

Colour of gas-pressure-sintered silicon nitride ceramics Part II. Thermodynamic considerations

M. Herrmann*, O. Goeb

Fraunhofer Institute for Ceramic Technologies and Sintered Materials (IKTS), Winterbergstrasse 28, D-01277 Dresden, Germany

Received 6 June 2000; accepted 13 August 2000

Abstract

Gas-pressure sintering is the most widely used process for manufacturing high-performance silicon nitride ceramics. Generally gas-pressure sintering of silicon nitride is conducted under reducing atmospheric conditions due to the use of graphite heaters. The interaction between the sintering atmosphere and the silicon nitride ceramics is often featured by an inhomogeneous grey coloration of the near surface area and a grey coloration of the bulk material. In the first part of this paper [Herrmann, M. and Goeb, O., Colour of gas-pressure-sintered silicon nitride ceramics Part I. Experimental data *J. Eur. Ceram. Soc.*, 2001, **21**(3), 303–314] the dependence of the colour of the material on the sintering parameters was investigated experimentally. It was shown that silicon inclusions, having sizes ranging from a few nm up to several μm , cause the coloration of the material. Gas pressure, temperature and sintering time influence the formation of the inhomogeneous grey coloration. In this second part, the dependence of the coloration in silicon nitride ceramics on the sintering parameters will be explained on the bases of thermodynamic considerations. The model developed explains the possibilities of governing the colour formation of silicon nitride materials. © 2001 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Colour; Gas-pressure sintering; Si_3N_4 ; Sintering; Thermodynamics

1. Introduction

Gas-pressure sintering is a state-of-the-art process used to obtain high-performance silicon nitride ceramics. Generally gas-pressure sintering is conducted under reducing atmospheric conditions due to the use of graphite heaters. The interaction between the sintering atmosphere and the silicon nitride ceramics is often featured by an inhomogeneous grey coloration of the near surface area and a grey coloration of the bulk material (Fig. 1).^{1–4}

The nature of the colour centres is not completely clear. It was shown that Si inclusions in the range of 10 to 50 nm are responsible for the coloration of glasses; however, larger metallic inclusions can also act as colour centres. Additionally, defects in the glass structure cannot be excluded as reasons for the coloration, as was found in the case of radiation damage of SiO_2 glasses.

In the first part of this paper,¹ the dependence of the colour of the material on the sintering parameters was shown experimentally. This data can be summarised as follows:

- The intensity of the grey coloration in silicon nitride ceramics was shown to correspond to the concentration of silicon precipitates that have dimensions of several nm to several μm and which act as colour centres.
- The colour of the bulk of the material is independent of the weight loss but depends strongly on the temperature and on the nitrogen pressure during isothermal sintering. The bulk colour additionally depends on the porosity. With increasing porosity the samples become brighter.
- Normally the near surface layer of the sintered samples consists of two differently coloured layers, an outermost bright-coloured layer followed by a dark-coloured layer beneath it.
- The dark colour of the near surface area depends on the weight loss and the oxygen partial pressure during sintering. The formation of the dark layers in the near surface area is connected with the reduction of Si^{4+} . This layer can only be formed in samples with closed porosity.
- The outer bright near surface layer is a result of decoloration processes occurring during the high-pressure step of isothermal sintering or during cooling from the sintering temperature.

* Corresponding author. Tel.: +49-351-2553527; fax: +49-351-2553600.

E-mail address: herrmann@ikts.fhg.de (M. Herrmann).

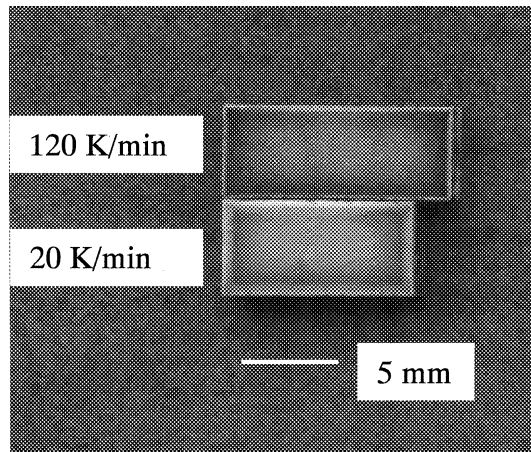


Fig. 1. Micrograph of a material sintered at 1750°C and 1.3 bar nitrogen pressure for 2 h (a: cooled at 120 K/min to 1000°C; b: cooled at 20 K/min).

The purpose of this work was to establish a model to explain the coloration of gas-pressure-sintered silicon nitride ceramics and to present the possibilities of governing the colour that is formed in silicon nitride materials.

2. Coloration of the bulk material

The coloration of the silicon nitride material depends on a number of parameters connected on one-hand with the composition of the material and on the other hand with the sintering conditions. The influence of the composition on the colour was explained previously,¹ the main emphasis being placed on the dependence of the colour on the sintering parameters.

The coloration is connected with the concentration of colour centres, i.e. with the concentration of free silicon.¹ This is formed from SiO according to Eq. (1) during cooling from the sintering temperature:



The formation of Si is strongly connected with the concentration of SiO in the melt. SiO is formed according to the following reaction:



(l — solved in the liquid; s — solid; g — gas).

For the formation of a dark colour, the concentration of SiO in the oxynitride liquid must be higher than the concentration of the physically dissolved nitrogen. Otherwise the dissolved nitrogen will react with SiO during cooling and no Si will be formed.

A ratio of solved SiO to solved $\text{N}_2 > 3$ seems to be reasonable, based on the fact that the structure of the

polar SiO molecule is more similar to the network of the liquid phase than is the structure of N_2 . The formation of SiO can be explained as O reduction of the network of the oxynitride liquid. The concentration of SiO in the material can be described by the equilibrium constant of the reaction shown in Eq. (2):

$$K_1 = \frac{a_{\text{SiO}}^6 \times a_{\text{N}_2}^2}{a_{\text{SiO}_2}^3 \times a_{\text{Si}_3\text{N}_4}} \quad (2a)$$

where a_{SiO} = activity of the SiO dissolved in the oxynitride liquid; a_{N_2} = activity of the nitrogen dissolved in the oxynitride liquid; a_{SiO_2} = activity of the SiO_2 in the oxynitride liquid; and $a_{\text{Si}_3\text{N}_4}$ = activity of the Si_3N_4 ($a = 1$).

Assuming that the nitrogen dissolved in the oxynitride liquid is in equilibrium with the nitrogen in the sintering atmosphere, the nitrogen activity can be expressed through the nitrogen pressure (under the assumption that nitrogen is an ideal gas):

$$K_H = \exp(-\Delta G_H/RT) = \frac{p_{\text{N}_2}}{a_{\text{N}_2}} \quad (3)$$

where K_H is the constant corresponding to Henry's law, when the activity coefficient is 1. The activity of the SiO can be expressed as follows:

$$a_{\text{SiO}} = \frac{(K_1 \times K_H^2)^{1/6} \times a_{\text{SiO}_2}^{1/2}}{p_{\text{N}_2}^{1/3}} \quad \text{or} \quad (4)$$

$$a_{\text{SiO}} = \frac{K_S \times a_{\text{SiO}_2}^{1/2}}{p_{\text{N}_2}^{1/3}} \quad (5)$$

where

$$K_S = (K_1 \times K_H^2)^{1/6} \quad (6)$$

Using the Beer–Lambert law, which relates the ratio of the intensity of the light to the initial intensity I/I_0 with the concentration of colour centres c (see also Part I), the following is obtained:

$$\ln(I/I_0) = -A \times c \quad (7)$$

$$\ln\left(\frac{I}{I_0}\right) \approx -A \times c_{\text{Si}} \approx -A \times \left[K_M \times \frac{\exp\left(\frac{-\Delta G(5)}{6 \times RT} \times \frac{1}{2}\right)}{p_{\text{N}_2}^{1/3}} - B \times p_{\text{N}_2} \right] \quad (8)$$

where

$$K_M = \text{constant ratio of SiO to Si}$$

$$B = 4,12 \times K_H \times f,$$

where f = activity coefficient; 4.12 is the factor relating the amount of nitrogen with the amount of reacted SiO, which will react with nitrogen according to the reaction in Eq. (2).

This equation is only valid when the SiO concentration calculated by the equilibrium is higher than the amount of SiO which can react with the dissolved nitrogen. Using the correlation between Grey level and Si content (see Part I), the amount of SiO dissolved in the oxynitride liquid in the bulk under sintering conditions at 1800°C and 5.1 MPa nitrogen can be estimated as 9 mg/cm³ for material I. Data about the solubility of nitrogen in oxynitride glasses at 1800°C do not exist. Using the data for alkali glasses determined at 1580°C,² the amount of the nitrogen that is physically dissolved in the grain boundary at 1800°C and 5.1 MPa nitrogen pressure can be estimated as 0.06 mg/cm³. This amount can react with 0.3 mg/cm³ SiO. The calculated amount of nitrogen is for nitrogen pressures < 50 MPa, much lower than the estimated SiO concentration. Therefore, the second part of Eq. (8) can be neglected under sintering conditions with pressures up to 50 MPa. Eq. (8) implies that a material will exhibit an “equilibrium colour”. It is possible to establish some main relationships between the colour, the sintering parameters and composition of the material using Eq. (8), but it is not possible to make quantitative calculations because most

of the constants in the formula are not known and must be determined experimentally for the different compositions.

Results of the calculations (Fig. 2) show that the colour depends very strongly on the nitrogen pressure at low pressures. At nitrogen pressures higher than 2.0–3.0 MPa, the colour changes only slightly. The intensity of the colour increases with increasing temperature; however, the increase is not uniform. At low temperatures (< 1600–1700°C), the colour changes only slightly with changing temperature, whereas when the temperature of decomposition of Si₃N₄ at the given nitrogen pressure is approached, the colour changes greatly (Figs. 2 and 3). This feature is also found for the pressure dependence. Near the equilibrium pressure of decomposition of Si₃N₄ the colour changes to a very dark one.

When the equilibrium pressure of the decomposition of Si₃N₄ is reached, the mechanism will be changed; i.e. Si will be formed directly by the following reaction:



The concentration of silicon and the colour depend in this case only on the kinetics of the decomposition.

Materials with a higher amount of Y₂O₃, rare earth or MgO additives will have a brighter colour due to the lower activity of the SiO₂ in the oxynitride liquid. The influence of the Al₂O₃ additives is not unequivocal. On one hand an addition of Al₂O₃ reduces the activity of SiO₂, but on the other hand the Al₂O₃ reacts with the Si₃N₄⁵ and forms additional SiO₂ by the following reaction:

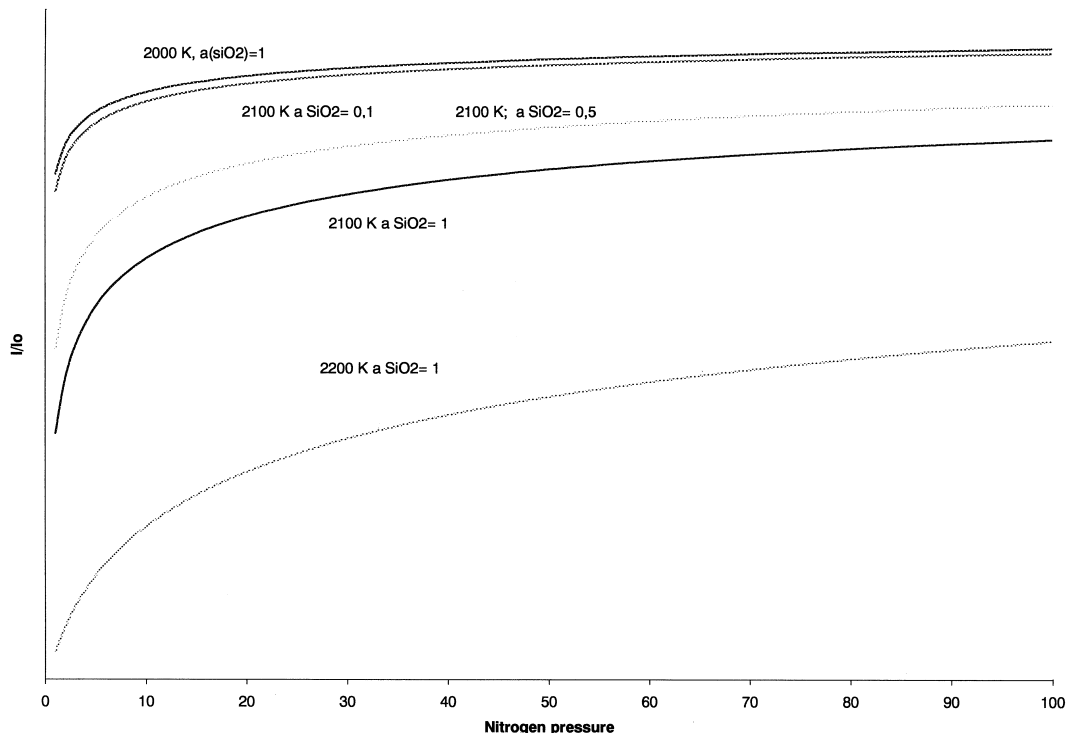


Fig. 2. Calculated dependence of the colour on the nitrogen pressure and on the temperature (low I/I_0 values mean black samples).

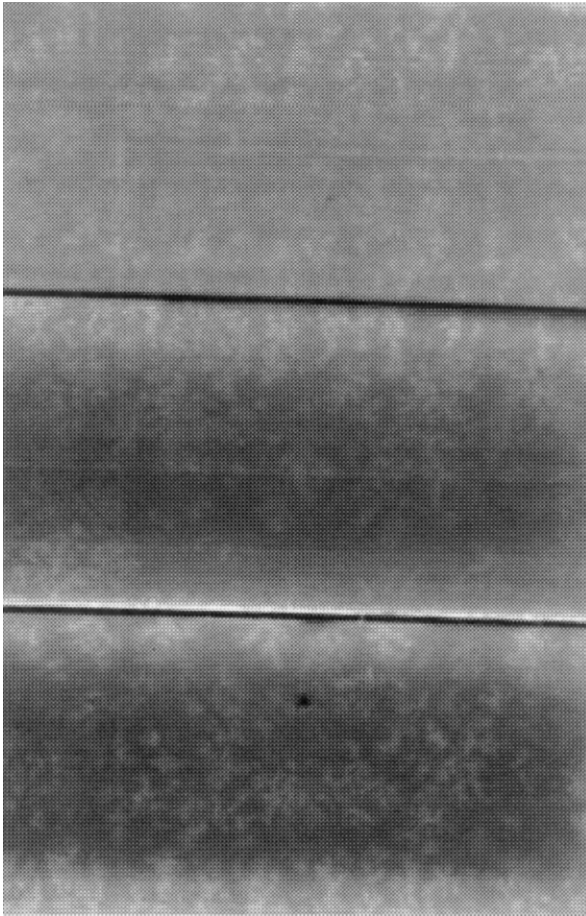
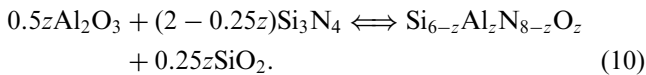


Fig. 3. Optical images of Si_3N_4 materials sintered under different conditions (samples sintered at 1750°C for 4 h, at 1825°C for 3 h and at 1900°C for 1.5 h with a pressure of 5 MPa N_2).



This means that Al_2O_3 works like a buffer. The more SiO_2 that evaporates during sintering, the more Al that dissolves in the silicon nitride grains and reproduces SiO_2 . The amount incorporated in the Si_3N_4 grains depends not only on the sintering parameters, but also on the activity of the Al_2O_3 in the oxynitride liquid, i.e. on the ratio of Al_2O_3 to the other additives.⁵ AlN additives reduce the SiO_2 activity and lead to a reduction in the dark coloration of the material. Evidence for this is provided by the fact that the α' -SiAlONs with nitrogen- and alumina-rich grain boundary phases are very bright or even translucent.⁶

The formation of an “equilibrium colour” means that the final colour is independent of the initial colour. The time needed for the formation of the “equilibrium colour” depends, of course, on the starting colour. The formation of the “equilibrium colour” assumes that the nitrogen in the oxynitride liquid is in equilibrium with the outer

nitrogen pressure. The nitrogen diffusion is very slow; therefore, the adjustment of the colour requires time.

Normally the materials are sintered to closed porosity at low nitrogen pressures. The consequence of this is that the materials are dark in colour; this has been found for pressureless-sintered silicon nitride. When the time for the second step of the gas-pressure sintering cycle with a high nitrogen pressure is too low, the material will exhibit a black centre and the equilibrium colour will be reached only in the outer regions.

The dependence of the colour on the porosity is given in Fig. 4, which shows that with increasing porosity, the brightness of the material increases. This dependence can be explained by the amount of nitrogen in the pores that will react with the existing SiO during cooling. The change in the concentration of silicon can be calculated based on the colour measurement and on the observed dependence of the colour on the silicon concentration (Part I). Alternatively, it can be calculated using the amount of nitrogen entrapped in the pores and Eq. (9). The two relationships are shown in Fig. 4.

The difference between the two curves depends on one hand on the error of the determination of the silicon, the porosity and the grey levels. On the other hand, the pores can also act as centres for light scattering, leading to a brighter colour due to the reduced penetration depth of the light (see also Part I).

3. Formation of the inhomogeneously coloured layers in the near surface area

Usually a small bright outer layer and a dark layer are observed in the near surface area (see Part I and Fig. 1). The outer, bright layer is formed during cooling and will be discussed in the next section. In this section, the formation of the dark layer is discussed. In Part I, it was shown that the thickness of the dark-coloured layer can be correlated with the weight loss and depends on the oxygen partial pressure. Fig. 5 demonstrates this behaviour very clearly. The sample sintered in the microwave furnace with a porous oxide insulation and therefore a high oxide partial pressure shows a weight loss of 32 mg/cm² and no formation of a dark surface layer at 1750°C , whereas a sample sintered in a gas-pressure furnace with a carbon heater shows a large dark surface layer even for lower weight losses (see Part I). The formation of the layer is connected with the interaction of the surface with the atmosphere, i.e. with the enhanced reduction of Si^{+4} in the near surface area of the samples.

For modelling the behaviour, three main systems are distinguished:

1. A thermodynamically closed system with a low ratio of the volume of the gas phase to the volume of the silicon nitride samples ($V_{\text{gas}}/V_{\text{solid}}$).

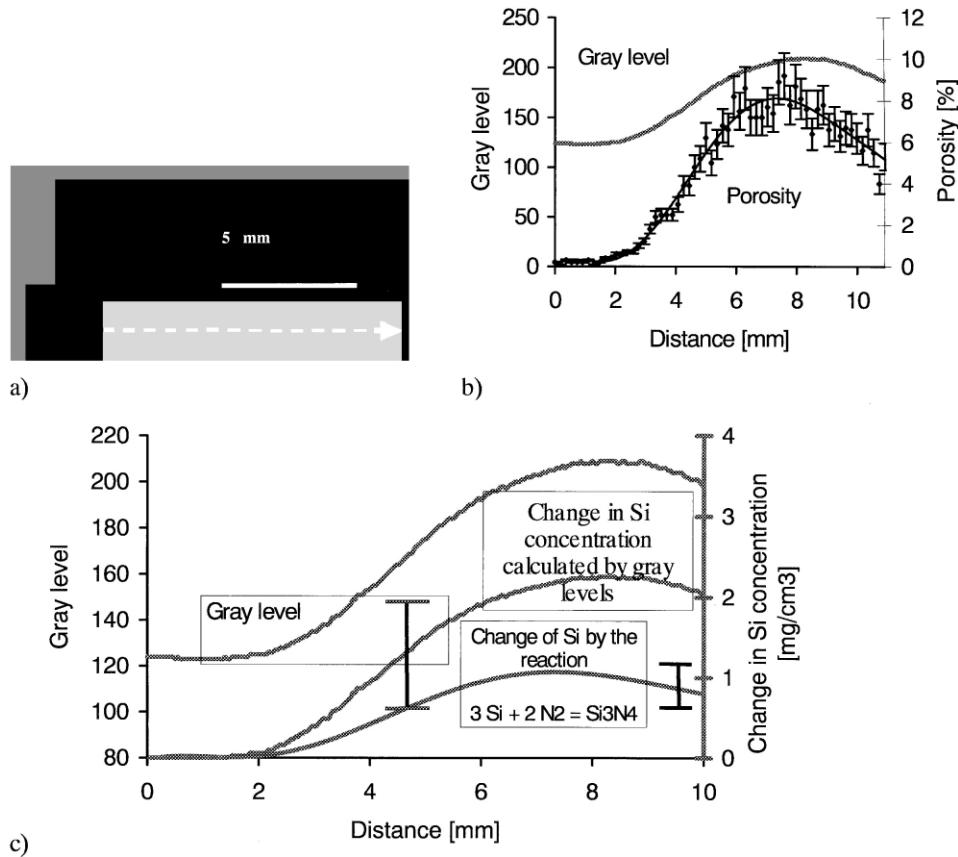


Fig. 4. (a) Optical image of a Si₃N₄ material with residual porosity, (b) measured colour and porosity, (c) calculated dependence of the colour on the porosity.

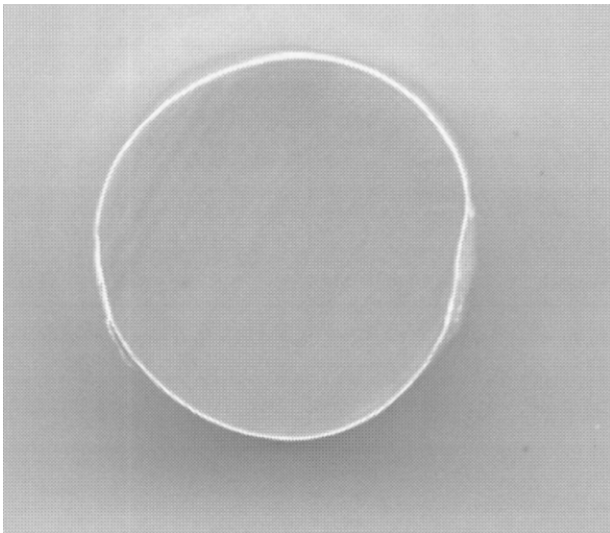


Fig. 5. Sample sintered in a microwave furnace with oxide insulation (high oxygen partial pressure) at 1750°C and 0.1 MPa nitrogen pressure (specific weight loss: 32 mg/cm²).

2. An open system or a closed system with a high ratio of the volume of the gas phase to the volume of the silicon nitride samples ($V_{\text{gas}}/V_{\text{solid}} \gg 1$).
3. A system with additional components able to react with the samples.

The real behaviour under sintering conditions can be described using one of these cases as the dominating system.

3.1. Closed system with low $V_{\text{gas}}/V_{\text{solid}}$

During sintering in a closed system with a low volume of gas phase in comparison to the volume of samples, the equilibrium composition of the gas phase is reached very quickly and therefore the weight loss of the samples is very low. The formation of a dark outer layer is not observed during sintering. This case corresponds, for example, to gas-pressure sintering in a closed BN, RBSN or SSN crucible.

3.2. Open system or closed system with a high ratio $V_{\text{gas}}/V_{\text{solid}} \gg 1$

The behaviour of the material depends on the oxide partial pressure. If the oxygen content in the atmosphere is much lower than the SiO partial pressure and the volume of the gas phase is large in comparison to the volume of the sample, a high weight loss and the formation of a dark outer layer are observed. The reason for the relatively high weight loss is that the equilibrium concentration of SiO in the gas phase is high and

a lot of SiO must be formed due to decomposition of the sample to reach the equilibrium pressure.

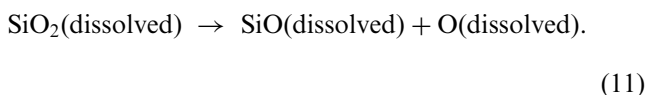
In Part I of this paper, it was shown that Si inclusions, formed by decomposition of SiO that is dissolved in the grain boundary, cause the material to be black in colour. Therefore, the formation of the dark outer layer must be caused by an increased concentration of SiO in the near surface area. At first glance it seems incomprehensible that when more SiO evaporates into the gas phase, the near surface area becomes enriched in SiO.

To explain this behaviour, the experimentally observed results must be taken into account:

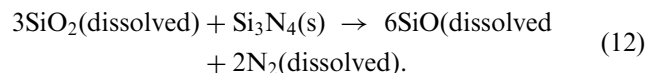
1. A higher SiO concentration in the liquid phase must exist in the near surface area under sintering conditions. The SiO evaporates at the surface, the evaporation being mainly caused by Eq. (2).
2. In the near surface area (20–200 μm), a reduction in the SiO₂ content is experimentally found.^{2,3} The change in the SiO₂ content is very dramatic in the first 10–50 μm below the surface. In the dark layer beneath, the concentration changes only slightly.
3. The thickness of the dark layer depends on \sqrt{t} . This indicates that diffusion is the rate-determining step.

Based on the experimentally observed changes in the concentrations of SiO and SiO₂ in the grain boundary, the concentrations of the components in the oxynitride liquid can be estimated assuming local equilibrium in the grain boundary phase.

Using the knowledge about the slight change in the SiO₂ concentration and an increased concentration of SiO in the near surface area, the concentration of the dissolved oxygen can be calculated using Eq. (11):



The nitrogen concentration (physically dissolved nitrogen) can be obtained by the equilibrium in Eq. (12):



The activity of Si₃N₄ is assumed to be 1. The results of these calculations are shown schematically in Fig. 6. They reveal a concentration gradient with respect to oxygen; i.e. the oxygen activity in the centre of the sintered material is higher than in the surface area. A decrease in the oxygen concentration at the surface leads to an increased SiO-formation, i.e. a more pronounced dark surface layer. These results seem to agree with the experimental results showing that in strongly reducing atmospheres, the formation of dark surface areas occurs. More surprising is the finding of a reduced nitrogen concentration in the near surface area. This

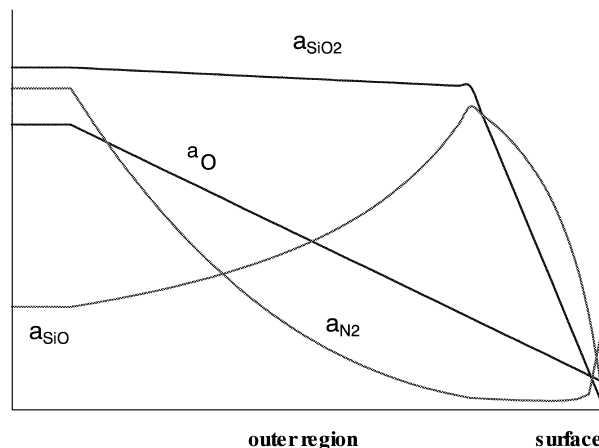
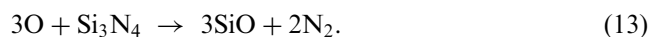


Fig. 6. Schematic change in the concentration of different components in the near surface area of the samples. The calculations are based on the experimentally observed change in the concentration of the SiO₂ and SiO under the assumption of local equilibrium.

can only be realised when the diffusion of nitrogen is slower than the diffusion of oxygen.

These profiles can be described in the following manner. The oxygen concentration is reduced at the surface because the oxygen reacts with Si₃N₄ at the surface to form SiO, which evaporates. This reduction in the oxygen activity is the reason for the pronounced diffusion of oxygen through the grain boundary phase to the surface. The reduction in the oxygen concentration causes the reaction in Eq. (11) to be shifted to the right; i.e. additional SiC is formed. However, this formed SiC will disturb the equilibrium shown in Eq. (12); to fulfill the equilibrium shown in Eq. (12), SiO must partially react with the nitrogen that is physically dissolved in the grain boundary phase. The result is a reduction in the nitrogen content in the grain boundary phase. This will cause the nitrogen to diffuse into the material. If this diffusion occurs more slowly than the diffusion of oxygen out of the material, then dark layers will be formed due to the enrichment of SiO in the near surface area. The nitrogen will also diffuse from the bulk of the material to the surface and reduce the coloration, but this diffusion will increase the extent of coloration in the bulk and lead to a deviation from the formation of the “equilibrium colour” of the bulk as explained above. No reliable data about the solubility and the diffusion of nitrogen and oxygen in the oxynitride liquid are available, but differences in the diffusion rates can be expected. By integrating the concentration of Si in the near surface area (using the relation of grey level and Si-concentration), the total amount of Si formed per surface area can be estimated. For 4 h at 1800°C and 6 bar, this amount is 0.1 mg/cm²; hence, the difference between the fluxes of oxygen and nitrogen must be 3×10^{-6} mol/cm². This is about 1% of the observed change in the oxygen content during sintering, which appears to be a reasonable value.

The model allows some relationships between the sintering parameters and the formation of the dark colour to be established. An increase in nitrogen pressure leads to a reduction in the equilibrium partial SiO-pressure in the sintering atmosphere and therefore a reduction in the weight loss, and a reduction in the rate of evaporation (see Part I). Additionally, a higher nitrogen pressure leads to a higher concentration of physically dissolved nitrogen. Both factors cause the formation of the dark outer layer to be hindered due to a lower rate of outward diffusion of oxygen and a increased inward diffusion of nitrogen. This is observed experimentally (see Part I). With increasing temperature, the formation of the dark surface layer is enhanced. An increase in the oxygen partial pressure in the atmosphere must hinder the formation of the dark layer according to this model. This is also found experimentally (Fig. 5, Part I Fig. 17). If the oxygen partial pressure in the system is much higher than the equilibrium pressure over the sample consisting of silicon nitride and the oxynitride liquid phase, active oxidation at the surface of the sample takes place:



The formed SiO evaporates; i.e. the weight loss is high. This means that a high oxygen partial pressure $p(\text{O})$ leads to a high weight loss due to a change in the evaporation mechanism. This process would be remarkable if the oxygen partial pressure were near to the equilibrium SiO partial pressure. Under sintering conditions, the oxygen partial pressure is not high enough to lead to passive oxidation; thus, a SiO₂ surface layer does not exist. (In air, passive oxidation of Si₃N₄ occurs at temperatures < 1600–1650°C.) The formation of the equilibrium concentration of SiO in the atmosphere is caused only by the surface reaction and hinders the formation of the dark surface layer (Fig. 5).

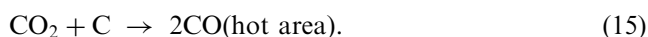
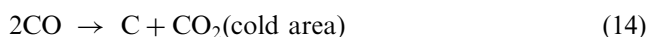
Under normal sintering conditions, the oxygen partial pressure is much lower than the SiO equilibrium pressure (especially in furnaces with carbon heating elements). Therefore, a mechanism similar to active oxidation does not play a decisive role under normal sintering conditions.

3.3. System with additional components able to react with the samples

The most important example of such a system is a system with carbon due to a carbon heater and the insulating systems found in most furnaces. In a system with carbon, the formation of the dark surface layer occurs to a greater extent than in a carbon-free system, if no additional measures are used. The influence of the carbon is connected on one hand with the reduction in the oxygen partial pressure (Fig. 9b in Part I). On the other hand, the formation of carbon monoxide leads to

increased SiO₂ reduction in the samples, which is necessary to reach the equilibrium composition of the gas phase.

The equilibrium partial pressure of CO is higher than or similar to that of the SiO partial pressure under the given sintering conditions. For this reason, more oxygen (SiO₂) in the samples must be reduced to reach the equilibrium pressure. The effect of the CO formation can, therefore, also be treated as an increase in the volume of the gas phase. To reduce this effect, attempts were made to achieve partial sintering with CO partial pressure.³ Such an approach has some disadvantages. For example, with increasing CO partial pressure, transport reactions become more pronounced:



These reactions lead to a reduction in the heater lifetime and in the reproducibility of the temperature control by pyrometric measurements. The second disadvantage is the increase in carbon content of the samples,³ which leads to black spots in the material. The problem is that the equilibrium CO pressure depends on the SiO₂-activity in the oxynitride liquid phase on the surface of the samples. Thus, in some samples the CO partial pressure is too low to compensate for the evaporation, and in other samples the CO partial pressure is higher than the equilibrium pressure and results in carbon enrichment. Due to reduction of SiO₂ on the surface during sintering, the CO equilibrium partial pressure is not constant during sintering. For this reason, the approach of reducing the influence of the carbon on the sintering atmosphere appears to be more suitable. For this, two main requirements must be fulfilled: (1) the amount of oxygen and water vapour impurities in the atmosphere must be reduced because they react with carbon to form CO, which increases the extent of the transport reactions and the influence of the carbon on the sintering; and (2) suitable crucible materials (RBSN, SSN BN or RSiC) must be used to further reduce the interaction of the volume inside the crucible with the gas phase in the furnace. The success of this concept was demonstrated by the experiments explained in Part I of this paper, in which weight losses lower than 1% and the avoidance of the formation of black-coloured surface layers were accomplished.

4. Formation of the outer bright near surface layer

The outer bright surface layer formation takes place during cooling, as shown by experiments using different cooling rates (Fig. 1). A greater extent of decoloration of the near surface area can be obtained using an additional

holding time during cooling (Fig. 7). The explanation of this process is identical to that of the coloration of the bulk phase. Fig. 9 (Part I) shows that at low temperatures and high nitrogen pressures, the equilibrium



is shifted to the left, i.e. the concentration of colour centres is reduced (Fig. 2). Additionally, Si formed during cooling due to disproportionation of SiO will react with the nitrogen diffusing inside the material. That is why the thickness of the bright layer depends on \sqrt{t} (Fig. 7). Based on the explanation of the coloration of the bulk, the reaction taking place during the decoloration process can be described as follows:



Assuming that the process has achieved a steady state and that the reaction of the nitrogen with the silicon is faster than the diffusion, the thickness of the decoloured layer x can be described as follows:

$$\frac{dx}{dt} = \frac{j}{N_0}$$

$$\begin{aligned} j_{\text{N}_2} &= D_{\text{N}_2} \times A_0 \times \frac{(c_{\text{ON}_2} - c_{\text{iN}_2})}{x} \\ &= D_{\text{N}_2} \times A_0 \times \frac{(c_{\text{aN}_2} \times \alpha' - c_{\text{iN}_2})}{x} \end{aligned} \quad (19)$$

where

A_0 = effective cross section of the grain boundary phase,

$$x^2 = B \times t \quad (20)$$

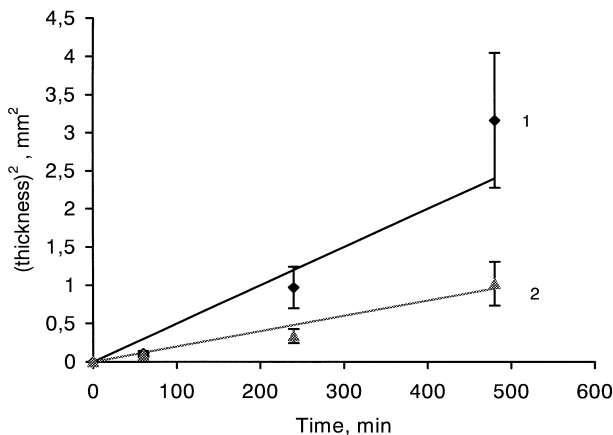


Fig. 7. Dependence of the thickness of the light-colored surface layer on the isothermal heating time at 1500°C and 0.6 MPa nitrogen pressure (1: material I, 2: material II; details see Part I).

where

$$\begin{aligned} B &= \frac{2 \times D_{\text{N}_2} \times A_0 \times (c_{\text{aN}_2} \times \alpha' - c_{\text{iN}_2})}{N_0} \\ &= \frac{2 \times D_{\text{N}_2} \times A_0 \times \left(\frac{p_{\text{aN}_2}}{RT} \times \alpha' - c_{\text{iN}_2} \right)}{N_0}. \end{aligned} \quad (21)$$

Whereas N_0 is the amount of nitrogen necessary for the decoloration of the colour centres in a given volume (taken as constant; this is only true when no dark-coloured surface layer exists), A is the cross section of the grain boundary phase, because the diffusion rate of nitrogen through the grain boundary phase is several orders of magnitude higher than through the Si_3N_4 grains. Using the data for the Si concentration determined in Part I by XRD and colour measurement, about 5×10^{-5} mol/cm³ for material 1, and a dissolved nitrogen concentration of $p_{\text{a}}/RT = C(\text{N}_2) \approx 10^{-7}$ mol/cm³, where α' is Ostwald's solubility coefficient,² the diffusion coefficients are calculated to lie in the range 10^{-4} to 10^{-5} cm²/s. These values are in the same order as the data found in the literature for different glasses.² The constant can only be determined approximately due to the fact that for the system $\text{Al}_2\text{O}_3/\text{Y}_2\text{O}_3/\text{SiO}_2$, no data were available for the solubility of nitrogen and for the error of determination of the silicon concentration. Additionally the SiO can diffuse from the centre to the surface. The diffusion of SiO/Si seems to be much lower (at least for temperatures below 1600°C) than the diffusion of nitrogen because the boundary between decoloration and the original colour is very sharp. Analysis of Eqs. (19)–(21) shows that the thickness of the bright layer depends on the concentration of the colour centres. A material which is not so dark will be decoloured faster than one that is darker. This is observed experimentally in Part I [compare thickness of the layer for sintering at 5.12 MPa and at 0.6 MPa (Fig. 14)]. The decoloration process is more intensive at higher nitrogen pressure during cooling. On the other hand, the decoloration processes are faster at higher temperatures due to the higher rate of nitrogen diffusion. But the reached “equilibrium colour” is not so bright. Therefore isothermal heating periods at different temperatures and pressures can be favourable for fast decoloration.

5. Conclusions

The results can summarised as follows:

1. The coloration is caused by the partial reduction of $\text{Si}^{+\text{IV}}$ to $\text{Si}^{+\text{II}}$ at sintering temperatures due to the sintering atmosphere. During cooling from sintering temperatures, the $\text{Si}^{+\text{II}}$ will undergo a disproportionation to $\text{Si}^{+\text{IV}}$ and metallic silicon.

2. The coloration of the bulk material is, even when the interaction with the atmosphere is suppressed (i.e. when nearly no weight loss occurs), an “equilibrium” one. This “equilibrium coloration” depends on one hand on the composition of the glassy phase (SiO_2 concentration) and on the porosity of the material and on the other hand on the temperature and nitrogen pressure.
3. The formation of the outer dark area results from the greater extent of SiO formation caused by the different diffusion rates of outwardly diffusing oxygen and inwardly diffusing physically dissolved nitrogen. The formation of the layer is diffusion controlled; i.e. the thickness depends on the square root of the sintering time. An increase in the nitrogen pressure or oxygen partial pressure causes a reduction in the extent of formation of the dark layer.
4. The outer bright layer is caused by the nitridation of the colour centres during cooling from sintering temperatures or during additional isothermal sintering at lower temperatures or higher nitrogen pressures. This process is diffusion controlled and the thickness of this layer depends on the concentration of the colour centres, the cooling rate and the applied nitrogen pressure.
5. Additional to the effects of the more or less intensive grey coloration explained in this paper, factors not explained in details here can affect the colour: for example, the carbon content of the samples, silicide-forming impurities and special colouring ions or inclusions.

References

1. Herrmann, M. and Goeb, O., Colour of gas-pressure-sintered silicon nitride ceramics Part I. Experimental data *J. Eur. Ceram. Soc.*, 2001, **21**(3), 303–314.
2. Göeb, O., Farbausbildungen und optische Inhomogenitäten beim Gasdrucksintern von Siliciumnitridkeramiken. Dissertation, TU Dresden, 2000.
3. Neidhardt, U., Partialdrucksintern von Siliziumnitrid, MPI Stuttgart, Dissertation, 1993.
4. Göb, O., Herrmann, M., Siegel, S. and Obenaus, P., Origins and avoidance of colour inhomogeneities in silicon nitride ceramics. *Key Engineering Materials*, Trans Tech Publications Ltd, Zuerich, 1997, **132–136**, 751–753.
5. Riedel, G., Bestgen, H. and Herrmann, M., Influence of sintering additives with differing proportions of $\text{Y}_2\text{O}_3/\text{Al}_2\text{O}_3$ on the sintering and material properties of Si_3N_4 ceramics, cfi. *Ber. DKG*, 1998, **75**, 30–34.
6. Shen, Z., Nygren, M. and Halenius, U., Absorbtion spectra of rare earth-doped α -sialon ceramics. *J. Mater. Sci. Lett.*, 1997, **16**, 263–266.