additives and sample are fed together into the crucible.

The analysis of ceramics encounters some difficulties as they are poor thermal conductors and in many cases are resistant to high temperatures. Therefore the sample is nearly always heated in a graphite crucible with metallic additives, e.g. Ni, Sn, Cu and Pt, in which the sample dissolves and enables a better reaction of oxygen with the graphite to CO. Both flux and bath technique can then be applied.

The flux technique, in which the sample is fed together with the additive into the crucible, is preferable because the bath technique, although ensuring a substantial removal of the blank, yields considerably lower oxygen contents depending on the additive.[11] From the many crucibles which are commercially available today, the cup-shaped type (EK 50, Rosemount Analytical, Hanau, Germany) has proved specially advantageous for the analysis of ceramics as temperatures as high as about 2900°C can be achieved.

In the analyser used in this study the formed CO is oxidized by CuO on the rare earth carrier at 600°C to CO_2, which is detected in an IR absorption cell down to 0·5 μg. The relative standard deviation was found to be ≤1% in the 20–500 μg range. The system is calibrated for oxygen with dried solid standards, i.e. ZrO_2, SiO_2, Bi_2O_3 and CuO. The results compare well with standard reference steel 501-553 (see reagents). It has to be mentioned, however, that sometimes outliers occur which cannot be explained as yet.

3 Results and Discussion

3.1 Characterization of some commercial Si_3N_4 powders
In order to obtain information on the oxygen contents of various powders, specimens of different manufactures and different preparation procedures (Table 1) were analysed for oxygen and water. Differing concentrations occur depending on the preparation process. Thus, for instance, a gas phase reacted powder (GP 1) has a relatively high oxygen content (Table 2) and a relatively low C content (Table 3). For sample GP 2—a batch which was especially reduced in surface oxygen content—the situation was just reversed.

In some cases a considerable deviation of the oxygen values from the manufacturer's specification was found. The difference might be due to a relatively high water content, which may scatter from batch to batch depending on storage conditions and thus to an ageing process. The situation

Table 2. Oxygen and water contents of some commercial powders (numbers in wt%, C = concentration, S = standard deviation)

Number	Type	Oxygen		Water	
		C	S	C	S
1	LC12S	1·49	0·015	0·48	0·015
9	GP 1	1·29	0·04	0·30	0·009
10	GP 2	0·4	0·01	0·19	0·011
11	ESP	1·02	0·04	0·305	0·011
12	E 10	1·11	0·02	—	—

Table 3. Carbon content of some commercial powders (numbers in wt%, C = concentration, S = standard deviation)

Number	Type and treatment	HF furnace		Tube furnace	
		C	S	C	S
1	LC12S	0·16	0·003	0·033	0·008
2	LC12S + water	0·31	0·100	0·100	0·007
3	LC12S + 2-propanol	0·216	0·007	0·127	0·002
9	GP 1	0·052	0·003 7	0·005	0·000 8
10	GP 2	0·191	0·001 3	0·08	0·001
11	ESP	0·215	0·009 3	—	—
12	E 10	0·149	0·006 2	—	—

cannot be helped by drying the powder at a given temperature prior to the oxygen determination as water can only be substantially removed at higher temperatures depending on the sample (Fig. 4) at the risk of increasing the oxygen content. A sample dried at 500°C for 1 h in flowing oxygen still contains 0·2% water. In this drying step the oxygen content rises by about 0·15 wt% (relative about 10%).

3.2 Determination of oxygen originating from different forms of binding

Almost all powder ceramic samples contain water (Table 2) which reacts with the hot graphite to give CO and H_2, as could be shown by addition of small volumes of water (dispensing 0·5 μl with a micro-syringe into a Ni capsule). The recovery of the added water was found to be between 90% and 94% when feeding the sample into a hot crucible (furnace setting: 4·0 kW outgassing, 3·8 kW analysing). If the sample is fed into a cold crucible, i.e. the temperature of the crucible is decreased after the outgassing step to about 50°C, only 8–12% of the added water is recovered (furnace setting: outgassing at 4·0 kW, analysis from 0·5 kW [analyse low*] to 3·8 kW [analyse high]). In the latter case, water escapes before it can react with hot graphite. When using the appropriate temperature setting, it is possible to analyse the specimen for oxygen with or without detecting the greatest part of the adsorbed water. No significant difference in total oxygen contents was established when heating the sample with a fast (maximum 225 units/s, corresponding to about 800°C/s) or a slow (minimum 1 unit/s, corresponding to about 4°C/s) heating rate.

During outgassing of the crucible the sample finds itself in the lock which is placed directly above the electrode furnace. At this stage already volatile components can partly be released by heat radiation. This might also be a reason for the scattering results obtained in the analysis of powders processed with organic additives. This is probably due to organic

components which reach the catalyst furnace, where they are oxidized to CO_2.

When a temperature ramp is applied to the sample without using metallic additives, different oxides[9] and differently bound oxygen can be distinguished depending on its thermal resistance. This technique has already been applied to AlN[12,13] and to Si_3N_4[13] for the determination of lattice oxygen. In this process the sample (5–10 mg) is blended with graphite powder (about 100 mg) to improve the contact of the sample with graphite. Blank values in the procedure have, of course, to be considered. The quantification of the individual oxygen components is, however, problematic as the resolution of the peaks is very poor when applying a linear temperature ramp. When using a step ramp the resolution of the peaks can be improved (Fig. 5). In this mode the power setting of the furnace is, however, the crucial point. Although the power setting for the evolution of the lattice oxygen can be correlated with the evolution of nitrogen (Fig. 6), the quantification is problematic, too, as the crucibles, even from the same lot, do not have the same thermal conductivity, giving rise to changes in temperature and thus to irreproducible results. The best results were obtained when using a linear ramp in the temperature sustain mode applying the following setting: outgassing 810 A (about 4·0 kW); analyse low 250 A
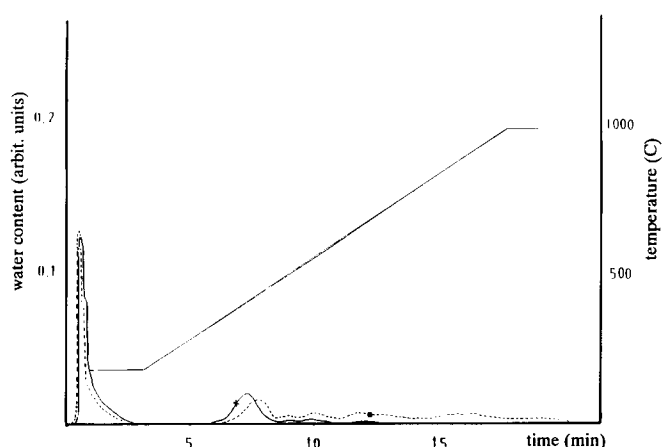
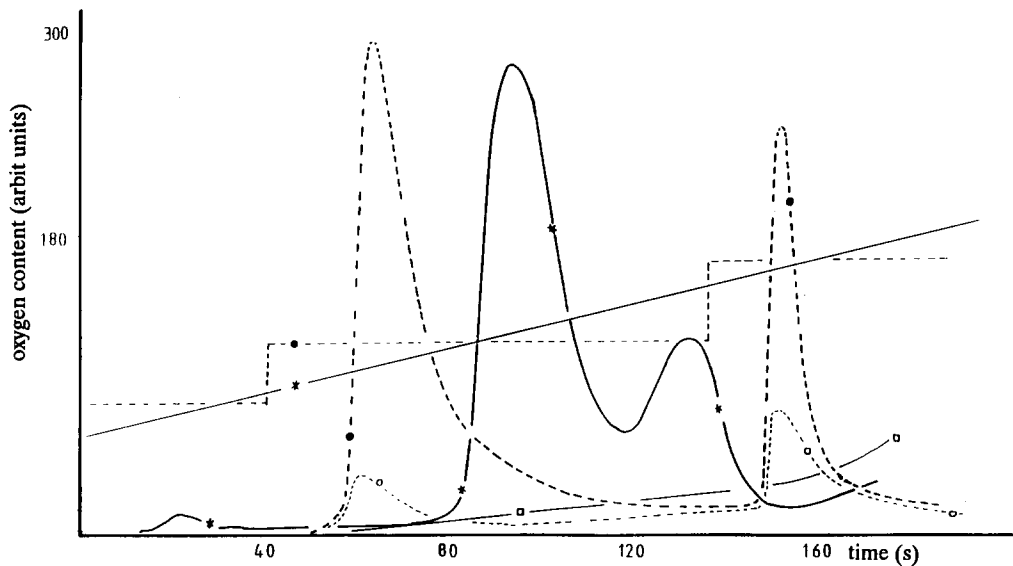**Fig. 4.** Evolution of H_2O from Si_3N_4 (LC12S, No. 1): ★, N_2-stream; ●, O_2-stream.

Fig. 5. Evolution of O_2 from Si_3N_4 (LC12S, No. 1) by linear and by step ramping: ★, linear ramp; ●, step ramp; □, blank linear; ○, blank step.

(about 0·5 kW); ramp 3 units/s where the linear heating stops at a given change in slope of the signal curve and sets in again after the point of inflection of the peak is reached (temperature sustain mode for Leco TC 436; furnace setting: outgassing 810 A (about 4·0 kW); analysing: about 0·5 kW followed by a ramp of 3 units/s*).

In Table 4 the distribution of differently bound oxygen for some Si_3N_4 powders is compiled. The results can only be considered as an aid for orientation. In some cases the relative standard deviation can amount to 20%. Even though the results reveal a wide scatter they give indications of the origin and the treatment of the sample. Samples 6 and 7, which were subjected to a differing temperature treatment (sample 6: 1800°C for 10 h, 0·1 MPa nitrogen pressure; sample 7: annealing in air

*These units refer to the Leco TC 436 apparatus.

at 1000°C for 1 h then at 1800°C for 10 h, 0·1 MPa nitrogen pressure),[14] show an essentially higher lattice portion and a lower oxide portion compared with the starting material. From both samples the same evologram was obtained (Fig. 7). The lattice oxygen content of GP 1 and GP 2 was expected to be similar, but the surface oxygen to be different as GP 2 was subjected to a reductive treatment. It seems that the lattice oxygen is also affected by this process.

3.3 Analysis for oxygen during processing
The experience gained in the analysis of starting materials was transferred to the determination of oxygen in samples obtained from processing (Fig. 2).

In order to investigate the influence of solvents and organic additives on the oxygen content, a pure powder (LC12S) was treated with 2-propanol, water and a deflocculant (KV 5088) dissolved in water. The
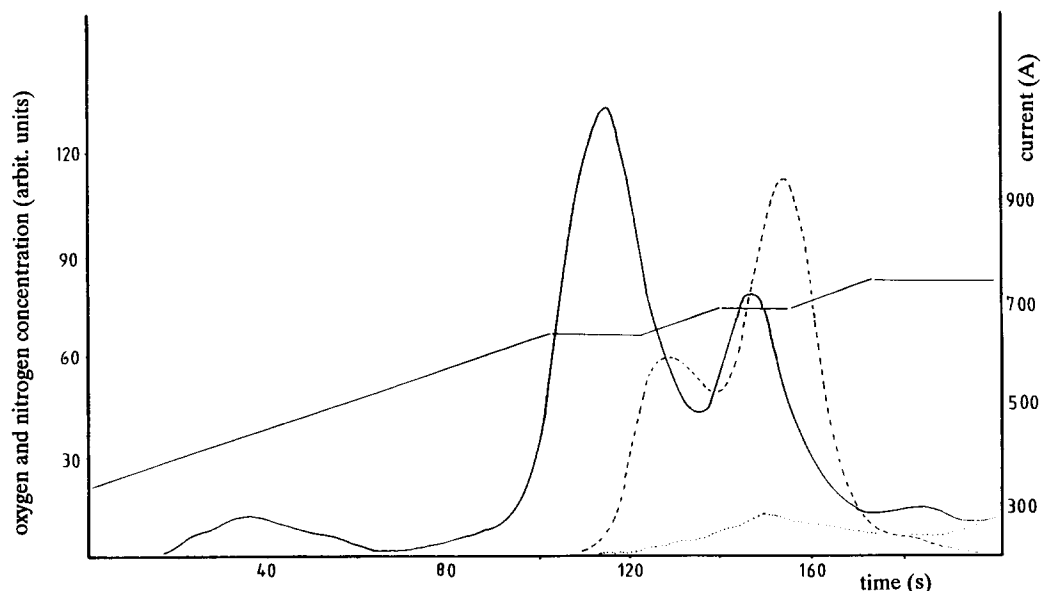

Fig. 6. Evolution of oxygen and nitrogen from Si_3N_4 (Ube ESP, No. 11): ——, oxygen; – – –, nitrogen; · · · ·, oxygen blank.

Table 4. Distribution of surface and lattice oxygen (numbers in wt%)

Number	Type	Oxygen content		
		Surface	Lattice	Total
1	LC12S	1·10	0·28	1·50
6	LC12S[a]	0·065	0·35	0·53
7	LC12S[a]	0·07	0·35	0·52
8	LC12SX	1·15	0·25	1·55
9	GP1	0·75	0·25	1·30
10	GP2	0·25	0·04	0·40
11	ESP	0·65	0·20	1·10
12	E10	0·70	0·20	1·15

[a] See Table 1.

resulting suspension was dried prior to analysis in a drying cabinet at 70°C for 18 h. Nevertheless, the samples contain irreproducible quantities of water or alcohol (Fig. 4) which affect the oxygen determination (see Section 3.2).

A differentiation of weakly bound and chemisorbed oxygen is possible with the furnace settings given in Section 3.2. Reactions are, however, neither complete nor reproducible and account for the serious problems encountered in the precise determination of oxygen in samples containing residues from solvents and additives. Table 5 and Fig. 8 show that the oxygen contents of differently treated Si_3N_4 powders—series 1—do not differ much from the starting powder if the crucible is cold at the beginning of the analysis (furnace setting: 0·5 kW/ 225 units s^{-2}/3·8 kW), i.e. the sample is fed into the cold crucible and heated with a fast temperature ramp. The relative standard deviation was found to be ≤1·2% (samples 1 and 5) and ≤1·7% (samples 2, 3 and 4), respectively. Without a decrease in the crucible temperature the values are higher and display a large scatter ($s_{rel} ≤ 25\%$) because volatile

Table 5. Oxygen content of Si_3N_4 (LC12S) powders in dependence on treatment and determination technique (hot and cold crucible) (numbers in wt%)

Number	Treatment	Oxygen content			
		Cold crucible		Hot crucible	
		C	S	C	S
As-received samples					
1	None	1·38	0·02	1·48	0·03
2	2-Propanol	1·43	0·03	1·49	0·04
3	Water	1·50	0·04	1·61	0·40
4	Water + deflocculant	1·51	0·04	1·80	0·40
5	No. 4, burned out	1·57	0·02	1·68	0·03
After nine months ageing					
1	None	1·51	0·05	1·61	0·04
2	2-Propanol	1·51	0·04	1·65	0·04
3	Water	1·55	0·02	1·71	0·05
4	Water + deflocculant	1·66	0·02	1·74	0·06
5	No. 4, burned out	1·56	0·05	1·69	0·03

oxygen-containing species do not react reproducibly with the hot graphite and do not reach the catalyst furnace in due time. Sample 5 indicates that the oxygen content rises to 1·57 wt% ($n = 7$) after a burning-out step at 500°C to remove carbon. The standard deviation of the results of this sample is better as volatile compounds and residual organics are removed.

After a storage time of nine months, the oxygen contents of the same samples have changed (Table 5), indicating that an ageing process must have taken place. A part of the weakly bound water must have reacted as the contents, when starting the analysis with a cold crucible, are higher. The scatter of the data was then small again.

Likewise, water and carbon contents increase with the processing steps and with additives (Table 6).
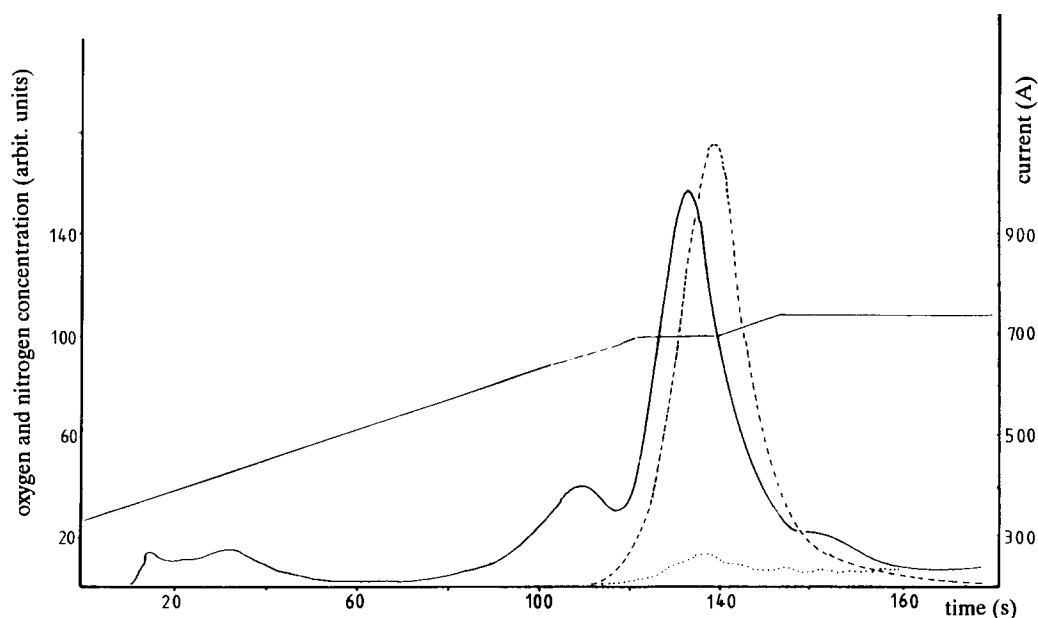

Fig. 7. Evolution of oxygen and nitrogen from heat-treated Si_3N_4 (LC12S, No. 13): ———, oxygen; – – –, nitrogen; ····, oxygen blank.

oxygen content (wt.%)

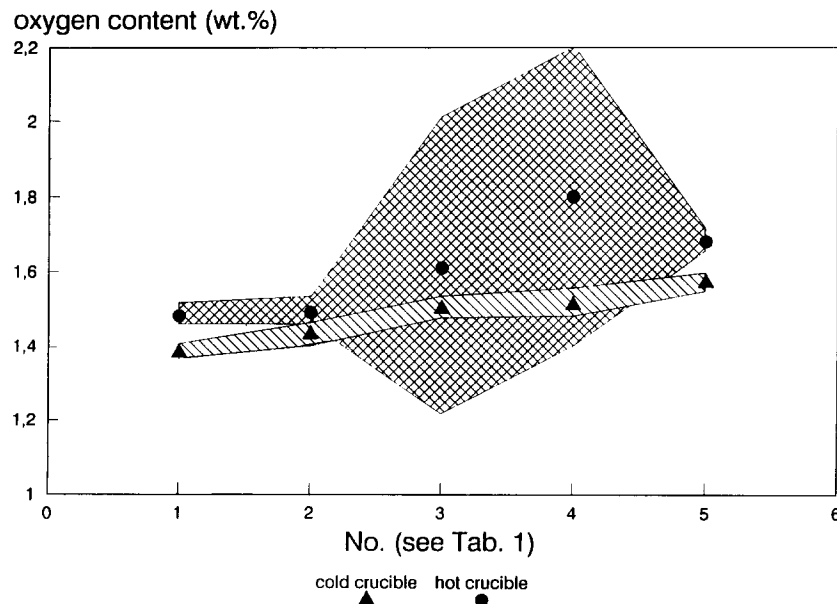

cold crucible   hot crucible
     ▲   ●

Fig. 8. (a) Result of oxygen determination (numbers in wt%) for hot (●) and cold (▲) crucible technique, samples 1–5. The presence of water results in high scatter for hot crucible technique. (b) After ageing for nine months the average level is approximately 0·1 wt% higher, associated with a comparably small scatter.

When using a temperature ramp for the determination of water and N_2 as a carrier gas, distinction between superficially adsorbed (physisorbed) and chemisorbed water is possible. The results for the adsorbed water contents agree exactly with Karl Fischer titration. When using oxygen as a carrier gas in the determination of water the values are higher, which points to the presence of hydrogen-containing species which are decomposed in oxygen atmosphere. When using a temperature ramp this effect is still greater, probably because the residence time of volatile components in the catalyst furnace is longer. This ramp technique cannot, however, be used for the determination of total carbon contents as at the maximum temperature of 1000°C SiC is not completely decomposed, but it provides clues to the presence of various carbon-containing species. For the determination of total carbon contents, the sample was heated in a HF furnace with additives (Fe, W). The results in Table 6 show the same tendency for two batches, but also that handling and drying processes take effect.

In a histogram plot, the individual contributions to the oxygen content of Si_3N_4 are shown when all the analytical methods and techniques used in this study are applied (Fig. 9). From the findings mentioned it can be concluded that the given concentrations of the individual components apply only for a given lot and batch. The oxygen content given in column A is composed of lattice oxygen (1), bound oxygen, e.g. oxide, compounds with Si–O–N bindings (2) and weakly bound oxygen, e.g. H_2O (3, 4) which can be divided into chemisorbed (3) and physisorbed H_2O (4). The hatched area in A corresponds to D. Position 5 indicates the increase in oxygen by the burning-out step. B is somewhat lower than A as H_2O is not completely detected if the analysis is started from a cold crucible.

In the determination of water, the contents are higher when using O_2 (C) instead of N_2 (D) as a carrier gas as carbonaceous components, e.g. hydrocarbons, are burnt in O_2 atmosphere. When using a ramp technique (E) physisorbed (1) and chemisorbed (2) water can be distinguished. The

Table 6. Water and carbon content of differently treated Si_3N_4 (LC12S) (numbers in wt%)

Number	Treatment	Water content					C-content (O_2-stream)
		N_2-stream			O_2-stream		
		T_{fix}	T_{ramp}		T_{fix}	T_{ramp}	
			Total	Ads.[a]			
1	None	0·45	0·44	0·19	0·70	0·90	0·16
2	2-Propanol	0·58	0·71	0·19	0·85	1·08	0·31
3	Water	0·52	0·63	0·18	0·86	1·18	0·22
4	Water + deflocculant	0·91	0·98	0·34	1·35	1·55	0·42

[a] This water contribution is considered to be physisorbed at the powder surface.
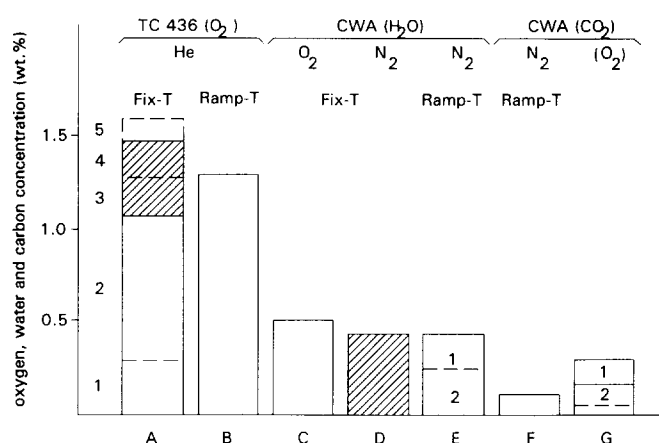
Fig. 9. Distribution of oxygen on various forms of binding in Si_3N_4 (LC12S, No. 1). TC 436 = N/O analyser, Leco; CWA = carbon/water analyser, Rosemount CWA 5003.

total value in this technique is sometimes a little lower, which can be referred to adsorption effects on tubing surfaces.

In the determination of carbon, only carbonate is detected if N_2 is used as a carrier gas (F), whereas in an O_2 atmosphere carbonaceous components are also detected (G). In a ramp technique hints to the occurrence of various species can be obtained (1, 2). The dotted line in (G) indicates the content of residual carbon after a burning-out step which is due to contamination during handling of the sample and to the presence of a small quantity of SiC, which in this case is quantitatively detected with a HF furnace.

4 Summary and Conclusion

Figure 10 shows that there are three general processing situations in which the actual oxygen content is of importance from the standpoint of processing.

To begin with, raw materials have to be character-ized. Usually the Si_3N_4 powders contain oxygen
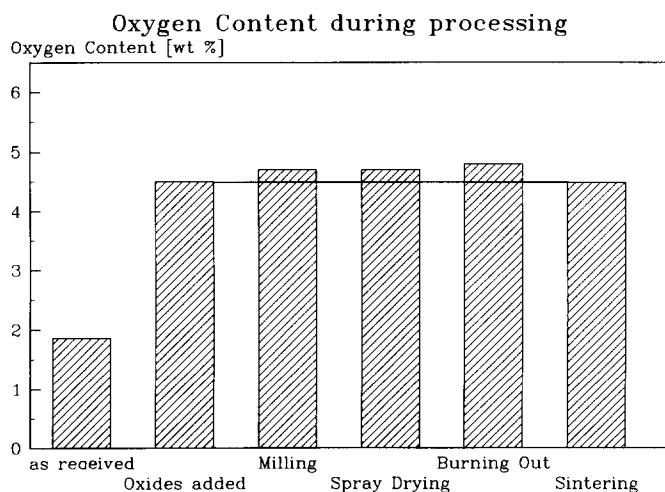

Fig. 10. Oxygen content during processing with Y_2O_3/Al_2O_3 additives.

strongly bound in the lattice and a second part is more loosely bound at the surface. Additionally, there is a considerable amount of water which contributes to the results. This situation can be solved in the best way by running slow temperature ramps. The volatile species, namely water, will be released from the specimen without reacting with the carbon, i.e. the largest part can be removed *in situ* and does not contribute to the results of the determination. Consequently, reliable values with a small scatter are obtained compared to the conven-tional hot crucible technique, as indicated in Table 5 and Fig. 8. The results of the hot crucible technique always appear to be higher. Hence the scatter of the data was found to be high when free water is present in the powders. This is mainly due to the incomplete recovery of the water during measurement. After ageing for longer times (nine months in this work) both the hot and cold crucible techniques give approximately 0·1 wt% higher values, which can be interpreted as a slow hydrolysis of the material. The scatter is then found to be small again.

Furthermore, the slow heating has the advantage of differentiating between surface and lattice oxygen (Table 4), which has, however, to be elaborated carefully. This technique allows the separation of the different oxygen contributions into individual peaks. Unfortunately this step heating programme has to be developed individually for every powder type.

During processing the samples appear as suspen-sions with both sinter additives and organic processing aids, i.e. there are additional contri-butions from the oxides and from the liquids. A large scatter of the results has to be expected if the standard hot crucible technique is applied. If large amounts of organic additives are applied, as is normal in ceramic manufacturing (the use of binders, pressing aids, plasticizers, etc.), the differen-tiation is more complicated. In order to achieve reliable data the organic should simply be burned out in a furnace prior to determination.

Specimens taken after processing (i.e. after spray drying or after pressure casting) have similar compositions to those taken from the suspensions during processing. Again a burn-out of the organics prior to determination is recommended. However, there are reasons to determine the free water content in these powders, because the granulate hardness is related to the moisture content. The binders and pressing aids change their properties considerably as a function of water content. Slow heating in the $C-H_2O$ analyser helps to differentiate between free water and water coming from OH groups of the organics. This topic is subject to further investi-gations.

The quality of the achieved data is good enough to judge the uptake of oxygen during processing, as can

be seen in Fig. 10. The raw powder shows a comparably low oxygen content (column 1), and the addition of the sinter additives increases the oxygen content (column 2). In the next two processing steps (milling and spray drying; columns 3 and 4) the samples contain a significant organic content. Due to the described procedure only a small alteration in the oxygen content occurs. Finally, column 5 shows the oxygen content after burn-out just before firing. The difference between column 5 and column 2 is interpreted as total oxygen uptake for the applied process.

The mentioned analysis techniques were found to give reliable data which could be used to pre-calculate the sample's composition with respect to the oxygen content. Finally, there is the experience that the calculated composition coincides well with the phase diagram and the results of the X-ray phase analysis.

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