

Colour of gas-pressure-sintered silicon nitride ceramics Part I. Experimental data

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Abstract

Gas-pressure sintering is the most widely used process for manufacturing high-performance silicon nitride ceramics. 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 Part I of this work 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. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Gas-pressure sintering is the most commonly used process for manufacturing high performance silicon nitride ceramics. Generally gas-pressure sintering is conducted under reducing atmospheric conditions in a graphite-heated sintering furnace. Due to the interaction between the sintering atmosphere and the silicon nitride ceramics, the sintered parts often display an inhomogeneous grey coloration of the near surface area and a homogeneous grey coloration of the bulk material. Normally, the near surface coloration consists of two differently coloured layers, an outermost light-coloured layer followed by a dark-coloured layer directly beneath it (Fig. 1).^{1–4}

This inhomogeneous coloration is on the one hand some times a reason for the customer to reject parts, on the other hand there exist unequivocal results about the influence of the colour on the properties.^{1–3} The absence of the understanding of the coloration makes a reproducible production of silicon nitride parts difficult, especially the production of near net shape parts or if the costs for finishing have to be reduced by minimising the thickness of sintering skins.

The coloration of the silicon nitride material depends on a number of parameters connected on one hand on the composition of the material and on the other hand on the sintering conditions. The influence of the composition on the colour will be explained here only very briefly, the main emphasis being placed on the dependence of the colour on the sintering parameters.

The bulk colour depends on the silicide-forming impurities (d elements excluding elements of the third and fourth group of the periodic table of the elements). With increasing concentration of these impurities the colour becomes darker. The addition of Ti-containing compounds leads to the formation of TiN. At low TiN concentrations the material will form a dark colour, whereas at higher concentrations it will form the typical brown or golden colour. At the surface the red-brown $\text{TiN}_{(1-x)}\text{C}_x$ can be formed. Under normal sintering conditions, Hf and Zr form HfO_2 and ZrO_2 , respectively, which can be stabilised by rare earths or MgO. Under strongly reducing conditions, yellow $\text{ZrN}_{(1-x)}\text{C}_x$ or red-brown $\text{HfN}_{(1-x)}\text{C}_x$ is formed.⁵

There are some indications that Cl impurities cause a darkening of the material.⁶ Materials containing free carbon impurities are black in colour.^{7,8}

Additionally, the different rare earth ions can change the colour of the material. For example, depending on its oxidation state, Yb can cause the material to be

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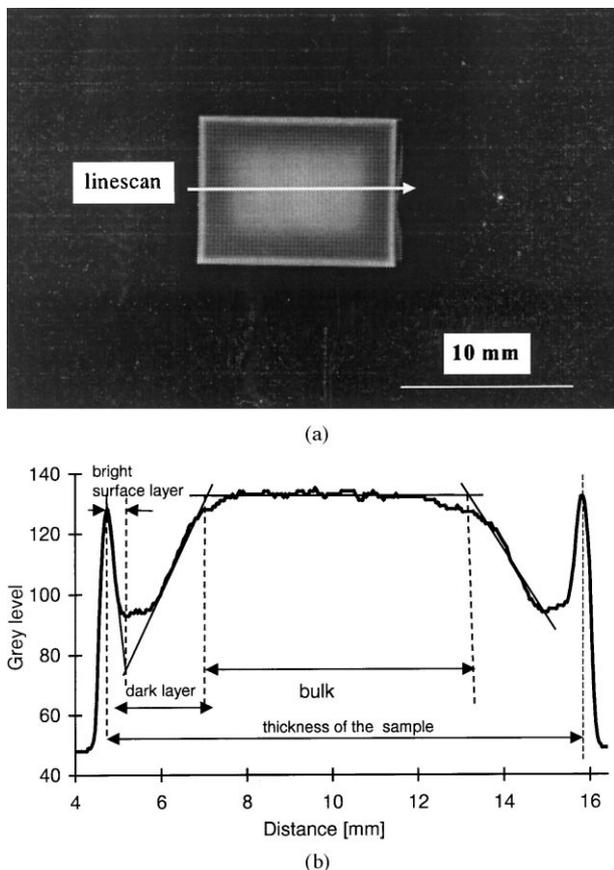


Fig. 1. (a) Optical image of the cross-section of the gas-pressure sintered material and (b) the results of the measurements of the colour.

brown or green. The effect of the rare earth ion on the colour of the material was investigated for α' -SiAlONs using different rare earths.⁹ Coloration of β -silicon nitride materials using different lanthanides is also possible if the dark coloration of the matrix is reduced or prevented.

The interaction of light with a ceramic material is shown schematically in Fig. 2. If the angle between the normal of the surface and the direction of the light is small, the fraction of reflected light at the outer surface is small. In a ceramic, unlike in a glass, reflection of the light can also take place at grain boundaries and defects (pores, cracks, inclusions with different refractive indexes from that of the bulk material). For this reason, ceramics with no colour centres are normally white and not transparent. Special measures (clean grain boundaries, avoidance of pores) must be taken in order to obtain translucent or transparent ceramics.

The black or grey colour of the silicon nitride materials is connected with the grain boundaries. Extraction of the grain boundaries by acid solutions causes the colour of the material to change from black to white (Fig. 3). The nature of the colour centres is not completely clear. It was shown that Si inclusions in the range of 10 to 50

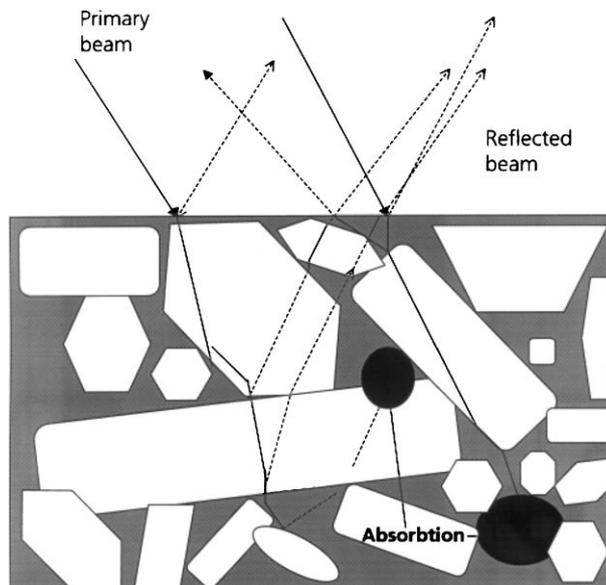


Fig. 2. Interaction of light with the ceramics (schematic view).

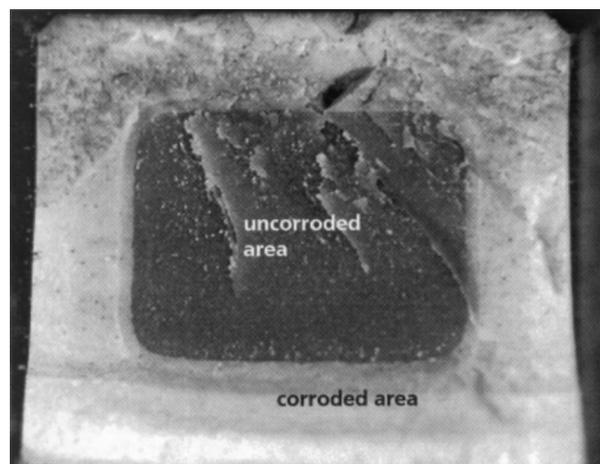


Fig. 3. Micrograph of a silicon nitride material corroded for 200 h in 1 N H₂SO₄ at 90°C.

nm are responsible for the coloration of glasses;^{10–12} however, larger metallic inclusions can also act as colour centres.¹³ Additionally, defects in the glass structure cannot be excluded as reasons for the coloration, as was found in the case of radiation damage of SiO₂ glasses.¹⁴ These defects are connected with oxygen vacancies.^{14–16} The absorption bands of such colour centres in SiO₂ glass usually have a high energy and are not active in the visible range of the spectra. However, the interaction of these centres with other impurities, such as Al or alkaline elements, can shift the absorption band to the visible range.¹⁵ The treatment of a pure oxide glass with hydrogen leads to a dark coloration of the glass.¹⁰ Swarts¹⁶ found a precursor for an absorption peak at 570 nm after treatment of the glasses under reducing

atmospheres which can be activated by UV- irradiation. These colour centres were connected with an oxygen deficit in the material.^{14–16} In Ref. 17, it was shown that in a strongly reducing atmosphere (weight loss during sintering >3%), the colour became darker; this was connected with the formation of Si inclusions. At the same time the high temperature strength increases due to the accelerated crystallisation of the grain boundary phase. The TEM investigations of oxynitride glasses were used to prove that FeSi_x and Si impurities are colour centres.¹³

The aim of this paper is to explain, on the basis of experiments, the influence of the sintering conditions on the coloration of the bulk and on the formation of a differently coloured outer layer.

2. Experimental

Different silicon nitride ceramics were gas-pressure sintered at a nitrogen pressure of 0.5 MPa until closed porosity (>97% theoretical density) was attained (Table 1). Samples (10×10×15 mm) were cut out of the homogeneous grey-coloured bulk material and tempered under various tempering conditions (Table 2). The specific weight loss (weight loss/surface area of the sample) and the density (Archimedes method) were measured after thermal treatment. The samples were analysed by grey-level analysis, X-ray diffraction, SEM and TEM.

The grey-level measurement was conducted with the grey-level analysing system² shown in Fig. 4. Measurement of the concentration of colour centres in glasses is usually made using transmitted light, but the preparation of thin ceramic foils that transmit sufficient light is quite difficult and not suitable for the systematic analysis of a large number of samples. For this reason, the analysis was made using reflected light (Fig. 4). To obtain reproducible data in all cases, a constant lapping procedure was used, the angle between the light sources and the normal to the surface was held constant (<30°) and the equipment was calibrated using standard samples. A

Table 1
Materials used for the experiments

Material	Si ₃ N ₄ powder	Additives	Density (g/cm ³)
I	SNE10 ^a	5Y ₂ O ₃ ^b , 2 Al ₂ O ₃ ^c	3.19
II	Baysinid ^d	6 Y ₂ O ₃ , 4 Al ₂ O ₃	3.10
IIa	Baysinid	6 Y ₂ O ₃ , 4 Al ₂ O ₃	2.97
III	Baysinid	8 Y ₂ O ₃ , 4 Al ₂ O ₃	3.28

^a UBE Industries.

^b Grade fine HCST.

^c ALCOA-A16.

^d Bayer AG.

Table 2
Parameter of the heat treatments^a

Number	Furnace	P_N (bar)	T_{max} (°C)	T_a (°C)	t_h (min)	t_a (min)
I	GPS	1.3	1700		5,60,240,480	
II	Carbon-free furnace	1.3	1700		5,60,240,480	
III	GPS	6	1600		5,60,240,480	
IV	GPS	6	1800		5,60,240,480	
V	GPS	51	1800		5,60,240,480	
VIII	GPS	6	1800	1500		60 60,240,480

^a P_N , nitrogen gas pressure; T_{max} , maximal temperature of heat treatment; T_a , temperature of annealing for decoloration; t_h , time of isothermal heat treatment; heating up and cooling was carried out with 20°C/min; GPS, gas-pressure furnace with a carbon heater.

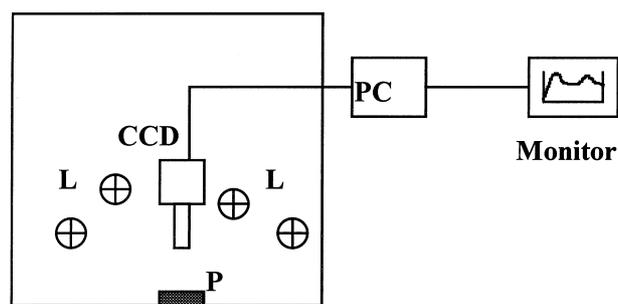


Fig. 4. Schematic drawing of the grey level measurement equipment (L, light sources; P, sample; CCD, CCD-camera).

black sample has the grey level 0 and the white sample has the grey level 256. The deviations between different measurements (measurement of the same sample at different times) were lower than 10%. Results and the parameters determined on the basis of these measurements are given in Fig. 1. A systematic error connected with the differing microstructures of the materials must be taken into account because the measured colour of the samples depends on the intensity of the light reflected at the internal grain boundaries, pores or inclusions. When the light that is reflected at internal grain boundaries, pores or inclusions is increased (due to higher porosity, finer grains, etc.), the penetration depth of the light decreases. The result is that materials with higher reflection abilities (porous materials, etc.) appear to be brighter than those with lower reflection abilities, even at the same concentration of colour centres, because the probability of the interaction of light with the colour centre is proportional to the medium depth of penetration of the light. On the other hand, when there is a high concentration of colour centres, the penetration depth is reduced by the increased absorption and scattering of the light by the inclusions.

TEM investigations were carried out using two different systems: CM200 (Philips) with a standard EDX

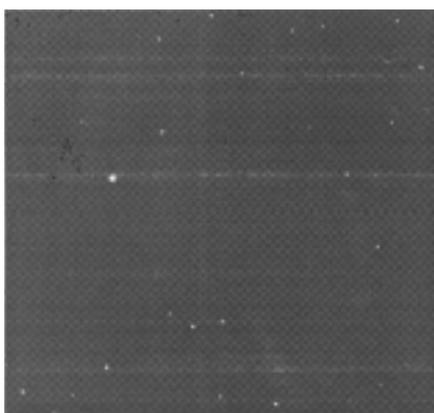
system (EDAX) and JEM 2010 (Jeol) with the EDX system Voyager 33050 (NORAN). The preparation of the samples was carried out using standard procedures for preparation of ceramic thin foils.

X-ray diffraction was carried out with the URD65 (Seifert-FPM) with Cu K_α radiation. An ELD detector was used for the detection of the low amount of silicon. The quantitative calculations were made using the method described in Ref. 18.

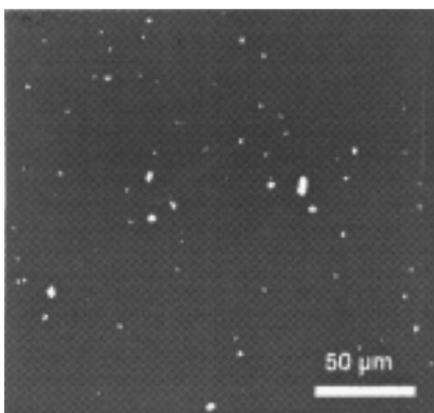
3. Results and discussion

3.1. Nature of the colour centres and mechanism of their formation

Samples of materials I and II with a wide range of grey levels were analysed by optical microscopy, XRD and TEM. The results (Figs. 5–8) show that Si inclusions in the range of a few nm up to several micrometers can be found in the material. Micrometer-sized inclusions also contain other metallic impurities. The TEM investigations



Grey level 100



Grey level 80

Fig. 5. Optical micrograph (bright field) of materials with different grey levels (material I Si inclusions are bright).

show that the metallic inclusions are very rich in Si. The Si content is higher than the content expected from thermodynamic calculations.¹⁹ This fact and the fact that the amount of such inclusions in the μm range can be correlated with the formation of the dark surface layer (Fig. 6) suggest that the high silicon amount in the silicide is not an equilibrium one but is determined by kinetic factors.

The darkness (grey level) corresponds to the concentration of metallic silicon inclusions. The amount of metallic inclusions, which was determined by optical microscopic measurements, can be correlated with those determined by XRD (Figs. 5, 8 and 9). The relationship between the amount of silicon and silicide inclusions and the grey level can be expressed at least for the lower Si concentration by the equation:

$$-\ln\left(\frac{GW}{GW_0}\right) = A_f \cdot x \quad (1)$$

GW : grey level of the sample
 GW_0 : grey level of the brightest sample (256)
 A_f : constant.

This is very similar to the Lambert–Beer law, which relates the transmitted light to the primary light intensity. At higher concentrations of colour centres, deviations from the linear dependencies were observed. This deviation can be explained due to the reduced penetration depth of the light and the change in the ratio of absorption to scattering with increasing particle size.¹²

The experimental data suggest that the colour of the material is caused by the silicon inclusions that have sizes of several μm up to several nm. This conclusion is in agreement with photoluminescence measurements, which show that the luminescence peaks are connected with pure Si or with (N) impurity centres in Si.² The results are also consistent with investigations of oxynitride glasses.¹⁰

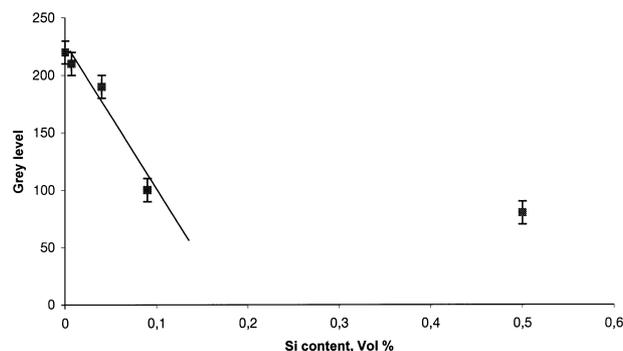


Fig. 6. Results of the quantitative analysis of the area fraction of the metallic inclusions analysis of the bright field images and the fitted curve.

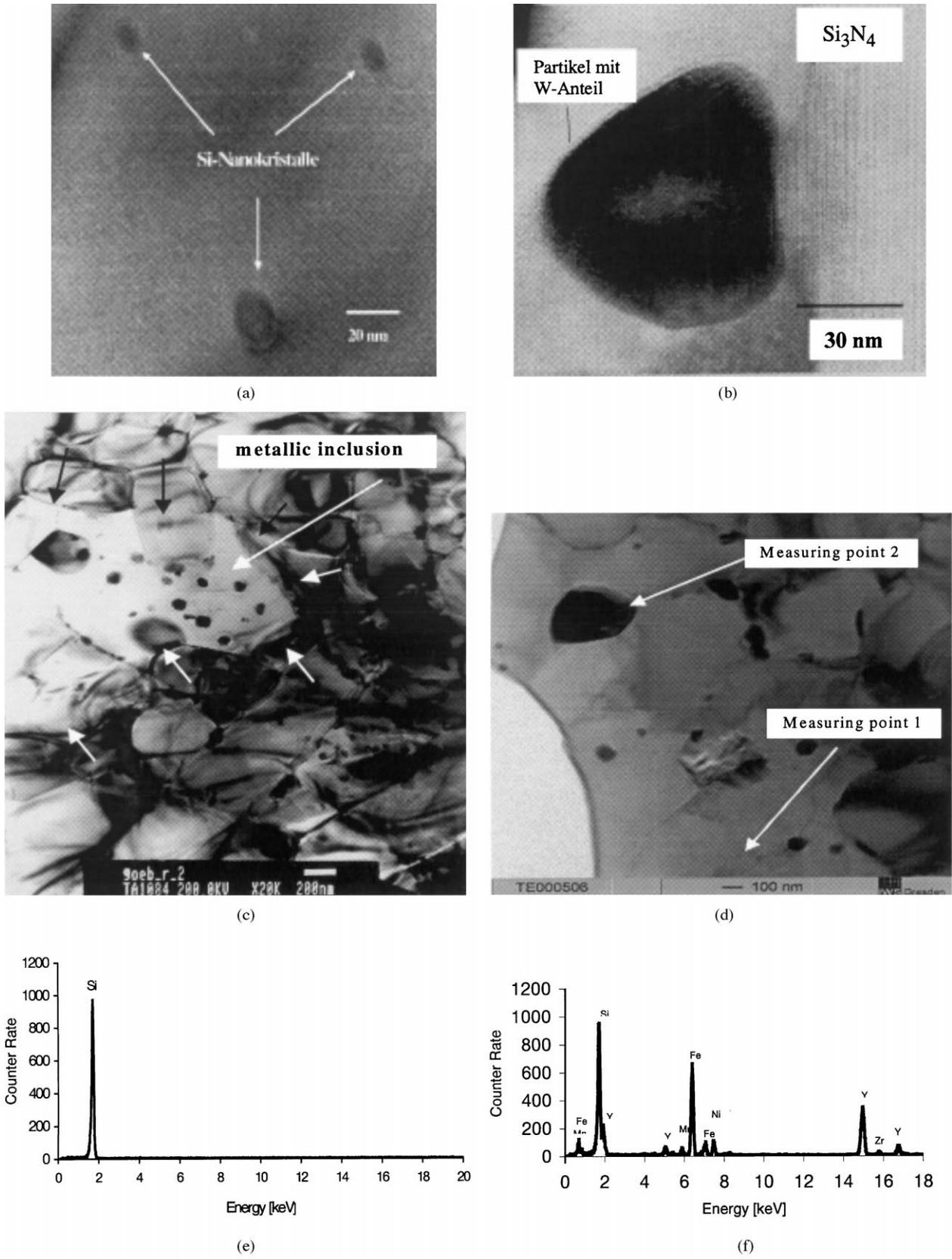


Fig. 7. TEM micrograph of a metallic inclusion in material I: (a) Si nano inclusions; (b) tungsten containing metallic inclusion in a material sintered in a furnace with tungsten heater; (c),(d) metallic inclusion in the micrometer range containing Si and FeSi_x ; (e),(f) results of EDX measurement [(e) measuring point 1; (f) measuring point 2].

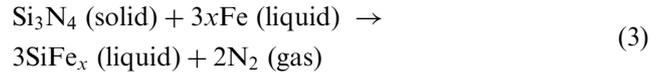
Therefore, the basis for the description of the dark colour of silicon nitride materials is the understanding of the mechanisms of formation of free silicon inclusions, which act as colour centres.

The formation of free silicon during sintering cannot take place by a simple dissociation of Si_3N_4 into silicon and nitrogen, as is often supposed,^{20,21} because the sintering takes place at nitrogen pressures higher than the equilibrium pressure of Eq. (2) (see Fig. 2: the pressure is about 0.1 MPa at 1900°C).



This mechanism is only possible when the activity of Si is lower than 1, i.e. when a solution of silicon is formed. This is the case when the materials contain impurities of the silicide-forming elements, for example

iron, which forms a silicide according to the following reaction:



The dependence of the composition of the iron silicide on the sintering parameters was investigated in Ref. 19. It was shown that at 1 atmosphere (0.1 MPa) nitrogen pressure, the composition of the silicide is FeSi_x with $x < 3.2$ at temperatures up to 1850°C. This is much lower than the composition of the silicides that were found in the dark samples, which was determined by TEM investigations (Fig. 7). This and the fact that pure Si inclusions were found ascertain that additional mechanisms for the formation of Si must exist.

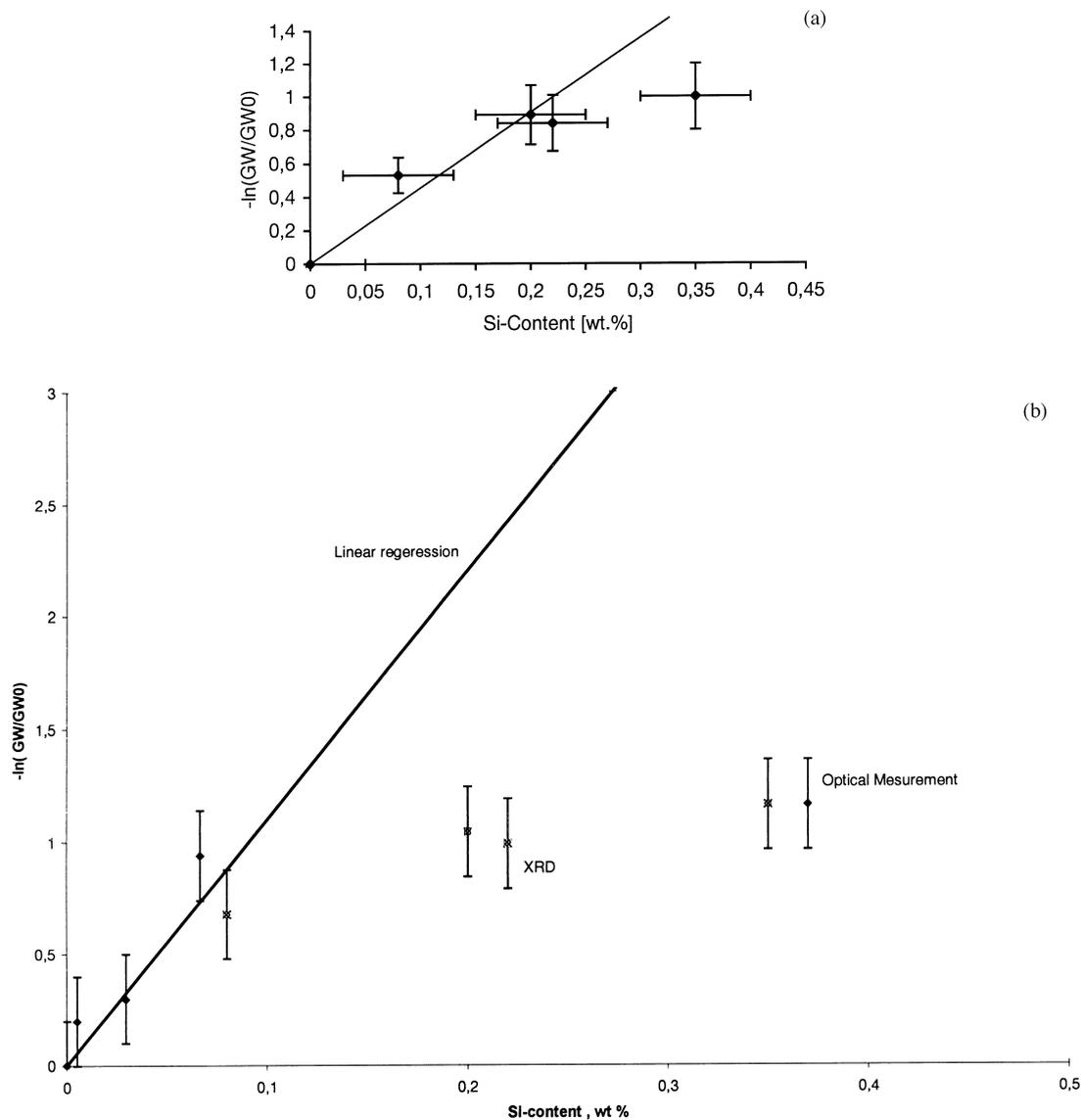
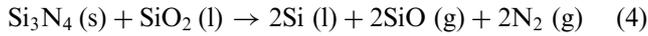


Fig. 8. (a) Correlation between the grey level of the material and the amount of silicon measured by XRD; (b) correlation between the grey level of the materials and the amount of silicon determined by XRD and optical measurements (Fig. 6).

The mechanism discussed in Ref. 11:



also cannot be responsible for the formation of free silicon because the liquid silicon that is formed will be nitrated again by the nitrogen, whose pressure is higher than the equilibrium pressure shown in Eq. (2) (Fig. 9).

Thermodynamic calculations show that the interaction of the oxynitride liquid with the silicon nitride leads to a high SiO partial pressure under the given sintering conditions. This partial pressure is 1000 times higher than the partial pressure of Si (Fig. 9). This interaction can be described by the reaction:

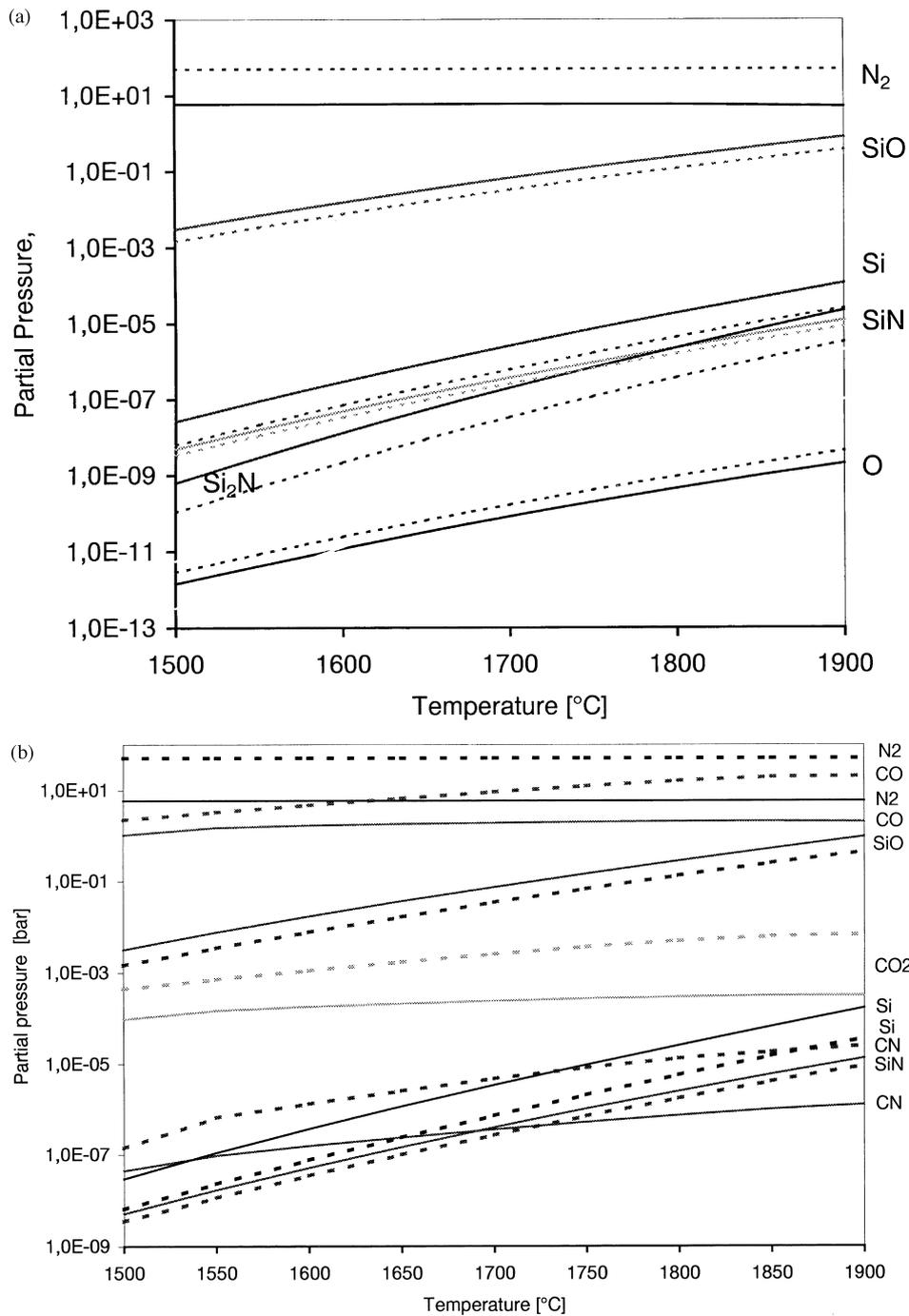


Fig. 9. (a) Composition of the gas phase over a mixture made of SiO₂ and Si₃N₄ as a function of temperature (—, 0.6 MPa nitrogen pressure; ---, 5.1 MPa nitrogen pressure); (b) composition of the gas phase over a mixture made of SiO₂ and Si₃N₄/SiC/C as a function of temperature (—, 0.6 MPa nitrogen pressure; ---, 5.1 MPa nitrogen pressure).

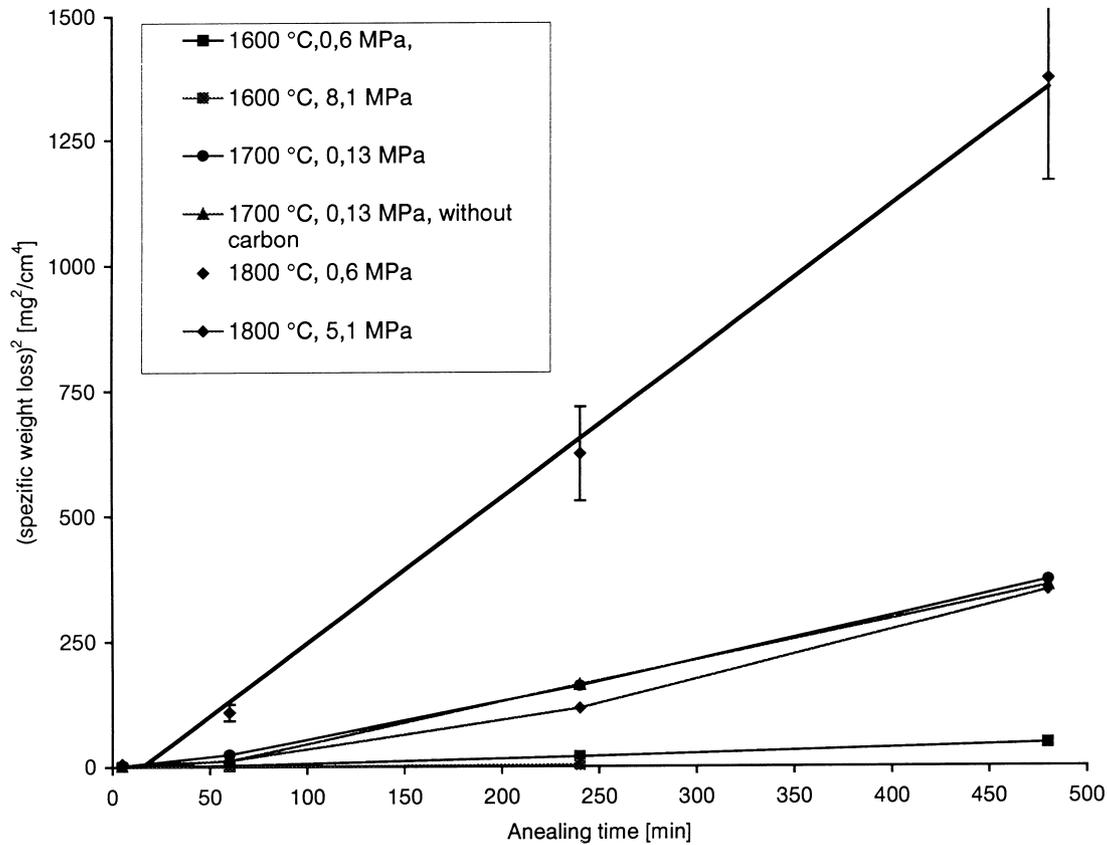


Fig. 10. Specific weight loss as a function of the isothermal sintering time at different temperatures. Material II; the temperature and the nitrogen pressure are indicated; without carbon-sintered in carbon-free furnace; all other samples are sintered in a furnace with carbon heater.

The SiO that is formed will not only exist in the gaseous phase but also dissolve in the oxynitride liquid. The solubility must be quite high, because the structure is very similar to the structure of the oxynitride melt. Alternatively, this process can be described as a simple formation of oxygen vacancies in the oxynitride melt or as a simple reduction of silicon from a valence of four to a valence of two:



Due to the decreasing stability of the divalent Si during cooling from sintering temperatures, the SiO will decompose during cooling:



The silicon that is formed is only kinetically stable due to the low diffusion rate of nitrogen through the dense ceramic. In Si_3N_4 ceramics with open porosity, the diffusion path is short enough that the nitrogen will react with the Si or directly with the SiO to form silicon nitride. This agrees with experiments showing that sintered Si_3N_4 ceramics with open porosity are lighter in colour than those with no open porosity.

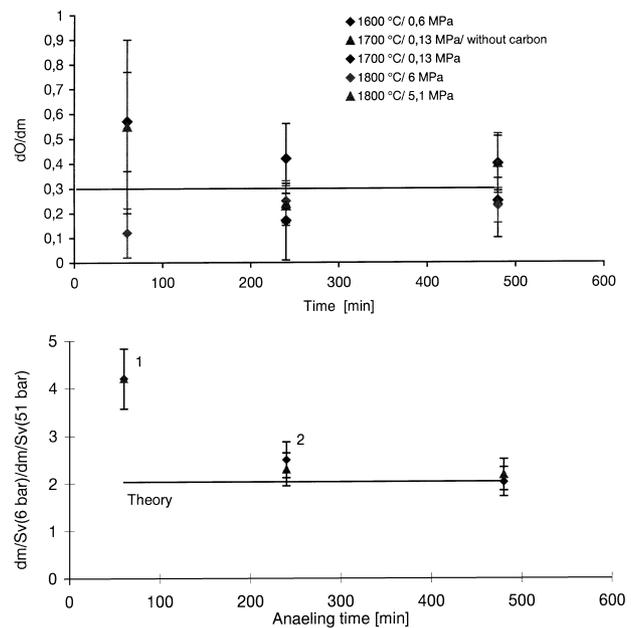


Fig. 11. (a) Ratio of the change of the oxygen content in the material to the specific weight loss as a function of the isothermal sintering time; (b) ratio of the specific weight loss of the samples sintered at 0.6 and 51 MPa at 1800 °C. The theoretical value is calculated on the bases of the silicon monoxide partial pressures (see Fig. 9).

This mechanism was also supposed by Geld et al.,²² who investigated the formation of free silicon in stags, and by Messier et al.,²³ who investigated oxynitride glasses. Additional evidence for such a mechanism of silicon formation can be found by analysing the weight losses during sintering (Figs. 10 and 11).² The main mechanism of the evaporation is connected with the formation of SiO according to reaction (5), as is indicated by the measured ratio of oxygen loss to weight

loss, which corresponds with the value 0.3 predicted on the basis of Eq. (5) (Fig. 11). The differences at low sintering times are due to the higher error of determination and additional mechanisms connected with surface reactions.

Evidence that the carbon monoxide formation has only a slight influence under the conditions used is provided by the fact that the difference between sintering in a furnace with a carbon heater and in a carbon-free

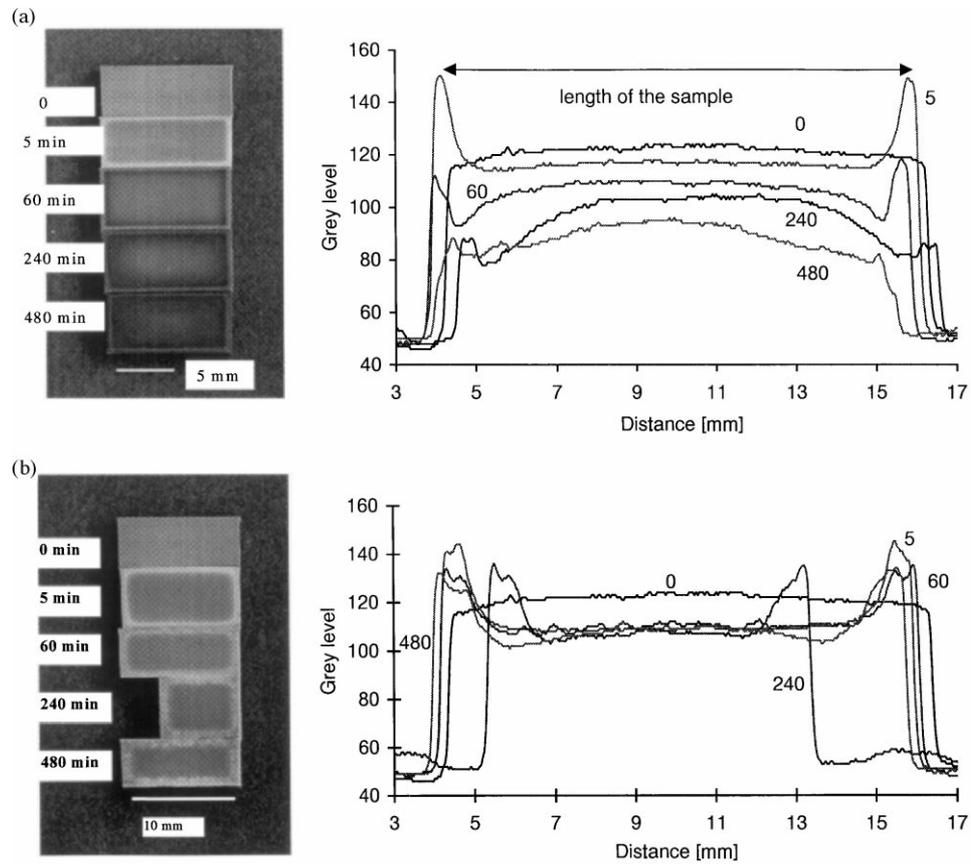


Fig. 12. Image of samples of material II and the measured grey levels: (a) sintering at 1800°C, 6 bar; (b) 1800°C, 51 bar (by the samples the time of isothermal sintering is given).

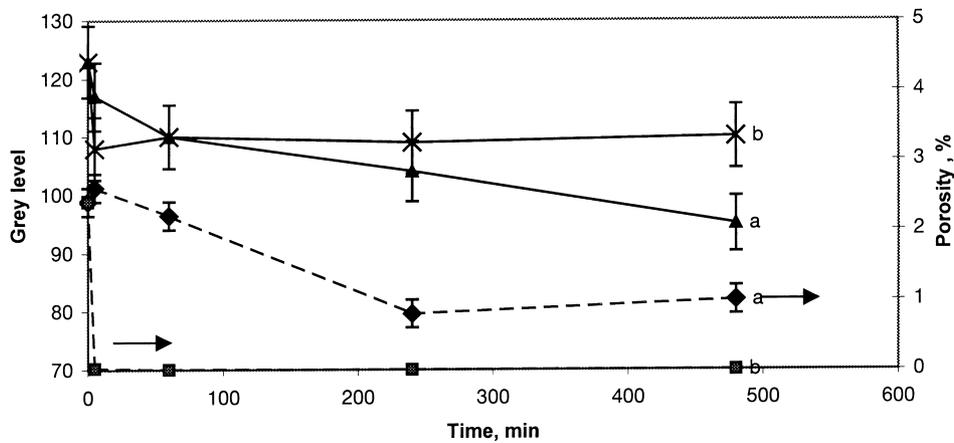


Fig. 13. Dependence of the measured medium grey levels of the bulk and the measured at polished sections porosity of the samples of material II on the isothermal sintering time: (a) sintering at 1800°C, 0.6 MPa; (b) 1800°C, 5.1 MPa.

furnace with a tungsten heater is quite small. With increasing nitrogen pressure the weight loss decreases in the same manner as it is predicted by Eq. (5) (Fig. 9). If the CO formation were the main mechanism of the decomposition, then the weight loss would have to increase with increasing nitrogen pressure, which was not observed.

All of the experimental results regarding weight loss and the formation of free silicon described in this paper can be explained by the mechanism of the formation of free silicon based on the SiO formation. This mechanism is the basis of the discussion of the correlation between the sintering parameters and the coloration of the materials.

3.2. Experimental results on the dependence of the coloration on sintering parameters

Selected micrographs and the grey levels measured for the samples sintered at 1800°C at 6 and 51 bar for different sintering times are shown in Figs. 12 and 13.

The experimental data (Figs. 12–14) show that the colour of the bulk for material II sintered at 5.1 MPa is constant for sintering times longer than 5 min, whereas the darkness of the materials sintered at 0.6 MPa increases with sintering time (grey level decreases). The same results were found for material I. The increase in the coloration of the bulk correlates with a decrease in the porosity. The bulk colour does not change when the porosity is held constant as it was found for the sintering at 5.1 MPa (Fig. 13). The samples sintered at lower nitrogen pressures have a darker bulk than samples with the same density sintered at 5.1 MPa nitrogen pressure.

The thickness of the dark surface layer increases with the square root of the sintering time (Fig. 14) and can be correlated with the weight loss (Fig. 15). The ascent of the curves relating the layer thickness with the specific weight loss depends on the composition of the materials, when the sintering conditions are held constant (Fig. 15).

The data for samples sintered at 1750°C and 0.13 MPa in a carbon-containing and in a carbon-free atmosphere are given in Fig. 16.

Comparison of the data obtained by sintering in a carbon-free furnace and in a gas-pressure furnace with a carbon heater under the same sintering conditions shows that for nearly the same weight loss, the formation of the dark surface layer is more pronounced in the case of sintering in a carbon-containing atmosphere. The thickness of the layer is greater and the colour of the layer is darker for the samples sintered in the carbon-containing atmosphere (Fig. 17). Measurements of the carbon content of the samples show no increase in the carbon content of the samples; in fact, the content remains constant at the level observed in the starting samples: $0.1 \pm 0.05\%$. This is an indication that the formation of

the dark surface layer is influenced by the different oxygen partial pressures occurring in the two systems.

The samples sintered at 5.1 MPa nitrogen pressure do not exhibit a dark surface layer. Only a bright layer with a nearly constant thickness was observed (Fig. 14). This layer is formed during cooling of the samples from the sintering temperature. This is confirmed by the investigation of samples cooled at different cooling rates (see Part II). The samples cooled at 120 K/mm have a remarkably thinner bright surface layer than the samples cooled at 10 K/mm. This indicates that the formation of the outer bright layer takes place during cooling and is determined by the cooling regime.

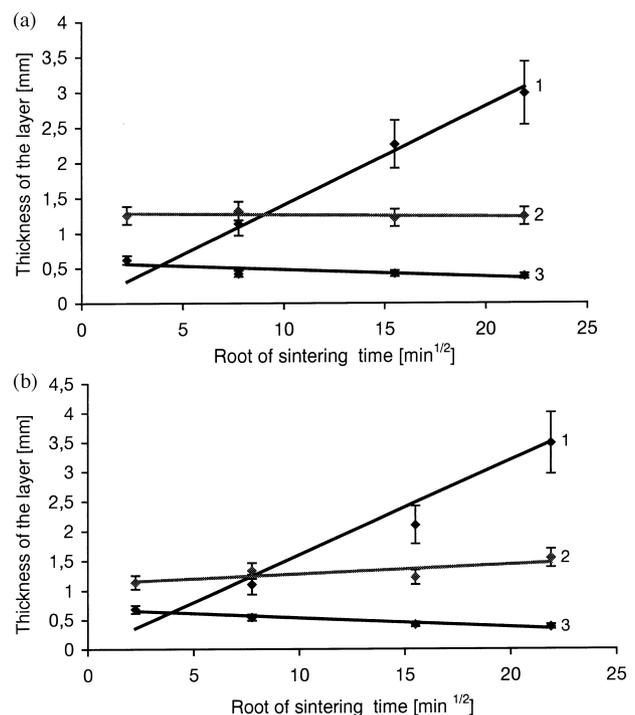


Fig. 14. Dependence of the thickness of the dark and bright near surface layer on the isothermal sintering time sintered at 1800°C at 0.6 and 5.1 MPa: (a) material I and (b) material II: 1, dark layer at 0.6 MPa; 2, bright layer at 5.1 MPa; 3, bright layer at 0.6 MPa nitrogen pressure.

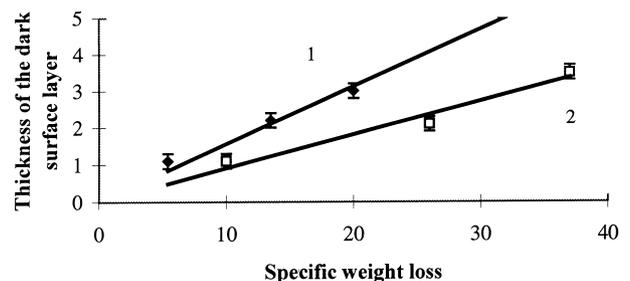


Fig. 15. Dependence of the thickness of the dark near surface layer on the specific weight loss: 1, material I and 2, II sintered at 1800°C 1, 4 and 8 h.

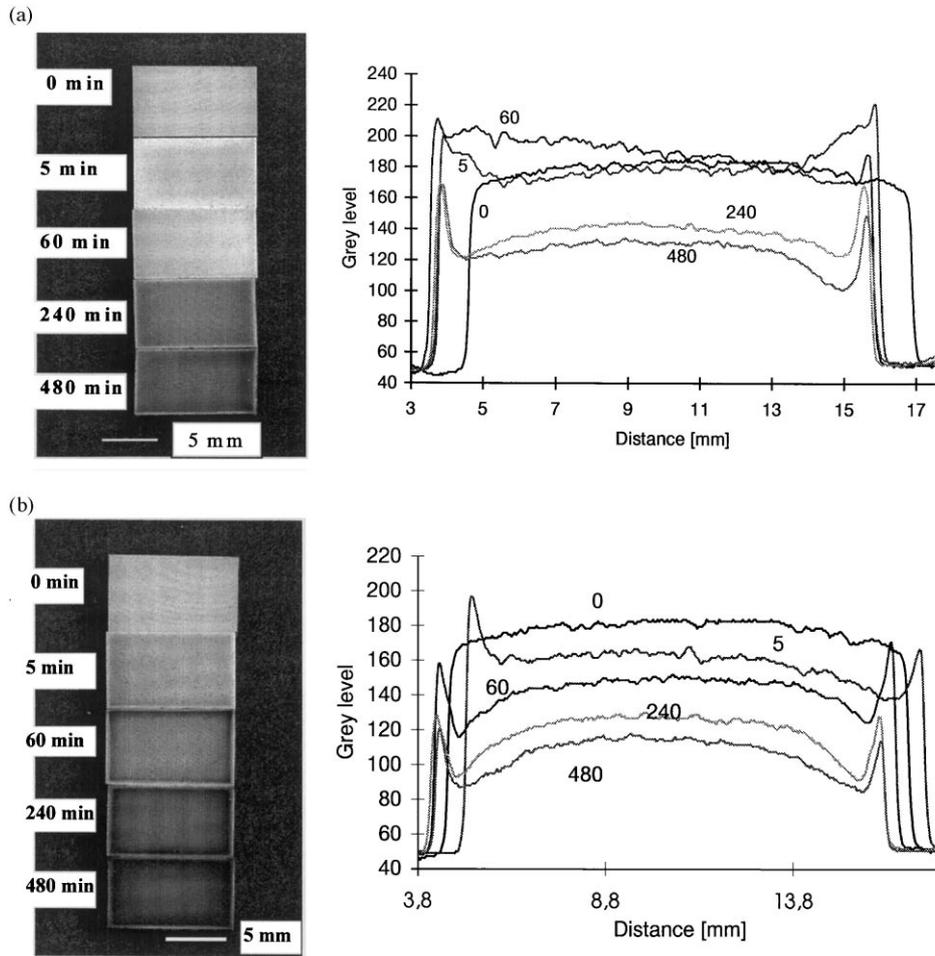


Fig. 16. Micrograph and measured grey levels of samples sintered at 1750°C at 0.16 MPa (a) in a carbon-free furnace (tungsten heater) and (b) in a furnace with carbon heater.

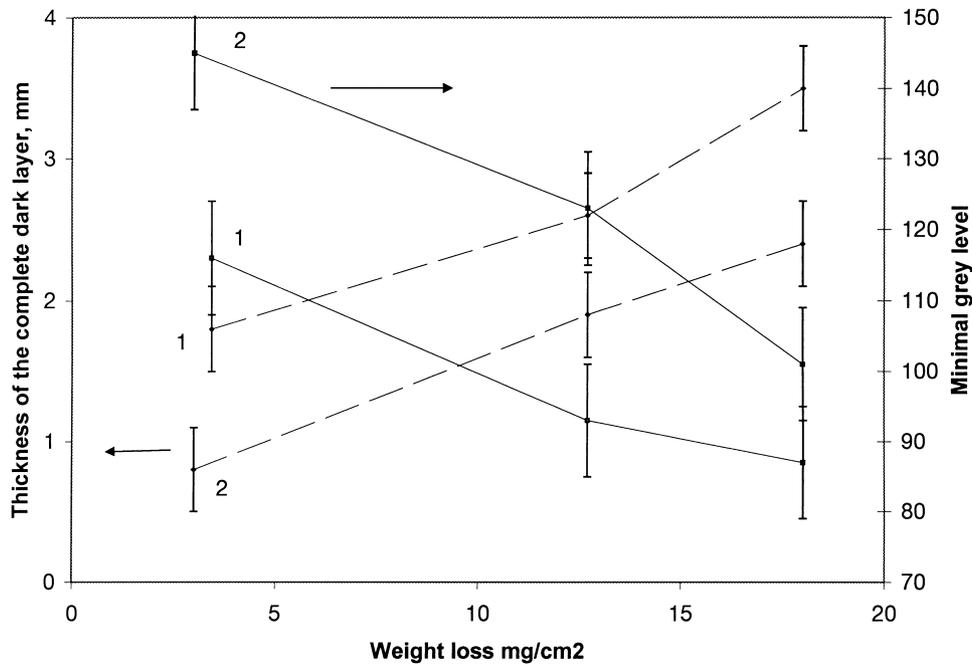


Fig. 17. Dependence of the thickness of the dark layer and the brightness (minimal grey level) on weight loss for heat treatment of the material I at 1750°C at 0.16 MPa in (1) a gas-pressure furnace with carbon heater and (2) in a carbon-free furnace.

4. Conclusions

The experimental data about the coloration 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. Impurities of the transition metals can act as nucleating agent for the formation of metallic silicon.
- 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 depends additionally 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.

The results of the investigations provide a model of the coloration behaviour based on the thermodynamic data developed in Part II.

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