

The oxidation of beta'-sialon

Citation for published version (APA):

van Dijen, F. K., & Metselaar, R. (1988). The oxidation of beta'-sialon. *Science of Ceramics*, 14, 327-332.

Document status and date:

Published: 01/01/1988

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

THE OXIDATION OF BETA'-SIALON

F.K. van Dijen and R. Metselaar

Oxidation studies have been performed on β' -sialon, $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$, with different sintering aids. Results are given for oxidation at 1000°C, 1200°C and 1400°C in air or oxygen. At 1200°C the parabolic rate constant is about $5 \times 10^{-13} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-2}$ for oxidation in air for all samples. At 1400°C the rates vary between $k \approx 10^{-11} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-2}$ for 3 wt% La_2O_3 , and $k \approx 10^{-9} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-2}$ for 3 wt% CaO doped sialon. The oxide scale consists of a mixture of mullite, cristoballite and other phases, and is enriched in the metallic component of the sintering aid. In the adjacent sialon surface layer a depletion of the sintering aid is observed. The results are compared with data from literature.

INTRODUCTION

The applicability of structural ceramics at high temperatures is often determined by their oxidation resistance. Since most non-oxide materials are thermodynamically unstable against oxygen or air their lifetime is determined by the formation of a protective oxide scale formed on the surface of the material. Actually the situation is quite comparable with that for metals. Here too the properties of the scale are determined by the composition of the alloy, its microstructure and of course temperature and partial oxygen pressure.

In the case of Si_3N_4 alloys many studies have been performed¹⁻⁷. We will mention here a few results which are most pertinent for our own study on β' -sialon. By far the highest oxidation rates are observed in reaction-sintered materials because of oxidation in the pores until a continuous surface layer of SiO_2 is formed. The lowest rates are observed for Si_3N_4 layers grown by chemical vapour deposition. Such layers are dense and chemically pure. The low oxidation rate is due to the formation of a coherent and protective SiO_2 layer. It has been shown for Si , SiC ^{8,9}, MoSi_2 ¹⁰ and Si_3N_4 that the activation energy for oxidation of these compounds corresponds to that of diffusion of molecular oxygen through a SiO_2 -glass layer. Hot-pressed Si_3N_4 materials occupy an intermediate position. Widely different rates are found in materials with different sintering aids due to the formation of different secondary phases. In general β -sialons seem to show a higher oxidation resistance than compositions close to the Si_3N_4 corner of the phase diagram.

The most recent study of β' -sialon, $\text{Si}_{6-x}\text{Al}_x\text{O}_3\text{N}_{8-x}$, with high x-value, is due to Pomeroy and Hampshire. These authors studied a pressureless sintered sialon with $x = 3$, doped with 3.8 wt% yttria. At 1380°C in air a short incubation time is found, followed by a linear regime for 3.5 hr and then a parabolic oxidation occurs. Other authors observed a parabolic oxidation only. The mechanism of oxidation is also unclear. Both outward cation migration and inward oxygen migration through the

TABLE 1. PROPERTIES OF THE RAW MATERIALS

	Kaolin ⁺ wt %	carbon black [*] wt %
SiO ₂	45.6	< 0.001
Al ₂ O ₃	38.6	< 0.001
Fe ₂ O ₃	0.34	< 0.01
TiO ₂	4.37	< 0.005
CaO	-	< 0.03
MgO	-	< 0.005
K ₂ O	0.06	< 0.02
Na ₂ O	-	< 0.02
S	-	< 0.5
ash		< 0.1
loss on ignition,	13.9	
BET(m ² g ⁻¹)	6.7	27

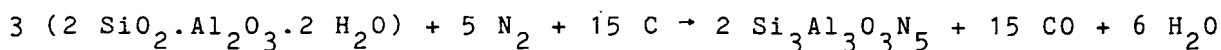
⁺Monarch
^{*}Elftex 120

oxide scale are reported to be rate determining mechanisms. From the work of Pomeroy and Hampshire it is clear that the scale formation occurs in different steps.

Since the oxidation process seems to be strongly dependent on both the x-value and the impurities or sintering aids, we have performed oxidation experiments on samples with different additives and a constant $x = 3$.

EXPERIMENTAL

The present study is restricted to sialons made by carbothermal conversion of kaolinite, according to the reaction



Details of the reaction have been published elsewhere¹¹ and we mention only the most important results here. As a starting material we used Monarch kaolin and carbon black. Table 1 gives data on the raw materials. As shown in this table Fe and Ti are the main impurities. The mixture of kaolinite and carbon is pelletized and heated under N₂ at 1500°C. The ratio C/kaolinite has to be adjusted carefully² to obtain the sialon phase. The resulting powder was milled and sintering was performed with powders of about 8 m²/g. After addition of sintering aids isostatically pressed pellets were sintered at 1675°C during 20 hours in a powder bed consisting of sialon powder with 5 wt% BN. Densities of the sintered samples varied between 2.9 and 3.3, depending on the sintering aid used (Table 2). The Ti and Fe impurities in the raw material lead to the formation of small TiN and FeSi₂ inclusions in the sintered samples. The grain size is relatively large due to the long sintering times (fig. 1). Only closed porosity is present.

TABLE 2. DENSITIES OF THE SINTERED SAMPLES

Sintering aid (3 wt%)	Y ₂ O ₃	La ₂ O ₃	CeO ₂	CaO	MgO
Density (g cm ⁻³)	3.3 ³	3.2 ³	3.3 ²	2.9	3.1

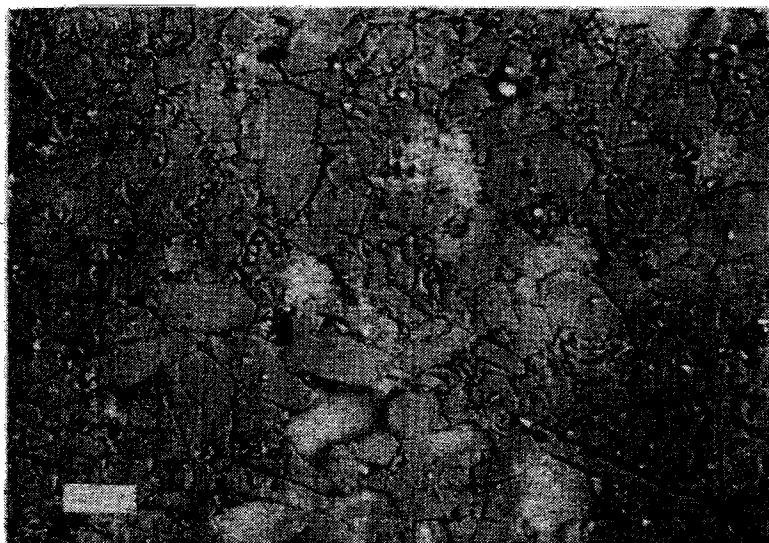


Fig. 1. Optical micrograph of an etched $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ with 3 wt% Y_2O_3 , sintered for 20 h at 1700°C . The length of the bar is $10\ \mu\text{m}$.

Oxidation experiments were performed in air or oxygen at 1000°C , 1200°C and 1400°C . The oxidation experiments in air were carried out in a tube furnace inside an alumina tube. The samples were heated up to the oxidation temperature within 2 hours. After oxidation they were pulled out of the hot furnace. The experiments in oxygen were performed in a thermobalance. (Setaram Microbalance MTB 10 - 8). In this case the samples were heated in nitrogen at a rate of 200°C per hour and next oxidized and cooled in oxygen. The cooling rate was again $200^\circ\text{C}/\text{h}$.

After exposure the samples were sectioned and polished and subsequently examined by optical microscopy and electron probe microanalysis (JEOL 733 Superprobe with both WDX and EDX analysis).

RESULTS

A number of measurements were performed in the thermobalance. Fig. 2 shows an example of the weight change. Some oxidation occurs already during the heating of the sample in nitrogen containing about 5 ppm of oxygen. The linear relation between the weight gain squared $(\Delta g)^2$ against time t shows a parabolic i.e. diffusion limited oxidation behaviour. The parabolic rate constant k is defined by $(\Delta g)^2 = kt A^2$, where A is the surface area of the sample. Table 3 shows the result of oxidation experiments in air at different temperatures for samples with different additives. The value of the sample with 3 wt% Y_2O_3 oxidized at 1400°C is of the same order of magnitude as observed by Pomeroy and Hampshire for a sample with 3.8 wt% Y_2O_3 oxidized at 1380°C ($k = 8.2 \times 10^{-12}\ \text{g}^2\text{cm}^{-4}\text{s}^{-1}$). The rate constant for the calcia doped sample is considerably larger than for other dopants, at temperatures above 1200°C . Best results were obtained for La_2O_3 doped samples. To investigate the influence of the partial oxygen pressure we have

TABLE 3. PARABOLIC RATE CONSTANTS FOR OXIDATION IN AIR AS A FUNCTION OF TEMPERATURE FOR SAMPLES WITH DIFFERENT SINTERING ADDITIVES (3 WT%)

Sintering aid	Y_2O_3	CeO_2	La_2O_3	CaO	MgO
1000°C	-	-	-	-	-
1200°C	0.1-0.6	0.1-0.6	0.1-0.6	0.1-0.6	0.1-0.6
1400°C	26	24	8	950	20

k in $10^{-12}\ \text{g}^2\text{cm}^{-4}\text{s}^{-1}$

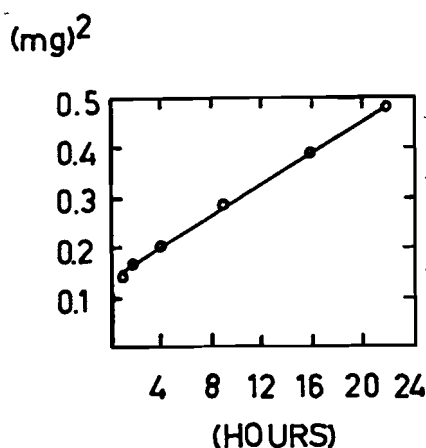
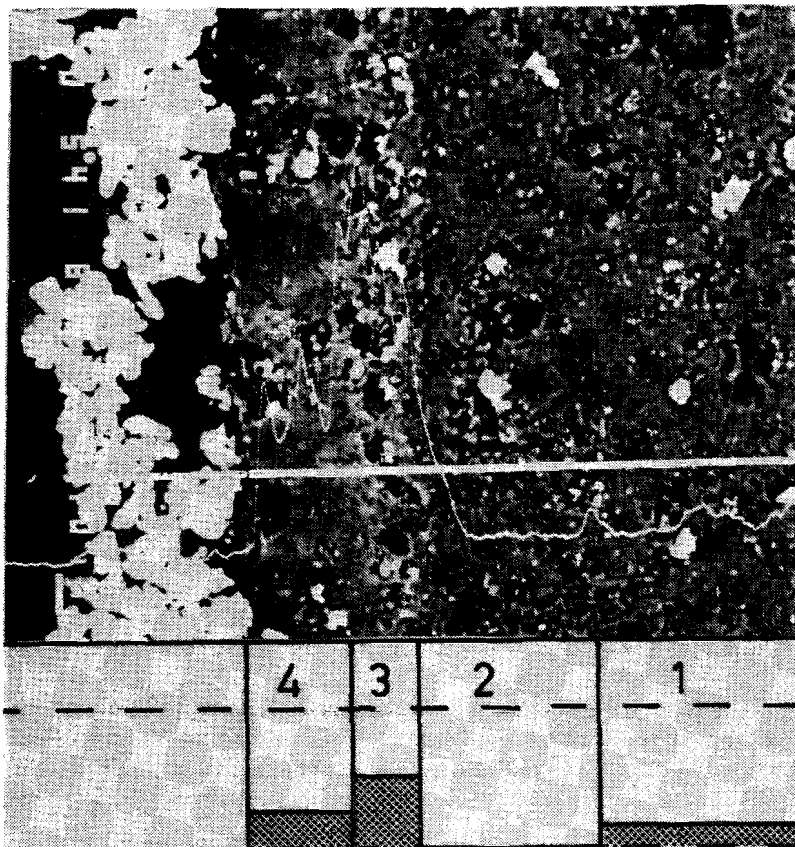
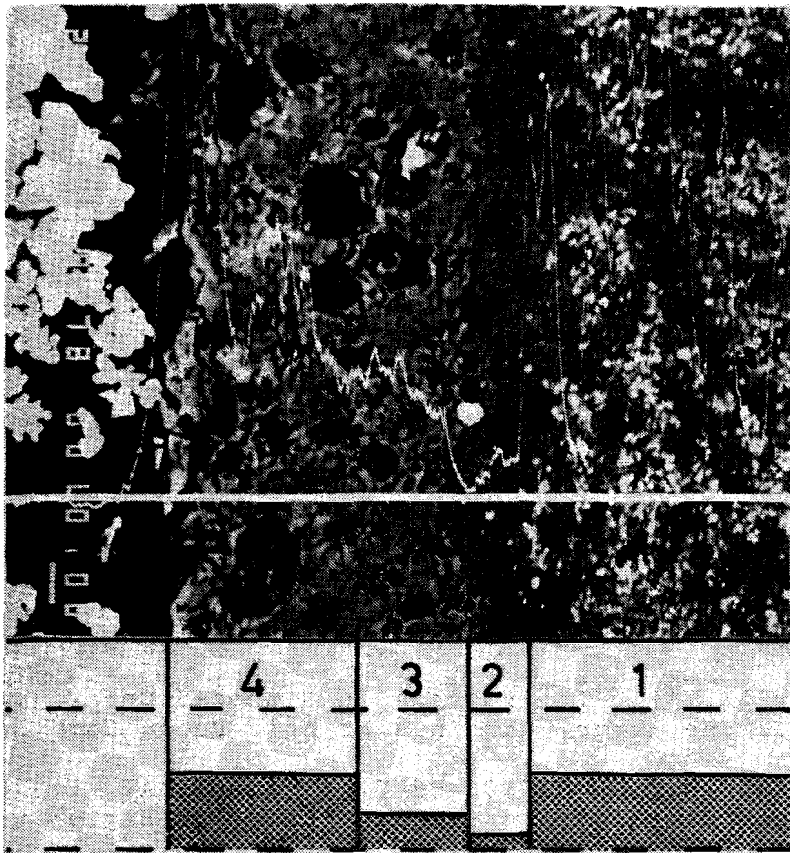


Fig. 2. Weight gain of $\text{Si}_3\text{Al}_3\text{O}_5\text{N}_3$ with 3 wt% CeO_2 , in oxygen at 1200°C as a function of time. Sample area 2.64 cm^2 .

heated a CeO_2 doped sample in pure oxygen instead of air. At 1000°C a catastrophic oxidation occurred and the sample cracked. However, at higher temperatures parabolic oxidation was observed. From the slope of fig. 2 we find at 1200°C $k = 0.6 \times 10^{-12}\text{ g}^2\text{ cm}^{-4}\text{ s}^{-1}$; at 1400°C $k = 260 \times 10^{-12}\text{ g}^2\text{ cm}^{-4}\text{ s}^{-1}$.

DISCUSSION

To get some insight in the oxidation mechanism we performed electron microprobe analyses on samples oxidized in air at 1200°C and 1400°C . Fig. 3a shows an example of an electron micrograph with superposed yttrium concentration profile. Independent of the nature of the additive always four different zones are observed. This is indicated schematically below the picture. In zone 1 the bulk concentration of the dopant is present. In zone 2 we are still in the matrix but a depletion of the sintering aid has occurred. The oxide layer consists of two parts, an inner layer (zone 3) and an outer layer (zone 4). The oxide layers are inhomogeneous and contain pores, mullite, cristoballite and other phases; therefore a concentration measurement is rather difficult. It was tried to carry out a line scan along a suitable part of the layer. The oxide layer clearly contains yttrium. A similar behaviour is observed for other dopants; e.g. fig. 3b shows results for a Mg doped sample. The impurity ions Ti and Fe of the kaolinite are present as TiN and FeSi_2 inclusions in the sialon and are not affected by the oxidation. The SEM picture also shows that large pores ($10 - 20\ \mu\text{m}$) are present in the oxidation layer. As mentioned in ref. 7 the surface of the scale shows signs of nitrogen eruption. Many questions, especially concerning the oxidation mechanism, are still unanswered. For instance, in HPSN 5 wt% MgO doped samples show an oxidation rate about two orders of magnitude higher than a sample with 6% SiO_2 + 12% Y_2O_3 . This has been attributed to the difference in viscosity of the liquid phase formed. However, the results shown in table 3 do not confirm this. Y_2O_3 and MgO doped samples show similar k-values, while CaO has a k-value about 36 x times larger. A matter which also deserves more attention is the influence of the partial oxygen and nitrogen pressures. For instance, for an undoped hot pressed β' -sialon with $z = 2.85$ Desmaison et al.¹³ find a parabolic oxidation kinetics at 1450°C in 1 atm oxygen ($p_{\text{O}_2} = 1\text{ atm}$) or 1 atm carbon dioxide ($p_{\text{CO}_2} \approx 10^{-15}\text{ atm}$). In most cases we observe parabolic oxidation, however, in the CeO_2 doped sample heated in 1 atm oxygen instead of air, catastrophic oxidation occurred at 1000°C . So far we can only say that both diffusion of cations and anions play a role.



REFERENCES

1. SINGHAL, S.C. in Nitrogen Ceramics, ed. RILEY, F.L., London: Noordhoff Publ. Comp. p. 607 - 626 (1977).
2. SCHLICHTING, J. in Nitrogen Ceramics, ed. RILEY, F.L., London: Noordhoff Publ. Comp. p. 627 - 634 (1977).
3. PORZ, F. in Progress in Nitrogen Ceramics, ed. RILEY, F.L., The Hague: Martinus Nijhoff Publ., p. 539 - 546 (1983).
4. THUMMLER, F. & GRATWOHL, G. in Progress in Nitrogen Ceramics, ed. RILEY, F.L., The Hague: Martinus Nijhoff Publ., p. 547 - 555 (1983).
5. SCHLICHTING, J. & GAUCKLER, L.J., Powder Metall. Int. 9, 36 - 39 (1977).
6. PORZ, F. & THUMMLER, F., J. Mater. Sci. 19, 1283 - 1295 (1984).
7. POMEROY, M.J. & HAMPSHIRE, S., Mater. Chem. Phys. 13, 437 - 448 (1985).
8. MOTZFELD, K., Acta Chem. Scand., 18 1596 - 1606 (1964).
9. FITZER, E. & EBI, R., Dechema Frankfurt (1972).
10. FITZER, E. & REINMUTH, K., in Hochtemperatur Werkstoffe, ed. BENESOVSKY, Wien: Springer Verlag (1969).
11. VAN DIJEN, F.K., Thesis, Eindhoven University of Technology (1986).
12. BABINI, G.N. & VINCENZINI, P., in Progress in Nitrogen Ceramics, ed. RILEY, F.L., The Hague, Martinus Nijhoff Publ. Comp., p. 427 (1983).
13. DESMAISON, J., BROSSARD, M., DESMAISON-BRUT, M. & GOURSAT, P., in Progress in Nitrogen Ceramics, ed. RILEY, F.L., The Hague: Martinus Nijhoff Publ. Comp., p. 439 (1983).