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Calculation of Heterogeneous Phase Equilibria in the System Si–Mg–N–O

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Abstract

The thermodynamic calculations of phase equilibria especially refer to the pseudoternary system Si_3N_4–Si_2N_2O–Mg_2SiO_4. With the model, the liquid phase is treated as a mixture of the quasicomponents 1/7 Si_3N_4, 1/3 SiO_2 and 1/2 MgO, for which an eutectic point was calculated at 1510°C with the composition 0·153 $Si_3N_4 + 0{\cdot}194$ $Si_2N_2O + 0{\cdot}653$ Mg_2SiO_4. For the equilibria Si_3N_4–liquid phase–gaseous phase the partial pressures of Mg and SiO were calculated in dependence on temperature, nitrogen partial pressure and composition of the liquid phase. The results of thermodynamic calculations and experimental studies of sintered Si_3N_4 materials with MgO additives are used to interpret the development of microstructure and the mechanical behaviour at high temperatures.

Die thermodynamischen Berechnungen der Phasengleichgewichte beziehen sich insbesondere auf das pseudoternäre System Si_3N_4–Si_2N_2O–Mg_2SiO_4. Mit dem Modell, das die flüssige Phase als Mischung der Quasikomponenten 1/7 Si_3N_4, 1/3 SiO_2 und 1/2 MgO betrachtet, wurde ein Eutektikum bei 1510°C mit der Zusammensetzung 0·153 Si_3N_4 + 0·194 $Si_2N_2O + 0{\cdot}653$ Mg_2SiO_4 berechnet. Für das Gleichgewicht Si_3N_4–flüssige Phase–Gasphase erfolgte eine Berechnung der Partialdrücke von Mg und SiO in Abhängigkeit von Temperatur, Stickstoffpartialdruck und Zusammensetzung der Schmelze. Anhand der thermodynamischen Berechnungen und experimenteller Ergebnisse von gesinterten Siliziumnitrid-Materialien mit MgO-Zusatz werden Aussagen zur Ausbildung der Mikrostruktur und zum mechanischen Verhalten bei hohen Temperaturen abgeleitet.

Les calculs thermodynamiques des équilibres des phases se rapportent en particulier au système pseudoternaire Si_3N_4–Si_2N_2O–Mg_2SiO_4. A l'aide du modèle considérant la phase liquide comme étant un mélange des quasi-composants 1/7 Si_3N_4, 1/3 SiO_2 et 1/2 MgO, on a pu calculér un eutectique à 1510°C composé de 0·153 $Si_3N_4 + 0{\cdot}194$ $Si_2N_2O + 0{\cdot}653$ Mg_2SiO_4. Pour l'équilibre phase liquide–phase gazeuse les pressions partielles de Mg et SiO ont été calculées en fonction de la température, de la pression partielle d'azote et de la composition de la phase liquide. Des calculs thermodynamiques et des résultats expérimentaux obtenus avec des matériaux frittés de nitrure de silicium avec addition de MgO ont été tirées des conclusions sur la formation da la microstructure et sur le comportement mécanique aux hautes températures.

1 Introduction

Although in the past years many oxides have been found to be suitable as sintering additives for Si_3N_4-based ceramic materials, magnesium oxide remains one of the most widely used densification aids for the sintering of Si_3N_4. The system Si–Mg–N–O can also be used as a model system for theoretical and experimental studies of high-temperature performance. The knowledge of the equilibria Si_3N_4–oxide–nitride melt is necessary for understanding the ceramic's behaviour at high temperatures. It has been shown by experimental studies[1] and computer calculations[2] that the stable equilibria Si_3N_4–Mg_2SiO_4 and Si_2N_2O–Mg_2SiO_4 exist in the system Si_3N_4–SiO_2–MgO. Table 1 shows the compositions and the eutectic temperatures of the interesting systems.

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Table 1. Compositions and temperatures of the eutectic points in the system Si_3N_4–Si_2N_2O–Mg_2SiO_4

Compositions (mole fractions)	*Temperature (K)*	*Reference*
0·19 Si_3N_4 + 0·81 Mg_2SiO_4	1 833	Ref. 1 (experimental)
0·39 Si_3N_2O + 0·61 Mg_2SiO_4	1 798	Ref. 1 (experimental)
0·10 Si_3N_4 + 0·30 Si_2N_2O + 0·60 Mg_2SiO_4	1 788	Ref. 1 (experimental)
0·62 Si_3N_4 + 0·38 Si_2N_2O	2 508	Ref. 11 (calculated)[a]
0·52 Si_3N_4 + 0·48 Si_2N_2O	2 124	Ref. 2 (calculated)[b]
0·61 Si_3N_4 + 0·39 Si_2N_2O	2 475	Ref. 3 (calculated)[a]

[a] Calculated for the condensed system Si_3N_4–SiO_2.

[b] Calculated for the system Si_3N_4–SiO_2 with consideration of the gaseous phase and the metallic silicon melt.

Up to now there have only been results from calculations obtained by Kaufman *et al.*[3] for the phase relations in the condensed system Si_3N_4–SiO_2–MgO. However, these results are not consistent with the experimentally obtained phase relations.[1] Also, the results obtained with consideration to the gaseous phase in the system Si–Mg–N–O[4] are not consistent with the observed phase relations in hot-pressed silicon nitride with MgO additives[1] and with the studies of the densification process of reaction-bonded Si_3N_4.[5]

The aim of these investigations was to calculate the system Si_3N_4–Si_2N_2O–Mg_2SiO_4. It is the most important region of the system Si–Mg–N–O with regard to Si_3N_4 ceramic materials with MgO additives. Furthermore, the microstructure and mechanical properties of some MgO-containing Si_3N_4 materials were investigated. The treatment is made with the assumption that all ions have their conventional valence. This allows the system to be treated as a ternary system at a given pressure.

2 Calculation Method and Thermodynamic Data

For this calculation two programs were used. The program GMIN[6] is based on the method of minimization of Gibbs free energy. The strategy of this program corresponds to the program developed by Eriksson.[7] It was used to calculate the multicomponent equilibria with solid stoichiometric phases and the gaseous phase, because with this program it is not possible to calculate mixing phases with a wide range of composition, e.g. silicate melts in ceramic materials. The second program performs a stepwise calculation of two phase fields for condensed binary and ternary systems. This program was based on the condition of equilibrium

$$\mu_i \text{ (phase I)} = \mu_i \text{ (phase II)}$$

and agrees with the method described by Kaufman & Bernstein.[8] The fields of three or four phases were obtained at the points of intersection of the two phase fields.

Table 2. Thermodynamic data of the condensed stoichiometric compounds[9,11]

	H (J/mol)	*S (J/mol K)*
SiO_2(s)	−820 704	155·721
SiO_2(l)	−811 122	160·521
Si_3N_4(s)	−530 943	357·217
'Si_3N_4(l)'	−321 643	437·710
MgO(s)	−515 000	119·220
MgO(l)	−437 596	144·240
Si_2N_2O(s)	−704 055	252·500
'Si_2N_2O(l)'	−545 880	313·125
Mg_2SiO_4(s)	−1 879 675	407·260
Mg_2SiO_4(l)	−1 808 548	440·020

The thermodynamic data were collected from Refs 9 and 10, except the data of silicon oxynitride. For Si_2N_2O the data selected by Dörner *et al.*[11] were used. These data were converted into the reference state used in Ref. 9 (stable modification of the pure element at 298·15 K). The authors also tried to use the data of Si_2N_2O published by Fegley,[12] but these enthalpy and entropy values do not result in a consistent set of data in connection with the data of the other compounds.

All the thermodynamic data used are listed in Tables 2 and 3. The Gibbs free energy of the condensed phases is described as a linear function of the temperature:

$$G = H - TS$$

Table 3. Thermodynamic data of the gaseous species[10] ($T_0 = 1700$ K)

Species	*H (J/mol)*	*S (J/mol K)*	*C_p (J/mol K)*
Si	479 728	204·93	21·51
Si_2	623 867	301·4	44·29
Si_3	727 737	377·31	69·62
SiO	−49 798	270·58	37·06
SiO_2	−242 543	323·49	60·92
SiN	453 255	276·46	37·79
Mg	176 239	184·72	20·79
MgO	100 035	291·15	49·20
MgN	339 453	287·50	41·87
N_2	45 427	246·16	35·38
N	501 817	189·37	20·79
O_2	47 942	262·57	37·07
O	278 631	197·75	20·83

The Gibbs free energy of the gaseous species is calculated according to the following equation

$$G = H - TS + c_p(T - T_0 - \ln(T/T_0))$$

where c_p is the molar heat capacity and T_0 is the temperature, for which the enthalpy (H) and entropy (S) were selected from the relevant table. The treatment of the liquid phase shall be mentioned later.

3 Results and Discussion

Two methods were applied to calculate the condensed pseudoternary system Si_3N_4–Si_2N_2O–Mg_2SiO_4. On the one hand the phases $Si_{3/7}N_{4/7}$, $Si_{2/5}N_{2/5}O_{1/5}$ and $Mg_{2/7}Si_{1/7}O_{4/7}$ were interpreted as quasicomponents; on the other hand $Si_{3/7}N_{4/7}$, $Si_{1/3}O_{2/3}$ and $Mg_{1/2}O_{1/2}$ were regarded as quasicomponents. The following symbols are employed for these quasicomponents:

SN = 1/7 Si_3N_4
SO = 1/3 SiO_2
MO = 1/2 MgO
SNO = 1/5 Si_2N_2O
FO = 1/7 Mg_2SiO_4

The first method treats the system SN–SNO–FO as a ternary system. The Gibbs free energy of the liquid phase is given by

$$\begin{aligned} G^{\text{liq}} &= xG^{0,1}_{\text{SN}} + yG^{0,1}_{\text{SNO}} + (1-x-y)G^{0,1}_{\text{FO}} \\ &\quad + RT(x\ln(x) + y\ln(y) \\ &\qquad + (1-x-y)\ln(1-x-y)) \\ &\quad + \frac{xy}{x+y}(xA^{1-2} + yA^{2-1}) \\ &\quad + \frac{x(1-x-y)}{1-y}((1-x-y)A^{1-3} + xA^{3-1}) \\ &\quad + \frac{y(1-x-y)}{1-x}((1-x-y)A^{2-3} + yA^{3-2}) \\ &\quad + xy(1-x-y)(xB^1 + yB^2 \\ &\qquad + (1-x-y)B^3) \qquad (1) \end{aligned}$$

where x is the mole fraction of SN and y is the mole fraction of SNO.

The description of the binary excess terms conforms with the model proposed by Kaufman *et al.*[3] The excess parameters for the systems SN–FO and SNO–FO were calculated to reproduce the eutectic points listed in Table 1. All excess parameters used are listed in Table 4.

Table 4. Excess coefficients (J/g-atom) for the model according to eqn (1)

$A^{1-3} = 15\,966$
$A^{3-1} = 40\,323$
$A^{2-3} = 18\,739$
$A^{3-2} = 11\,549$
$A^{1-2} = 30\,000$
$A^{2-1} = 30\,000$
$B^1 = 150\,000$
$B^2 = 30\,000$
$B^3 = 150\,000$

The results obtained with this rather formal method are shown in Fig. 1. A phase diagram of 'classic' ternary shape is obtained, in which the ternary eutectic point is located at 1750 K with the composition

$$0{\cdot}11\ Si_3N_4 + 0{\cdot}22\ Si_2N_2O + 0{\cdot}67\ Mg_2SiO_4$$

Of course the compounds Si_3N_4(s) and Si_2N_2O(s), respectively, practically decompose into Si(l) and N_2, and Si(l), SiO(g) and N_2, respectively. Therefore the phases 'Si_3N_4(l)' and 'Si_2N_2O(l)' have to be regarded as metastable phases and the melting points are hypothetical values.

Secondly the system SN–SNO–FO was treated as a subsystem in the pseudoternary system SN–SO–MO. The Gibbs free energy of the liquid phase is calculated corresponding to the following equation:

$$\begin{aligned} G^{\text{liq}} &= xG^{0,1}_{\text{SN}} + yG^{0,1}_{\text{SO}} + (1-x-y)G^{0,1}_{\text{MO}} \\ &\quad + RT(x\ln(x) + y\ln(y) \\ &\qquad + (1-x-y)\ln(1-x-y)) \\ &\quad + \frac{xy}{x+y}(xD^{1-2} + yD^{2-1}) \\ &\quad + \frac{x(1-x-y)}{1-y}((1-x-y)D^{1-3} + xD^{3-1}) \\ &\quad + \frac{y(1-x-y)}{1-x}((1-x-y)D^{2-3} + yD^{3-2}) \\ &\quad + xy(1-x-y)(xE^1 + yE^2 \\ &\qquad + (1-x-y)E^3) \qquad (2) \end{aligned}$$

(x = mole fraction of SN, y = mole fraction of SO). The excess parameters are listed in Table 5. The results obtained with this model are shown in Figs 2–5. The composition of the ternary eutectic point is

$$0{\cdot}153\ Si_3N_4 + 0{\cdot}194\ Si_2N_2O + 0{\cdot}653\ Mg_2SiO_4$$

at 1785 K.

The comparison between Fig. 1 and Fig. 5 shows that the shape of the liquidus lines depends strongly on the model for calculation. For all further studies the second model was used.

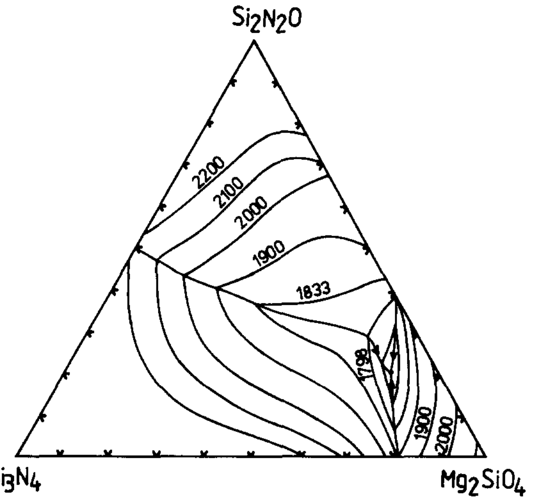

Fig. 1. Condensed system Si_3N_4–Si_2N_2O–Mg_2SiO_4 calculated according to eqn (1).

Table 5. Excess coefficients (J/g-atom) for the model according to eqn (2)

Interaction SN–MO:	$D^{1-3}=$	10000
	$D^{3-1}=$	10000
Interaction SO–MO:	$D^{2-3}=$	−9598
	$D^{3-2}=$	−9598
Interaction SN–SO:	$D^{1-2}=$	42500
	$D^{2-1}=$	42500
Ternary interaction parameters:		
	$E^1=$	−50000
	$E^2=$	−75000
	$E^3=$	−75000

No attempt has been made to approach the real state with a more complicated description. This seems unreasonable because of the little experimental data known in this system.

The partial Gibbs free energies (μ_i) of the quasicomponents in the liquid phase were used for

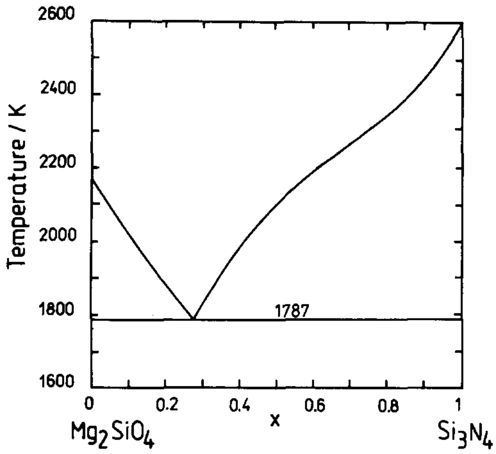

Fig. 2. Section Si_3N_4–Mg_2SiO_4 of the condensed system Si_3N_4–SiO_2–MgO calculated according to eqn (2); x = mole fraction of Si_3N_4.

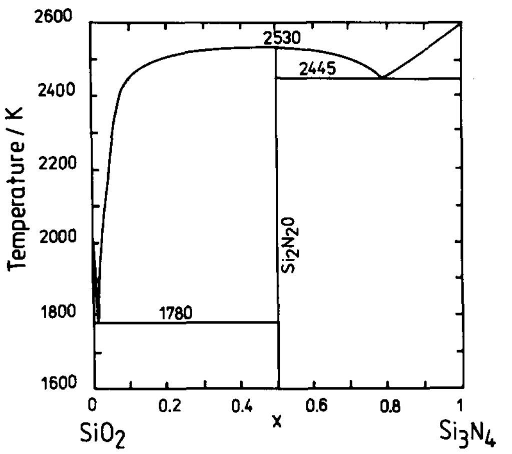

Fig. 4. Quasibinary system Si_3N_4–SiO_2 within the condensed system Si_3N_4–SiO_2–MgO calculated according to eqn (2); x = mole fraction of Si_3N_4.

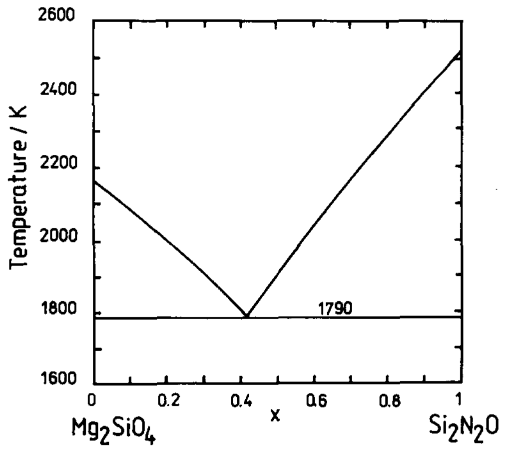

Fig. 3. Section Si_2N_2O–Mg_2SiO_4 of the condensed system Si_3N_4–SiO_2–MgO calculated according to eqn (2); x = mole fraction of Si_2N_2O.

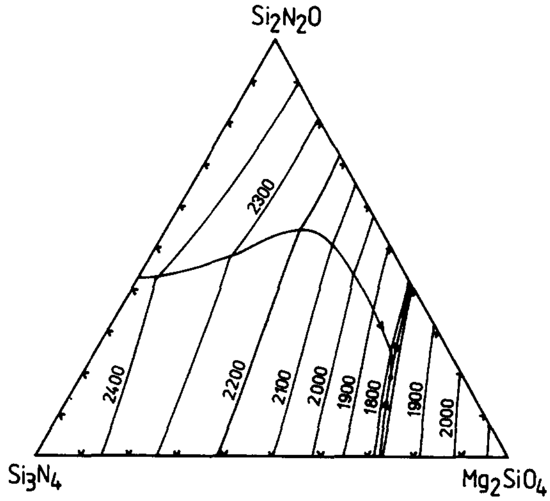

Fig. 5. Pseudoternary system Si_3N_4–Si_2N_2O–Mg_2SiO_4 within the condensed system Si_3N_4–SiO_2–MgO calculated according to eqn (2).

calculation of the partial pressures (p_i) of SiO_2 and MgO because of the relations

$$\mu_i^l = \mu_i^g$$

and

$$\mu_i^g = \mu_i^{0,g} + RT \ln p_i$$

where the gaseous phase is treated as an ideal mixture. The following equilibria were used to calculate the partial pressures of SiO and Mg

$$Si_3N_4(s) = 3\,Si(g) + 2\,N_2$$
$$SiO_2(g) + Si(g) = 2\,SiO(g)$$
$$SiO(g) = Si(g) + 1/2\,O_2$$
$$MgO(g) = Mg(g) + 1/2\,O_2$$

The partial pressures of SiO_2 and MgO were obtained from the calculated partial Gibbs free energy of these components in the melt. For a given partial pressure of N_2 the partial pressures of Si, SiO, O_2 and Mg can be calculated. The partial pressures of SiO and Mg were calculated for several mole relations SiO_2/MgO in the melting phase. The SiO partial pressure increases with increasing amount of SiO_2 in the melt at simultaneous decreasing of p_{Mg} (Fig. 6). The increase of the N_2 partial pressure causes a reduction of p_{Mg} and p_{SiO}, but not in the same order (Fig. 7).

With the aforementioned program, GMIN, the equilibrium $Si_3N_4(s)$–$Si_2N_2O(s)$–$Mg_2SiO_4(s)$–gaseous phase was calculated. This four-phase equilibrium is unambiguously determined, because the remaining two degrees of freedom are given to temperature and pressure in this four-component system. Figure 8 shows the partial pressures of all considered gaseous species. The calculation was carried out for a total pressure $p = 50$ bar.

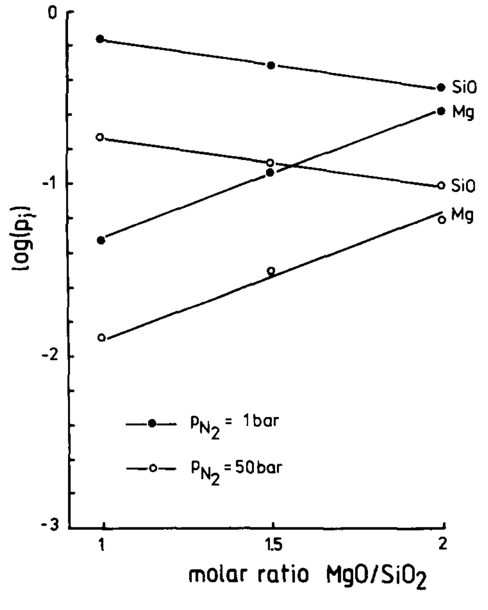

Fig. 6. Calculated partial pressures (p_i) of the equilibrium Si_3N_4–liquid at different molar ratios MgO/SiO_2; $T = 2200$ K.

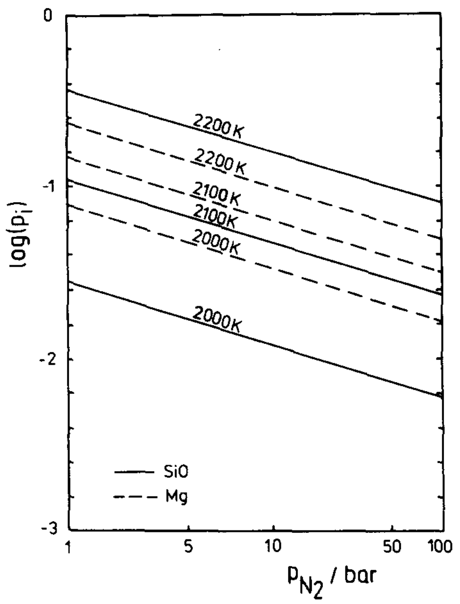

Fig. 7. Calculated partial pressures (p_i) of the equilibrium Si_3N_4–liquid in dependence on the partial pressure of N_2; molar ratio $MgO/SiO_2 = 2$.

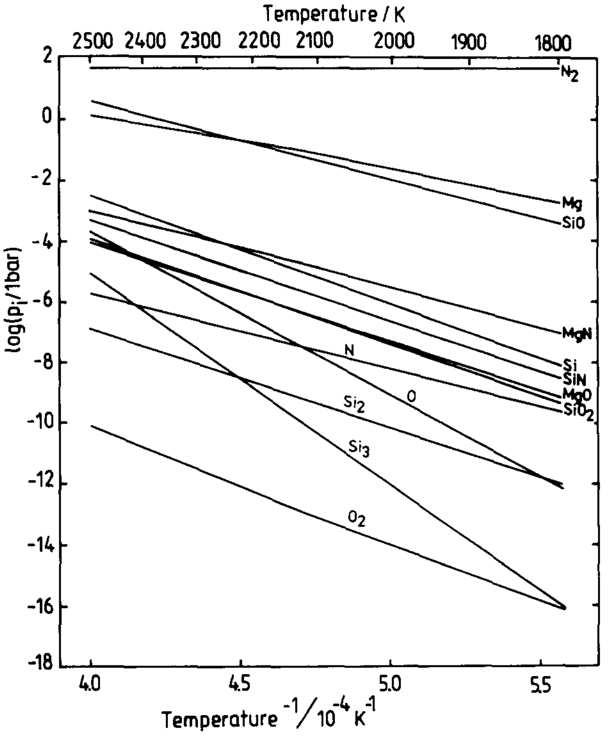

Fig. 8. Calculated partial pressures (p_i) of the gaseous species in the system Si–Mg–N–O for the equilibrium Si_3N_4–Si_2N_2O–Mg_2SiO_4–gas; p_N total pressure = 50 bar.

As expected, the partial pressures of SiO and Mg are somewhat higher in the case of neglecting the liquid phase, but the latter results are sufficiently exact if only the tendency of the gaseous phase composition is of interest.

4 Application

The calculated equilibria were used for the interpretation of the microstructure and high-temperature performance of Si_3N_4-ceramic materials. It is assumed that the calculated results are also valid for the multigrain junctions and the grain boundaries between two grains. This assumption seems to be reasonable because the creep behaviour of Si_3N_4-ceramics can be explained in terms of glasses.[13]

Sintering experiments were carried out in a gas pressure furnace at 1850°C and 50 bar nitrogen pressure. The details of the sample preparation and of the analysis are given in Ref. 14. SRBSN (sintered reaction-bonded silicon nitride) and SSN (sintered silicon nitride) materials were investigated.

The sintering experiments at various temperatures show that the aspect ratio of the grains increases with increasing temperature (see Fig. 9). This effect is caused by the higher solubility of Si_3N_4 in the liquid phase at higher temperatures. At 1750°C (2023 K) the solubility is 42·4 wt% and at 1850°C (2123 K) it is 52·2 wt% for the molar ratio $MgO/SiO_2 = 2$ (see Fig. 2). This will affect the viscosity of the liquid phase. The viscosity will be increased by higher concentration of Si_3N_4 in the melt, whereas the higher temperature decreases the viscosity.

The temperature dependence of the viscosity (η) can be described with an energy of activation in the range 670–900 kJ/mol for internal friction[15] and creep[13] of hot-pressed silicon nitride. The change of $\log \eta$ caused by increasing the temperature from 1750 to 1850°C is in the range $-1{\cdot}8$ to $-2{\cdot}5$. The increase of the viscosity ($\log \eta$) due to the increasing nitrogen content from 50 to 65 equivalent % is about 2.[16] It means that the viscosity of the liquid phase will remain approximately constant. But the amount of the liquid phase increases with increasing temperature. For example, a material with 4 wt% MgO and 3 wt% SiO_2 contains 12 wt% liquid phase at 1750°C (2023 K) and 14·5 wt% liquid phase at 1850°C (2123 K) (see Fig. 2).

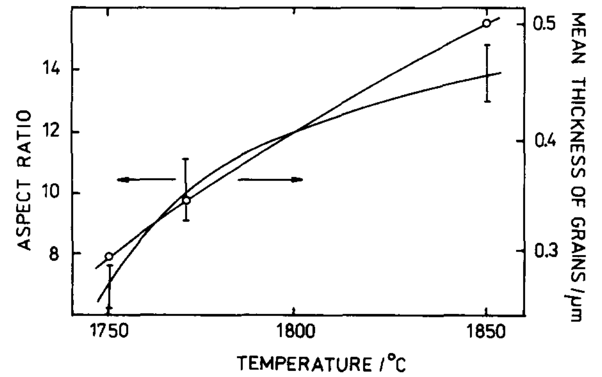

Fig. 9. Dependence of the maximal measured aspect ratio and mean grain size on the sintering temperature (SRBSN; isothermal sintering time, 90 min).

Table 6. Composition and properties of SRBSN- and SSN-materials after sintering at 1 850°C (nitrogen pressure: 50 bar, sintering time: 90 min)

Material	*Content (wt%)*		*Three-point bending strength (σ_{3B}/MPa)*	
	Mg	*O*	*Room temperature*	*1 200°C*
SRBSN1	1·8	0·6	790 ± 60	509 ± 50
SSN1	3·3	3·2	730 ± 70	421 ± 50
SSN2	3·2	0·8	745 ± 70	545 ± 50

The composition and the amount of the liquid phase will also alter during sintering due to the evaporation of sintering aids. The calculation shows that up to the molar ratio $MgO/SiO_2 = 2$ the partial pressure of silicon monoxide is higher than of the atomic magnesium (see Fig. 6). Using MgO in the powder bed it is possible to avoid the evaporation of magnesium, but the evaporation of SiO is accelerated by the reducing atmosphere (carbon heater and crucible during the sintering process.[17] These processes are more important for the preparation of SRBSN than for SSN because the densification of reaction-bonded silicon nitride occurs at higher temperatures in comparison with SSN.[14]

The end of the crystallization which occurred during cooling after the sintering process depends on the molar ratio MgO/SiO_2. The crystallization process of β–Si_3N_4 finishes within the glass-forming region in the system Si–Mg–N–O near the ternary eutectic point (Si_3N_4, Si_2N_2O, Mg_2SiO_4). If the molar ratio MgO/SiO_2 is higher than 2 the crystallization is stopped at the ternary eutectic point (Si_3N_4, Mg_2SiO_4, $MgSiN_2$) outside the glass-forming region. The high temperature performance is influenced by those different endpoints of crystallization. Table 6 shows that the bending strength (at 1200°C) of the material SSN2 with a low oxygen contents is about 30% higher in comparison with the material SSN1 which has a higher oxygen content. Also the SRBSN material with low Mg and oxygen contents has higher strength at 1200°C.

5 Conclusions

The presented calculations of the pseudoternary system Si_3N_4–Si_2N_2O–Mg_2SiO_4 show that the data set, including the model for description of the Gibbs free energy of the liquid phase is consistent with the known experimental results. The calculated results are suitable for better understanding of high-temperature performance of Si_3N_4 materials with MgO additives and they allow prediction of optimal sintering and recrystallization conditions.

References

1. Lange, F. F., Silicon nitride polyphase systems: Fabrication, microstructure and properties. *Int Met. Rev.*, **25** (1980) 1–20.
2. Müller, R., Konstitutionsuntersuchungen und thermodynamische Rechnungen im System Mg,Si/N,O. PhD Thesis, Stuttgart University, 1981.
3. Kaufman, L., Hayes, F. & Birnie, D., Calculation of quasibinary and quasiternary oxynitride systems. *High Temp.-High. Press.*, **14** (1982) 619–31.
4. Weiss, J. & Lukas, H. L. Calculated phase equilibria in silicon nitride systems. In *Materials Science Forum*, Vol. 47, ed. D. A. Bonnel & T. Y. Tien. Trans Tech Publications, Switzerland, 1989, pp. 43–57.
5. Pabst, J. & Herrmann, M., The kinetics of postsintering of reaction-bonded silicon nitride with different α/β phase content. *Science of Sintering*, **21** (1989) 155–60.
6. Sommer, K.-H., Program GMIN, Documentation for Users. ZFW, Dresden, 1987.
7. Eriksson, G., Thermodynamic studies of high-temperature equilibria. *Acta Chem. Scand.*, **25** (1971) 2651–8.
8. Kaufman, L. & Bernstein, H., *Computer Calculation of Phase Diagrams*. Academic Press, New York, 1970.
9. Barin, I. & Knacke, O., *Thermochemical Properties of Inorganic Substances*. Springer Verlag, Berlin–Heidelberg–New York, 1973, Supplement 1977.
10. Glushko, V. P. *et al.*, *Termodinamiceskie svoistva individualnych vescestv*, Vols 1–3. Moscow, 1978, 1979, 1981.
11. Dörner, P., Gauckler, L. J., Krieg, H., Lukas, H. L., Petzow, G. & Weiss, J., Calculation of heterogeneous phase equilibria in the SiAlON system. *J. Mat. Sci.*, **16** (1981) 935–43.
12. Fegley, M. B., The thermodynamic properties of silicon oxynitride. *J. Am. Ceram. Soc.*, **64** (1981) C124–C126.
13. Schaeffer, H. A., Sauerstoff- und Siliziumdiffusion in silicatischen Gläsern. PhD Thesis, Erlangen University, 1980.
14. Herrmann, M., Keßler, S., Pabst, J., Richter, H.-J. & Hermel, W., Sinterverhalten und Gefügeentwicklung in Siliziumnitridkeramiken. *Keramische Zeitschrift*, **42** (1990) 250–3.
15. Mosher, D. R., Raj, R. & Kossowsky, R., Measurements of viscosity of the grain-boundary phase in hot-pressed silicon nitride. *J. Mat. Sci.*, **11** (1976) 49–53.
16. Drew, R. A. L., Hampshire, S. & Jack, K. H., Nitrogen glasses and glass ceramics. In *Proceedings of the International Symposium on Ceramic Components for Engines*, Japan, 1983, pp. 394–403.
17. Richter, H.-J. & Herrmann, M., Zur Wechselwirkung von Siliziumnitridpulver mit kohlenstoffhaltigen Ofenmaterialien. In *Tagungsband Festkörperchemie und Keramik*, Holzhau, GDR, 1988, pp. 164–6.