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Calculation of heterogeneous phase equilibria in the SiAlON system

P. DÖRNER, L. J. GAUCKLER, H. KRIEG, H. L. LUKAS,
G. PETZOW, J. WEISS
Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaften,
D-7 Stuttgart 80, W Germany

Two available computer programs have been adapted for the calculation of phase equilibria in salt systems. Missing thermodynamic data have been estimated from known values and compared with experimental literature data. With one program the condensed quasibinaries Al_2O_3–AlN and SiO_2–Si_3N_4 have been calculated. The other program was used to calculate heterogeneous phase equilibria in the SiAlON system. The results clearly show the importance of composition and partial pressures of the gas phase on the condensed equilibria.

1. Introduction

In order to determine optimal fabrication and application conditions for Si_3N_4 ceramics, the thermodynamic properties of Si_3N_4 at high temperatures have been studied by both experimental investigations [1–3] and by computer calculations [4].

For the .calculations two different programs were used. The Lukas program [5, 6] is based on the Newton–Raphson-iteration method and performs a stepped calculation of the different n-phase fields for condensed binary and ternary systems without using an overall composition.

The second program was developed by Eriksson *et al.* [7–9]; it calculates for a given temperature, pressure and overall concentration, the compositions and amounts of the equilibrium phases by minimization of the Gibb's free energy. This program was modified for the calculation of phase equilibria in salt systems; the mixing entropy is described by introducing the ionic charge for the salt liquid. This oxide–nitride liquid [3] is described as being formed of single ions with the overall charge of this phase set to zero and shall be called "salt liquid" below. The crystalline β-solid-solution (β-ss) phase [1–3] is described by exchanging Al^{3+} for Si^{4+} on the cation sublattice while on the anion sublattice three of the four N^{3-} are exchanged for O^{-2} anions. Thereby the ionic charge serves to limit the solubility range of both phases and not to describe the bonding character, which is mainly covalent in β-ss and mostly ionic in the salt liquid, where the simplified description of single ions is better than a description of molecular species like SiO_2 and Al_2O_3. An even better description would take into account the real existing ionic groups like SiO_4^{4-} and polymeric ions $(SiO_3^{2-})_x$. However, up till now no information has been available on which ionic species really exists in the liquid phase investigated here.

These modifications allow a treatment of salt solutions and ionic crystalline phases as ideal or regular mixtures. For this treatment these phases have to be split up into their single elements whereby the concentration of each element in the sublattice, where it is placed, has to be calculated. The modifications are described in detail in previous papers [10, 11].

The thermodynamic data used for the calculation in both programs were collected from the Janaf Tables [12] as far as possible. The AlN polytype phases [1, 2] are neglected except the X_2 phase, which is treated as a stoichiometric phase with the composition $Si_3Al_{13}N_{11}O_9$. The aluminium–oxynitride spinel (γ, AlON) [13, 14] was also treated as a stoichiometric phase with a composition $Al_7O_9N_1$. Missing data for the phases X_2, AlON and X_1 were estimated by using experimental phase diagrams [1–3]. The same was done with regular terms introduced into solution phases. The procedure for this estimation

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TABLE I Thermodynamic data used for the calculation [11]: Enthalpy and entropy of formation of the gaseous species and solid phases (reference states: (O_2), (N_2), [Si], [Al], (Ar)

Species	H_0 (J mol^{-1})	$-S_0$ (J k mol^{-1})
Gaseous species		
Ar	0.0	0.0
O_2	0.0	0.0
O	255 742.5	−67.010
N_2	0.0	0.0
N	480 695.8	−67.100
NO	90 476.6	−12.690
Si	391 083.6	−111.63
Si_2	470 398.7	−113.64
Si_3	448 449.5	−90.449
SiO	−166 118.5	−45.270
SiO_2	−362 659.1	32.020
SiN	311 821.8	−61.150
SiN_2	279 914.9	−45.270
Al	290 775.4	−105.095
AlO	57 354.2	−57.98
Al_2O	−185 382.0	−40.72
Solid phases		
Al_2O_3	−1673 913.8	318.940
AlN	−325 854.1	114.990
AlON*	−5315 213.2	1054.520
Mullite†	−6919 128.0	1350.640
X_1-phase‡	−23808 261.0	5453.830
X_2-phase§	−8099 374.8	2030.680
Si_2N_2O	−940 000.0	305.400
Si	−50 208.0	29.8
Quartz	−949 225.7	200.293
Tridymite	−946 651.7	197.912
Cristobalite	−944 893.64	196.91

*AlON = Al_7O_9N
†Mullite = $Si_2Al_6O_{13}$
‡X_1-phase = $Si_{12}Al_{18}O_{39}N_8$
§X_2-phase = $Si_3Al_{13}O_9N_{11}$

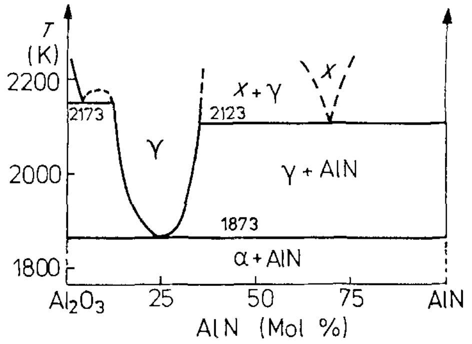


Figure 2 The Al_2O_3–AlN system after [13]. γ is aluminium oxynitride spinel and X is AlN polytype phase.

and the treatment of the regular terms (polynomial terms) are explained in detail [10, 11]. All data are listed in Tables I to III.

2. Calculation of the condensed quasibinaries Al_2O_3–AlN and SiO_2–Si_3N_4 with the Lukas Program

The results for the calculation of the condensed oxide quasibinary SiO_2–Al_2O_3 are given by Dörner *et al.* [11]; therefore, here only the two quasibinaries Al_2O_3–AlN and SiO_2–Si_3N_4 shall be discussed.

For simplification it is assumed, that the mixing entropy for the liquid phase is formed solely from the anions; the contribution of the cations is neglected. Both of these systems, however, are hypothetical in the higher temperature range without considering the gas phase. The calculated system Al_2O_3–AlN (Fig. 1) is compared with the results of Collongues *et al.* [13]

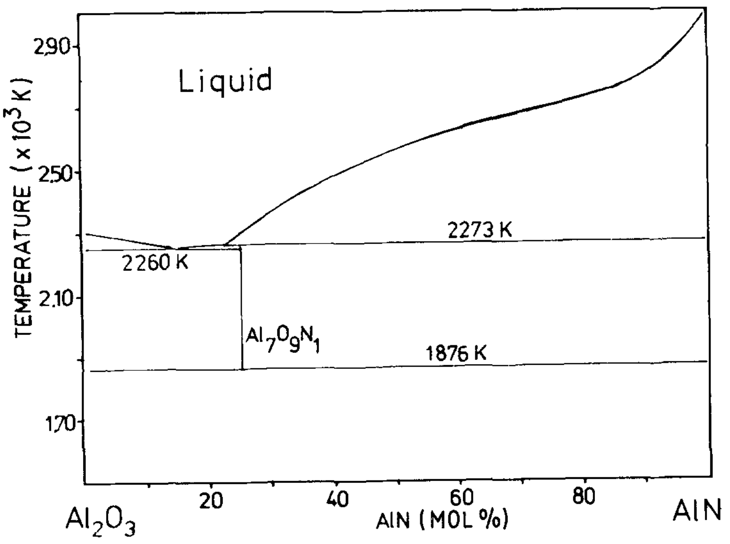


Figure 1 The calculated condensed system Al_2O_3–AlN. $Al_7O_9N_1$ is aluminiumoxynitride spinel treated as a stochiometric phase.

TABLE II Data of the condensed solution phases β-Si_3N_4 solid solution and the metallic melt of the Al–Si system

	Species	H_0 ($J g^{-1} atom^{-1}$)	$-S_0$ ($J K^{-1} g^{-1} atom^{-1}$)
β-Si_3N_4			
Phase stabilities	Si_3N_4	−124 601.9	57.946
	Al_2O_3N	−284 139.1	64.960
Al–Si			
Phase stabilities	Al	0	0
	Si	0	0
Regular solution terms	Al–Si	−10000	0

TABLE III Salt liquid of the system Si–Al–O–N. For data evaluation and mathematical description of this phase in the programs see Dörner *et al.* [11]

	Species or system	H_0 ($J mol^{-1}$)	$-S_0$ ($J K^{-1} mol^{-1}$)
Phase stabilities for liquid, pure compounds	Al_2O_3	−1555 511.34	267.79
	SiO_2	−935 312.28	192.1
	AlN"L"	−256 854.1	91.99
	Si_3N_4"L"	−662 913.38	325.12
Regular solution terms used in the description for the liquid phase in the Lukas Program	$AlO_{1.5}$–SiO_2	33 000.0	0
	AlN–$Si_{0.75}N$	33 000.0	0
	$Al_{0.67}O$–AlN	35 000.0	0
	$Si_{0.5}O$–$Si_{0.75}N$	35 000.0	0

shown in Fig. 2, and with those of McCauley and Corbin [14].

In the SiO_2–Si_3N_4 system thermodynamic data may be found in the literature for the solid phases Si_3N_4 and Si_2N_2O [15–22]. For β-Si_3N_4 the Janaf data of Pehlke and Elliott [16] are used. They agree with those of Blegen [19]. The α-modification of Si_3N_4 is not considered in the calculations, since there are no consistent results in the literature about the nature of the α–β relationship in Si_3N_4. For Si_2N_2O several results exist which differ widely [15, 19–23]. Here the data of Blegen [19] were used since the entropy found there is comparable to that of Si_3N_4. This seems reasonable considering the great structural and chemical similarity between both phases [24, 26], which should result in similar entropies. In Fig. 3 the condensed system SiO_2–Si_3N_4 is given, showing that a eutectic exists close to SiO_2 between SiO_2 and Si_2N_2O. Data which became available for the authors after completion of this paper are given by Ehlert *et al.* [27].

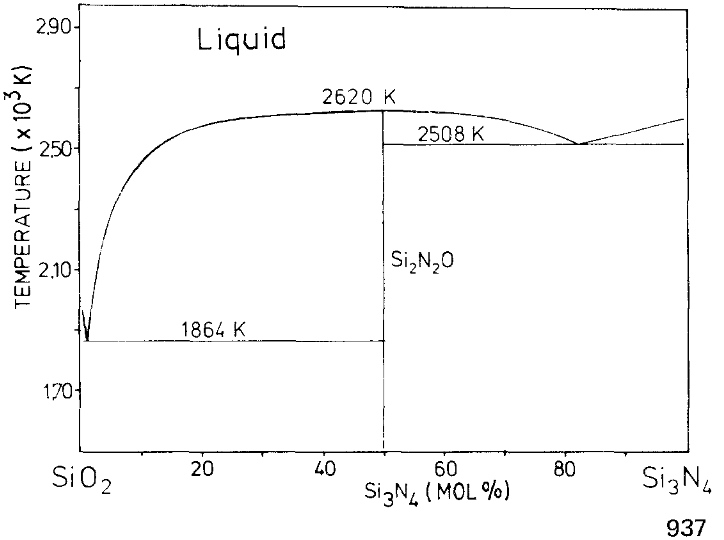


Figure 3 The calculated condensed system SiO_2–Si_3N_4.

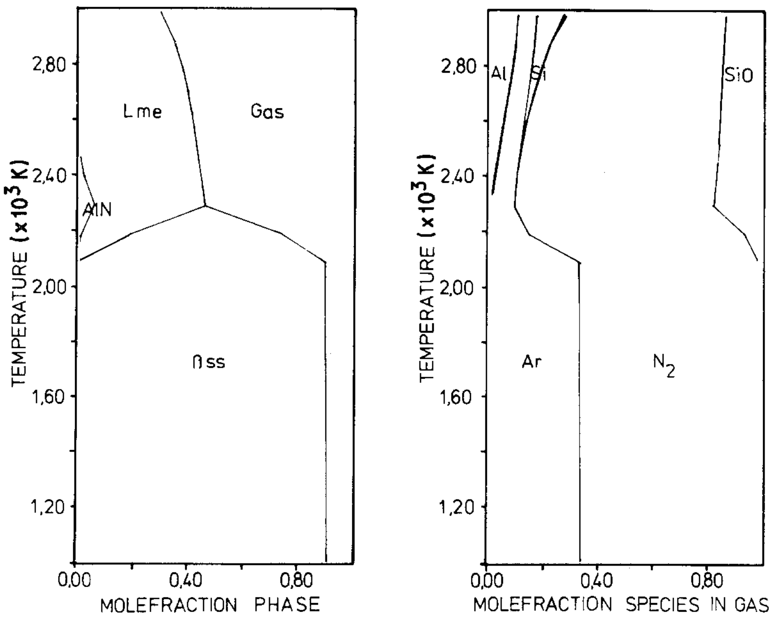


Figure 4 Calculated phase equilibria for a composition of $Si_5AlN_7O + N_2 + 0.5\,Ar$. (6.1 at% O, 54.6 at% N, 30.3 at% Si, 6.1 at% Al, 3.0 at% Ar). L me is metal liquid.

3. Calculation of heterogeneous equilibria in the SiAlON system with the Eriksson Program

In the SiAlON system the heterogeneous equilibria were calculated for several compositions. In these calculations the gas phase at low temperatures was always assumed to consist of N_2 and Ar. Figs 4 and 5 show such calculations for β-ss in this atmosphere with varied Al^{3+} concentration in the β-ss. It may be seen that, on the Si_3N_4 side of β-ss at elevated temperature, this phase decomposes to liquid metal by losing SiO (Fig. 4). With increasing Al^{3+} content β-ss decomposes to X_2 and AlN by losing SiO (Fig. 5). These results are in good agreement with the literature [28–31]. The further decomposition gives an oxide-rich salt liquid due to the oxygen content of β-60 (β-$Si_2Al_4N_4O_4$), instead of the metal liquid found for the composition in Fig. 4 (Si_5AlN_7O). Fig. 6 shows a composition of Si_2N_2O, SiO_2 and X_1, where a liquid forms above 1800 K from SiO_2 and X_1, with Si_2N_2O decomposing to further liquid and gas

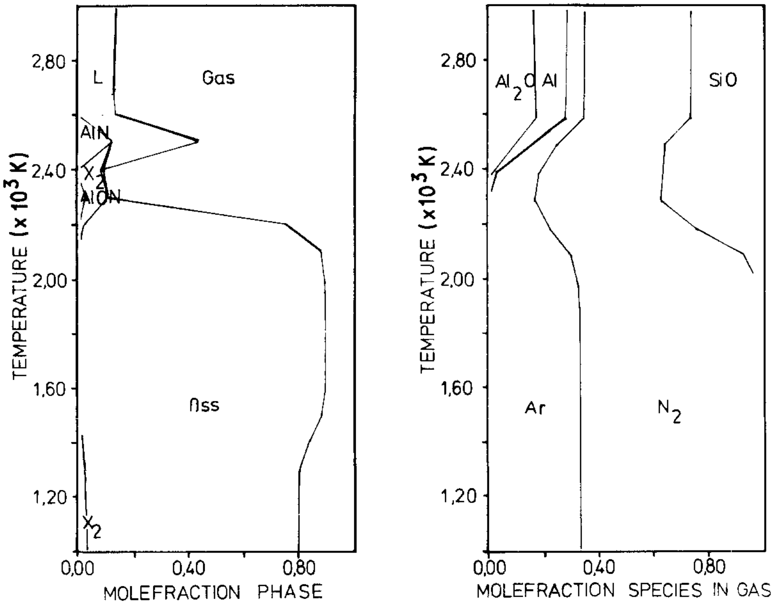


Figure 5 Calculated phase equilibria for a composition of $Si_2Al_4N_4O_4 + N_2 + 0.5\,Ar$ (β-60) (24.2 at% O, 36.4 at% N, 12.1 at% Si, 24.2 at% Al, 3.0 at% Ar). L is salt liquid.

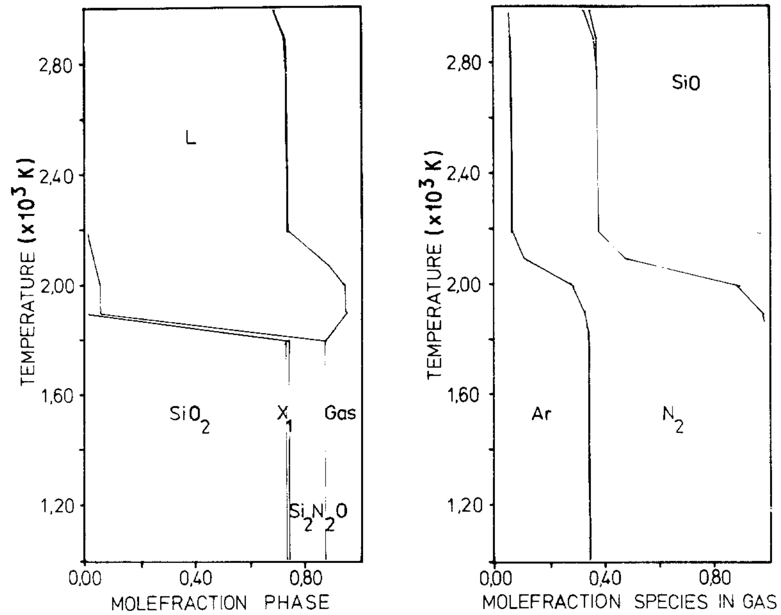


Figure 6 Calculated phase equilibria for a composition of $Si_2N_2O + SiO_2 + X_1$. (51.7 at% O, 13.5 at% N, 29.2 at% Si, 4.5 at% Al, 1.1 at% Ar).

above 2000 K. Fig. 7 shows a composition of $Si_2N_2O + SiO_2$ on the quasibinary SiO_2–Si_3N_4. Comparing this diagram to Fig. 3 shows that the liquid phase which forms at a composition of 25 mol% Si_3N_4 will decompose totally to SiO and N_2 above 2200 K. The gas phase in the SiAlON system consists of N_2, SiO, Al_2O, Si (v) (v = vapour) and Al (v) with Ar always added to the overall composition. However, only the first two species show a significant partial pressure while the other species only form above 2300 K (Figs 4 and 5). This shows the importance of choosing a suitable atmosphere for sintering β-ss materials to complete density and that it is necessary to balance the forming solid equilibrium with a certain SiO partial pressure in order to avoid a loss of SiO from the condensed material thus resulting in the formation of pores. This, above all, is valid for the more oxygen-rich transient liquid phase which plays an important role in the sintering process by solution of the starting compounds in this liquid and reprecipitation of β-ss [31, 32].

The calculation at several different compositions in the SiAlON system allows comparison

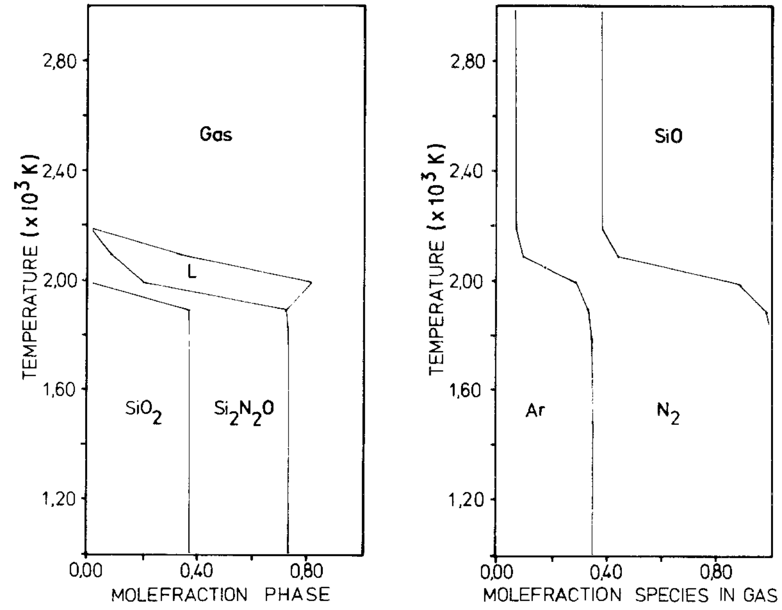


Figure 7 Calculated phase equilibria for a composition of $Si_2N_2O + SiO_2$. (32.4 at% O, 32.4 at% N, 32.4 at% Si, 2.7 at% Ar).

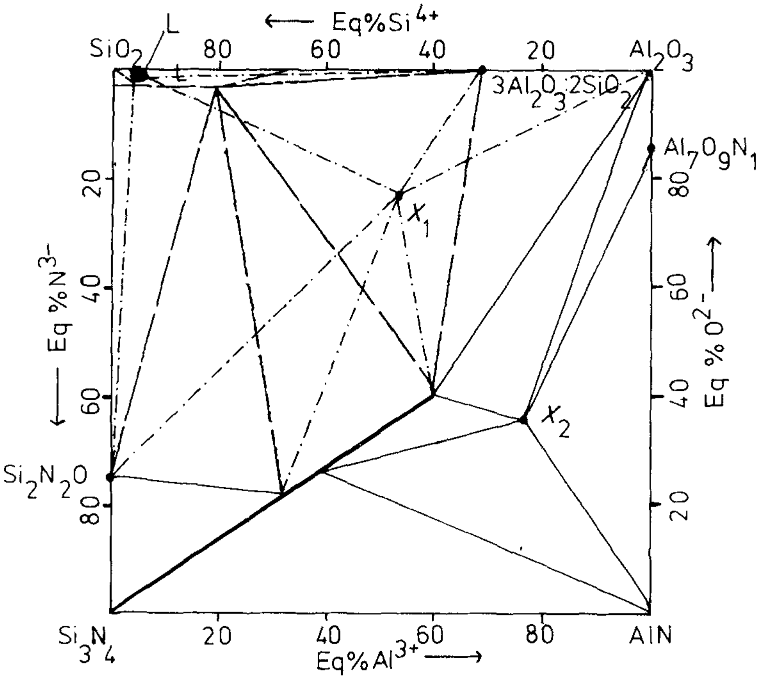


Figure 8 The calculated condensed phase equilibria in the SiAlON system. ——— 2100 K, —·—·— 1900 K. L is liquid and the drawn out lines apply for both temperatures.

of the phase relations of the condensed phases, as shown in Fig. 8, with the experimentally-determined SiAlON system in Fig. 9 [1, 2]. A comparison of these figures shows that, with the simplifications made, the relations in the concentration triangle Si_3N_4–AlN–Al_2O_3 are reproduced by the calculation. In the concentration triangle Si_3N_4–SiO_2–Al_2O_3 two important differences exist:

(1) The calculation in Fig. 8 shows no two-phase field Al_2O_3–liquid but a two-phase field $3Al_2O_3 \cdot 2SiO_2$ (mullite)–β-ss (thereby the joining three-phase fields differ as well). The reason for this difference lies in the errors of the estimated

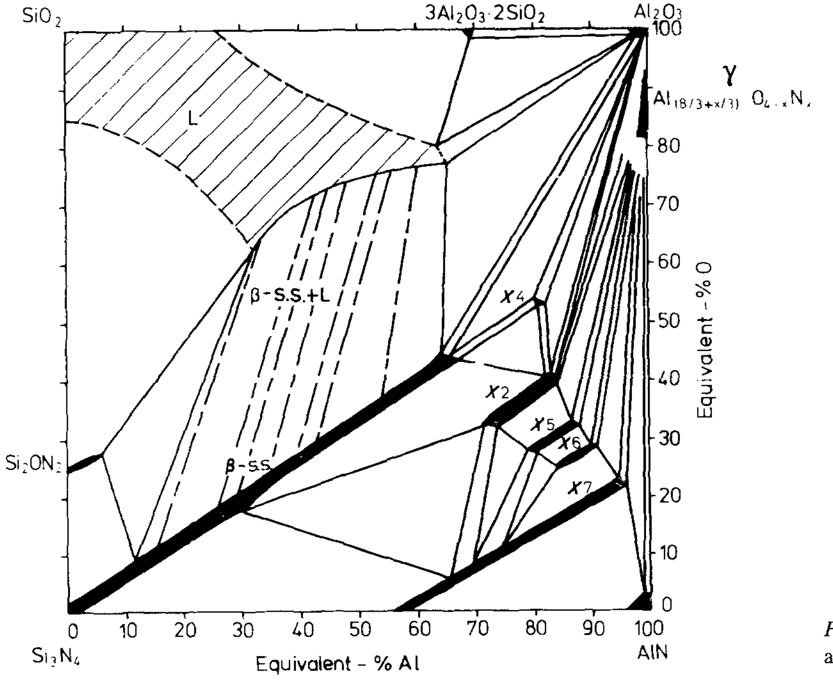


Figure 9 The SiAlON system after [3] at 2023 K.

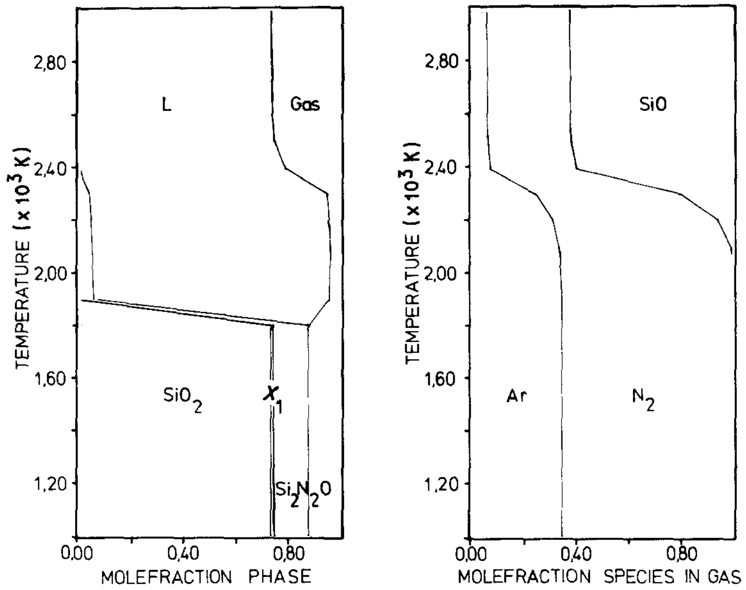


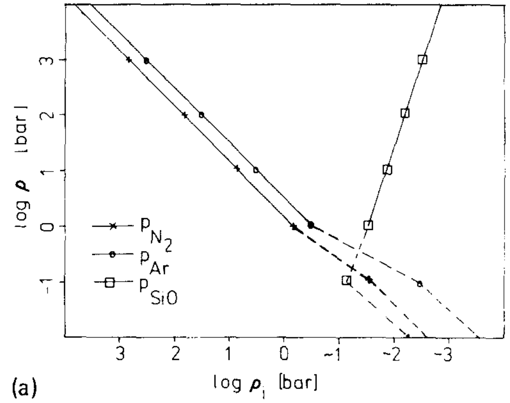
Figure 10 Calculated phase equilibria for a composition of $Si_2N_2O + SiO_2 + X_1$. Pressure 10.1 bar. (51.7 at% O, 13.5 at% N, 29.2 at% Si, 4.5 at% Al, 1.1 at% Ar).

thermodynamic data, probably mainly due to the description of the liquid phase by the introduction of simple regular terms in the quasibinaries. A better approach to the real state would need a more complicated description. This, however, seems unreasonable at the present time with the little experimental data known in this system.

(2) The liquid phase contains less nitrogen than found in the experimental data of Fig. 9. This can be explained by the fact that in the calculation the concentrations of the liquid and the gas phases are fixed by the minimum of the Gibb's free energy. In the experiment the composition of the gas phase is fixed by the reducing conditions in a graphite pipe furnace, thereby forming a more nitrogen-rich liquid phase. Further there is a possibility that the liquid in Fig. 9 has not yet reached final equilibrium by losing N_2 and SiO. This would shift the composition towards the quasibinary Al_2O_3–AlN.

4. Influence of pressure

Several calculations were made with a pressure of 10.1 bar. The pressure has little effect on the nitrogen solubility of the liquid, while the decomposition temperature of the condensed phases rises. Comparing Figs 10 and 6 shows that,



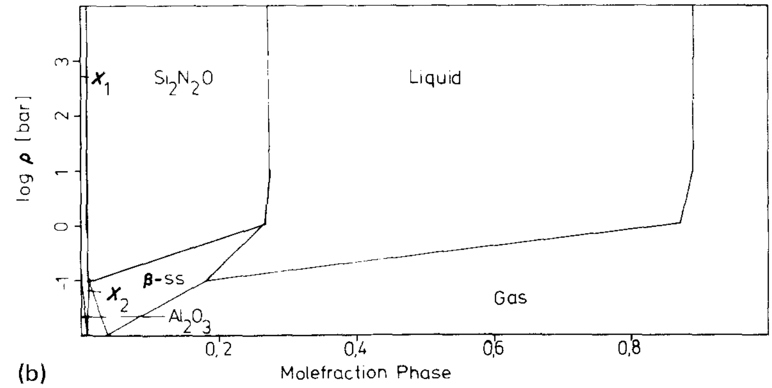


Figure 11 (a) Partial pressures of the vapour species plotted against log p and (b) the influence of pressure on the phase relations at a chemical composition of 5 SiO_2 + 2 Si_3N_4 + Al_2O_3 + N_2 + 0.5 N_2 (35.6 at% O, 27.4 at% N, 30.1 at% Si, 5.5 at% Al, 1.4 at% Ar) at 1900 K.

for a composition consisting of Si_2N_2O, SiO_2 and X_1, this pressure raises the vapourization of Si_2N_2O and liquid from 2000 K up to 2300 K. Fig. 11a shows the influence of the variation of pressure on the phase relations for one composition at 1900 K. Fig. 11b shows the partial pressures of the vapour species drawn logarithmically against the overall pressure. On lowering the overall pressure the liquid decomposes to β-ss and SiO. Further lowering of the overall pressure decomposes β-ss to X_2 and additional SiO vapour. At 1900 K no other species besides SiO, N_2 and Ar are found to be of importance for the gas phase. This too shows the importance of the SiO partial pressure for the equilibrium of the condensed phases.

5. Conclusions

The calculations in the SiAlON were carried out to test, to which extent the calculation of heterogeneous phase equilibria in such complex salt systems would be possible. The results of these calculations of the SiAlON system agree to a large extent with experimental data in the literature. The accuracy of these calculations suggests the possibility of using this method for determination of areas worthy of further experimental research in similar salt systems whereby in condensed binary or ternary systems the Lukas Program may be used, while for higher component systems with significant vapour pressures the Eriksson Program is the suitable program. The calculations show the influence of the composition of the gas phase on the composition and stability of the condensed phases. This allows prediction of optimal sintering conditions for β-ss based SiAlON materials.

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