

Determination of phase equilibria in the system Si–Al–Zr/N–O by experiment and thermodynamic calculation

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The phase relations in the system Si–Al–Zr/N–O are studied by experiment and by thermodynamic calculations. The results show the conditions under which such ceramics can exist and thereby explain contradictions between earlier results. The knowledge of these phase equilibria makes it possible to choose suitable material compositions in order to apply the toughening effects of ZrO₂ on a SiAlON matrix.

1. Introduction

Si₃N₄ can be sintered to full density only by the addition of sintering aids. ZrO₂ has been tested as an additive in several investigations with differing results [1–7]. ZrO₂ dispersions in various matrix materials also improve the fracture toughness, caused by the tetragonal–monoclinic transformation of ZrO₂ [8–11]. These toughening effects may be applied to Si₃N₄-based materials.

As a precondition for the introduction of ZrO₂ dispersions to a Si₃N₄ matrix both compounds must be compatible under fabrication and application conditions. The phase relations in the system Si–Zr/N–O have been studied several times [12–15] and extended to the system Si–Al–Zr/N–O by Rae *et al.* [15] and Layden and Holmquist [16], but there are no experimental details given [15] and some results contradict those of the other investigation [16].

The purpose of this work was to determine the phase relations in the system Si–Al–Zr/N–O with the main interest focused on those existing between the salt compounds Si₃N₄–AlN–ZrN–SiO₂–Al₂O₃–ZrO₂ in order to find the optimal composition and optimal sintering conditions for Si₃N₄-based ceramics containing ZrO₂ dispersions.

Furthermore, an attempt was made to clarify the contradictions between the earlier investigations.

The determination of these phase relations requires great experimental effort. Therefore, it seemed a good idea to reduce this effort by the use of thermodynamic calculations, especially since, in higher component systems, the phase relations are mainly fixed by the phases in the quasibinary and ternary systems because the probability of the existence of higher component intermediate phases is small. For these calculations two computer programs were used; these proved to be successful in the calculation of salt equilibria. The first program calculates n-phase-fields in condensed binary and ternary systems by the Newton–Raphson iteration method [17, 18] without using an overall composition. The second calculates, for a given overall composition, temperature and pressure, the composition and amount of the phases present by minimization of the Gibbs free energy [19–21]. The modifications made to the programs, as well as the data collection and estimation of missing data for phases in the SiAlON system, are outlined in detail in previous papers [22–25]. This paper presents the results of the experiments and calculations on the system Si–Al–Zr/N–O.

TABLE I Starting materials

Powder type		Powder specifications supplier's data (wt %)
Si ₃ N ₄	Kawecki Berylco Industries Inc. Lot. No. D 206, powder No. 76119	59.58 Si, 38.62 N, 1.8 O
SiO ₂	Rovin Ceramics (Flint No. 25)	—
ZrN	Apache Chemicals Inc. No. 9447 Lot No. T	325 mesh 99%, 11.4 N
ZrO ₂	Apache Chemicals Inc. No. 9453	2% HfO ₂ , 99% pure
Si ₃ N ₄	Amorphous GTE Sylvania SN 402 Lot No. 10-48	1.52 O, 4.0 Cl
Zirconium-n-propoxide (C ₃ H ₇ O) ₄ Zr·2C ₃ H ₇ OH (liquid)	Alfa Products No. 88733 Lot No. 011676	95% pure
Aluminium-i-propoxide Al(OC ₃ H ₇) ₃ (solid)	Alfa Products No. 11122 Lot No. 121776	98% pure
AlN	HCST Starck No. T 983	33.5 N, 0.07 C, 0.12 Fe

2. Experimental procedure

The specimens were prepared from the starting powders listed in Table I, mixed in agate jars with agate balls under acetone for 2 h, then dried at 373 K in air. To obtain more homogeneous samples, several additional mixtures were made from organic bonded oxides; these samples are listed in Table IIC. They were mixed for 2 h under water-free benzene. After drying in air, these samples were heat treated at 673 K in air for 1 h to remove the organic binder [26] and obtain an ultra-fine powder mixture. The samples were either hot pressed under flowing nitrogen in BN coated graphite dies or prepressed with a uni-axial pressure of 35 MPa and then sintered in a BN packing powder in order to avoid any chemical reaction with the graphite. Temperature was controlled by optical pyrometry during the heat treatment in a graphite tube furnace. The weight loss was measured and phase analysis was carried out by X-ray diffraction (XRD) using a Philips goniometer with a graphite monochromator and CuK α radiation. Heat treatment conditions, results of phase analysis and weight loss measurements are listed in Table II. For the determination of the phase relations only samples exhibiting less than 3% weight loss were used.

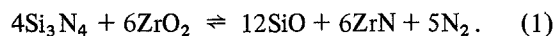
3. Results and discussion

3.1. The subsystem Si–Zr/N–O

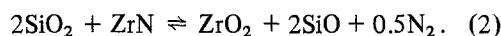
The solid equilibria in the system Si–Zr/N–O between the condensed phases Si₃N₄–ZrN–SiO₂–ZrO₂ are shown in Fig. 1. The reason for choosing this representation is that zirconium in this system shows two different valencies in ZrO₂ and ZrN, therefore the system Si₃N₄–ZrN–SiO₂–ZrO₂ cannot be presented like a reciprocal salt system in a square. The thermal stability of the different phase regions shown in Fig. 1 differs significantly;

thermal decomposition takes place at different temperatures. These decomposition reactions are described below:

ZrN shows no reaction with ZrO₂ up to 2173 K except formation of cubic, nitrogen-stabilized ZrO₂; this will be discussed in detail later. Si₃N₄ is stable with ZrO₂ up to 1873 K. Above this temperature it reacts according to [14]



The presence of the gas phase caused by this reaction causes the normal pressure to exert a great influence on the equilibrium. The least stable nitride–oxide composition exists between SiO₂ and ZrN; at 1673 K the following reaction takes place



All nitride–oxide compositions in this system do not react to form a liquid phase because of their immediate thermal decomposition according to Equation 1 or 2 and therefore shows poor sintering behaviour. The only stable liquid phase in the salt system Si₃N₄–ZrN–SiO₂–ZrO₂ forms between ZrO₂ and SiO₂ on the oxide quasibinary ZrO₂–SiO₂.

Several other phases are reported in the literature to exist in the system Si–Zr/N–O in addition to those shown in Fig. 1 and to those of the binary system Si–Zr [27]. Among these phases are Zr₃N₄, Zr₂N₂O and Zr₇O₈N₄. The existence of these compounds at temperatures above 1273 and 1473 K, respectively, can be ruled out, since they decompose irreversibly to ZrO₂, ZrN and N₂ [28, 29] and have not been observed in this investigation. The only compound reported to exist at higher temperatures is Zr₇O₁₁N₂ [29]. This compound has been determined to have a cubic CaF₂ structure [12]. The cubic high-

TABLE IIA Fabrication conditions and phase analysis

Composition (mol %)				Hot pressing conditions		Phase analysis*	Weight loss (%)
Si ₃ N ₄	SiO ₂	ZrN	ZrO ₂	T (K)	t (h)		
90	—	10	—	2023	1	β s, ZrN w	—
10	—	90	—	2023	1	ZrN s, β w, ZrO ₂ c vvw	—
60	20	—	20	2023	1	ZrN m, β m, ZrO ₂ c w, ZrO ₂ m w, Si ₂ N ₂ O vw	—
—	60	20	20	1873	1	ZrO ₂ m s, ZrSiO ₄ m, ZrO ₂ c w, Si ₂ N ₂ O w, ZrN vw	2.78
25	50	—	25	1873	1	ZrSiO ₄ s, w, ZrO ₂ m w, Si ₂ N ₂ O w, β vw	—
—	—	50	50	2173	0.5	ZrN s, ZrO ₂ c s, ZrO ₂ m m	—
60	—	20	20	2023	1	β s, ZrN s, ZrO ₂ c vvw	—
50	—	—	50	1873	4	ZrO ₂ c s, ZrO ₂ m mw, β m, SiO ₂ N ₂ O w, Gas vw	2.0
—	50	50	—	1673	2	ZrN s, SiO ₂ s, ZrO ₂ c w, ZrO ₂ m vw, Si ₂ N ₂ O vvw, Gas vvw	1.0

*s = strong, m = medium, w = weak, vw = very weak, vvw = traces.

TABLE IIB Fabrication conditions and phase analysis

Composition (mol %)				Hot pressing conditions		Phase analysis*	Weight loss (%)
AlN	Al ₂ O ₃	ZrN	ZrO ₂	T (K)	t (h)		
—	50	50	—	2273	1	ZrN s, Al ₂ O ₃ m, ZrO ₂ c w	0.6
33.3	33.3	33.3	—	2273	1	ZrN s, AlON w, X ₂ vw	2.1
33.3	33.3	—	33.3	2023	1	ZrN s, ZrO ₂ c s, Al ₂ O ₃ m, AlN w, AlON w, X w, ZrO ₂ m w	—
33.3	—	33.3	33.3	2073	1	ZrN s, ZrO ₂ c s, ZrO ₂ m w, AlON w, Al ₂ O ₃ w, X w	—

*s = strong, m = medium, w = weak, vw = very weak, vvw = traces.

TABLE IIC Fabrication conditions and phase analysis

Composition (mol %)				Hot pressing conditions		Phase analysis*	Weight loss (%)
Si ₃ N ₄	Al ₂ O ₃	AlN	ZrO ₂	T (K)	t (h)		
65.92	13.03	13.03	7.89	1973	1	β s, Si ₂ N ₂ O w, ZrO ₂ m w, ZrO ₂ c vw, ZrN vvw	5.8
46.99	24.22	24.22	3.61	1973	1	β s, ZrO ₂ c vw, ZrN vw, SiO ₂ vw	4.6
32.26	32.26	32.26	3.23	1973	1	β s, ZrN w, ZrO ₂ c vvw	6.6
31.25	31.25	31.25	3.13	1973	1	β s, ZrN w, X ₂ vvw, ZrO ₂ m vvw	3.2
19.51	38.82	38.82	2.91	1973	1	β s, ZrN m, X ₂ m	6.9

*s = strong, m = medium, w = weak, vw = very weak, vvw = traces.

temperature modification of ZrO₂ shows the same structure and is stabilized to lower temperatures by oxygen deficiency [30–32] or, to room temperature, by nitrogen stabilization [33]. The cubic ZrO₂ modification (ZrO₂ c) observed in our work must be nitrogen stabilized as it forms at 2173 K from pure ZrO₂ in N₂ atmosphere, while heat treatment in Ar at the same temperature results in monoclinic ZrO₂ (ZrO₂ m) after cooling. We assume that, due to the structural coincidence and the small compositional difference, a homogeneity range between the two types of the cubic ZrO₂ modification should exist at elevated temperatures, as drawn with dashed lines in Fig. 1. The experimental determination of the solid solubility range of this phase, however, has not yet been proved.

The lack of a liquid phase during densification in the system Si₃N₄–ZrN–SiO₂–ZrO₂ explains the low density and poor mechanical properties found in previous investigations [1, 4, 5, 14, 15]. On the other hand, the good density and properties reported by others [3, 6, 7, 15, 16] can be explained by the presence of additional Al₂O₃ [6, 7, 15] and impurities which form low melting phases like WC, which reacts to give Si₂W [3].

3.2. The subsystem Al–Zr/N–O

In the subsystem Al–Zr/N–O no reaction between Al₂O₃ and ZrN has been observed up to 2273 K although the densification is good. This can be explained by liquid formation between Al₂O₃ and

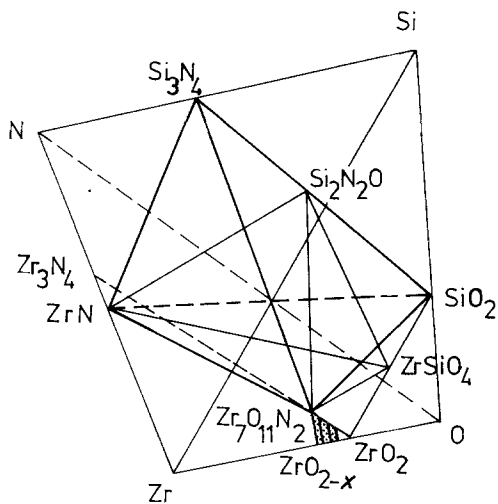


Figure 1 The phase relations between the solid phases of the system Si_3N_4 - ZrN - SiO_2 - ZrO_2 .

ZrO_2 impurities of ZrN which form a eutectic at 2163 K [34]. The two compounds AlN and ZrO_2 were found to react at 1973 K:



At 1900 K two four-phase equilibria exist in this subsystem: Al_2O_3 - $\text{AlON}(\text{spinel})$ - ZrN - ZrO_2 and AlN - AlON - ZrN - ZrO_2 . At 1973 K a liquid forms from AlON - ZrN - ZrO_2 with a composition near the AlON -phase. This liquid formation is possible because Al_2O_3 shows a higher thermal stability

under a reducing atmosphere if compared to SiO_2 , where the latter decomposes to yield SiO as described above. For the same composition, between 1973 and 2173 K several samples showed small amounts of an unidentified phase. The X-ray pattern did not fit with any other phase known in this system. Attempts to obtain a larger amount of this phase failed and since this part of the system is of less interest in the studies of SiAlON materials with ZrO_2 dispersions, no further attention was given to this phase. Above 2173 K AlN -polytype phases form in the quasibinary AlN - Al_2O_3 , in good agreement with other observations [35].

3.3. The system Si-Al-Zr/N-O

Samples with a composition of β - Si_3N_4 solid solution (βss) and ZrO_2 show much better sintering behaviour than those of Si_3N_4 and ZrO_2 only. This is due to the formation of βss by a transient liquid, as previously described [36, 37]. The fast densification inhibits a vapour reaction [1], therefore only traces of ZrN could be observed in some of the samples. The only reaction observed with ZrO_2 was the formation of nitrogen-stabilized ZrO_2 c, which accounted for about one third of the weight fraction of ZrO_2 . This shows, that βss materials can be hot pressed to full density and be in thermodynamic equilibrium with ZrO_2 dispersions [7].

The thermodynamic calculations presented in

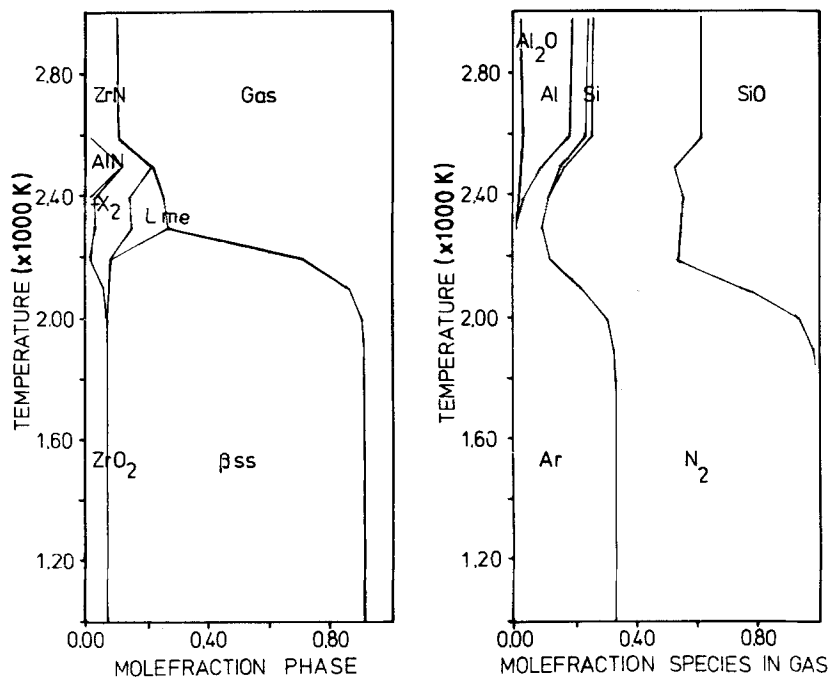


Figure 2 Calculated phase equilibria for a composition of $\beta\text{ss} + \text{ZrO}_2$ (20.5 at% O_2 , 41.0 at% N_2 , 20.5 at% Si , 10.6 at% Al , 5.1 at% Zr , 2.6 at% Ar) L me = metal liquid.

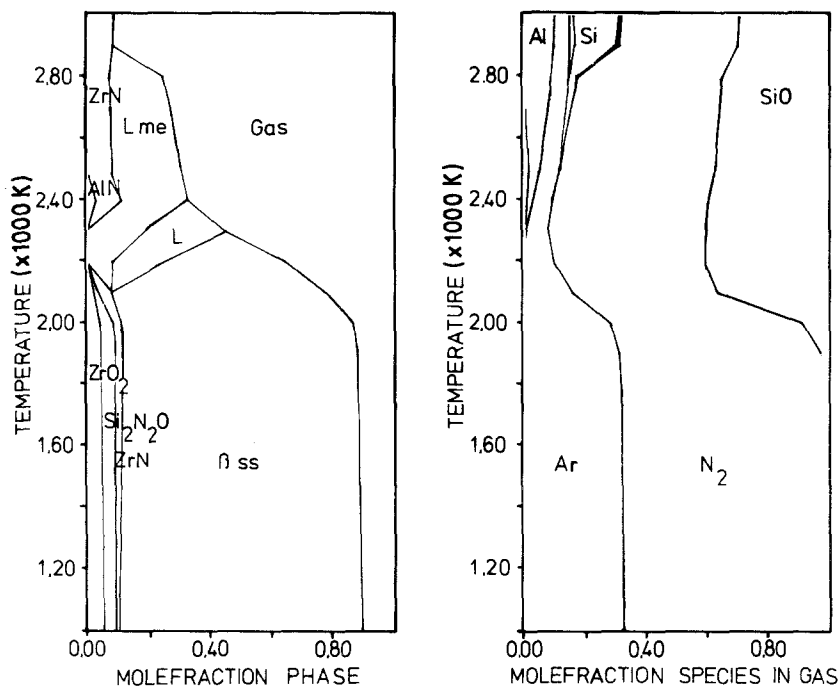


Figure 3 Calculated phase equilibria for a composition of $\beta ss + Si_2N_2O + ZrN + ZrO_2$ (15.4 at% O_2 , 41.6 at% N_2 , 25.6 at% Si, 5.1 at% Al, 5.1 at% Zr, 2.6 at% Ar) L = salt liquid.

this paper were carried out with the modified program by Eriksson *et al.* [19–25]. For several compositions the calculated results are drawn in the phase stability diagrams [38] shown in Figs 2 to 7. Fig. 2 shows that βss can coexist in equilibrium with ZrO_2 at a higher Al^{3+} content while at lower Al^{3+} content Si_2N_2O and ZrN are present in addition to βss and ZrO_2 (Fig. 3). The other

phase equilibria are set up by further calculations for various compositions. In the Figs 4 to 7 several significant examples are given. They show that βss , Si_2N_2O , X_2 (an AlN polytype phase), AlON and Al_2O_3 coexist with ZrN and $ZrO_2 \cdot SiO_2$; mullite ($3Al_2O_3 \cdot 2SiO_2$) and X_1 can only coexist with ZrO_2 or $ZrSiO_4$ at 1900 K and AlN only coexists with ZrN at this temperature. In the vapour

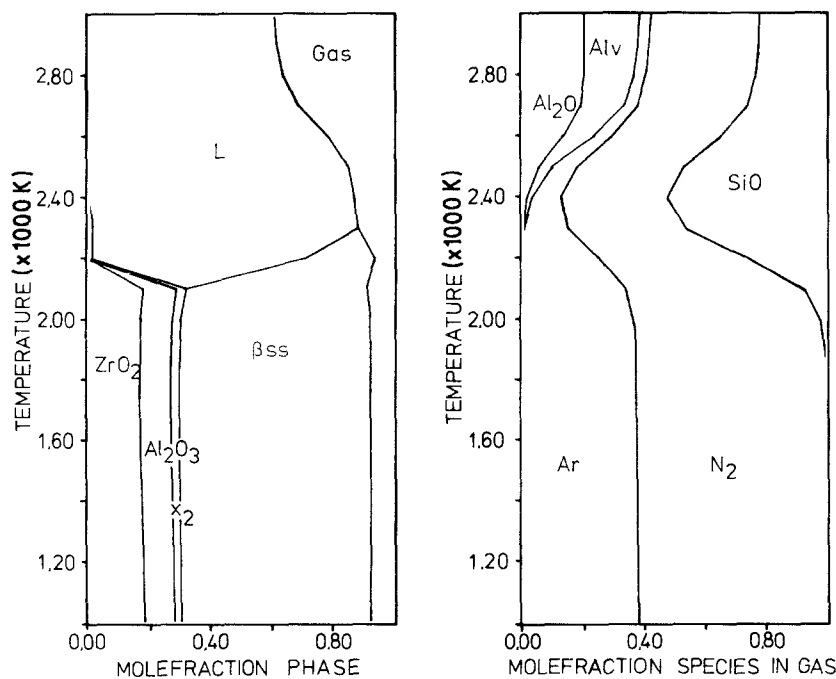


Figure 4 Calculated phase equilibria for a composition of $\beta ss + X_2 + Al_2O_3 + ZrO_2$ (36.6 at% O_2 , 21.5 at% N_2 , 6.5 at% Si, 28.0 at% Al, 6.5 at% Zr, 1.1 at% Ar).

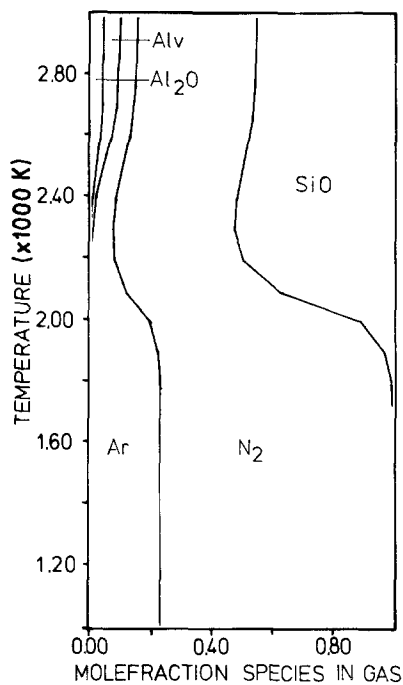
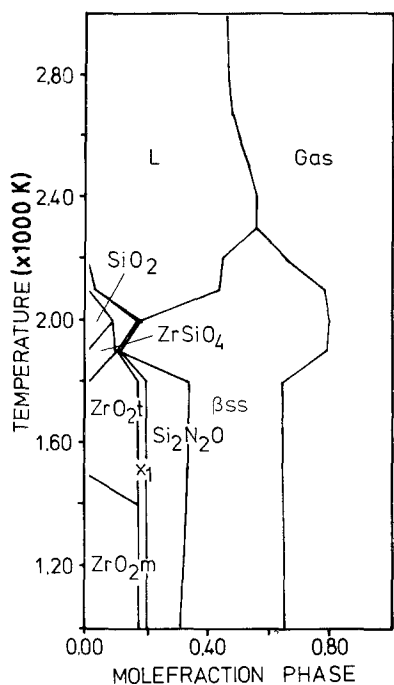


Figure 5 Calculated phase equilibria for a composition of $\beta ss + Si_2N_2O + X_1 + ZrO_2$ (36.7 at % O_2 , 28.6 at % N_2 , 16.3 at % Si, 12.2 at % Al, 4.1 at % Zr, 2.0 at % Ar).

phase of this system up to 2300 K, only N_2 and SiO are of importance; Al_2O , Al and Si vapour become significant only above this temperature.

The results of Layden and Holmquist [16] in Fig. 8 agree well with the equilibria found in this work shown in Figs 2 to 7 and 9a and b except the relation $ZrN-X_1$. The representation must not

be considered to be that of a concentration prism for a quinary reciprocal salt system. Due to the two valencies of zirconium in its compounds such a representation is impossible, since a precondition for it is that all elements have only one valency in the compounds included in the system. A simplification made is that ZrO_2 and $ZrO_2 c$ are treated as a single phase in all figures.

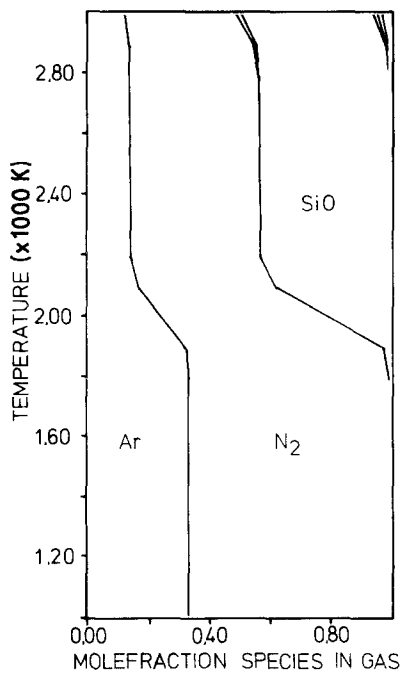
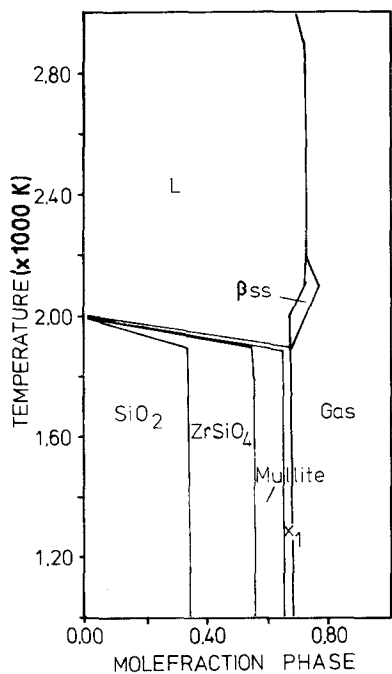


Figure 6 Calculated phase equilibria for a composition of mullite + $X_1 + SiO_2 + ZrSiO_4$ (55.4 at % O_2 , 9.2 at % N_2 , 15.4 at % Si, 15.4 at % Al, 3.1 at % Zr, 1.5 at % Ar).

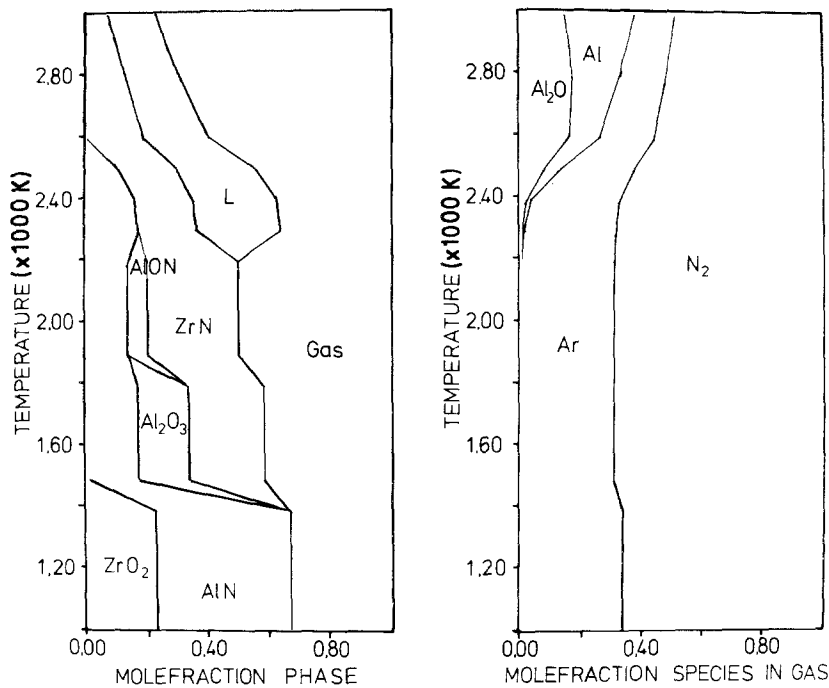


Figure 7 Calculated phase equilibria for a composition of AlN + AlON + ZrN (21.1 at % O₂, 42.1 at % N₂, 21.2 at % Al, 10.5 at % Zr, 5.3 at % Ar).

4. Conclusions

The studies of phase relations in the system Si-Al-Zr/N-O show a good agreement between experimental data and thermodynamic calculation. The results indicate that preparation of dense Si₃N₄ bodies containing ZrO₂ is difficult due to the absence of a densifying liquid and the chemical reaction between the components at 1873 K which produces a gas phase. Both problems can be overcome by adding Al₂O₃ and AlN to form βss by a transient liquid resulting in a βss matrix with ZrO₂

dispersions. The transient liquid allows fast densification thereby inhibiting gas producing reactions. The phase relations indicate that ZrO₂ is stable with oxygen-rich and ZrN with nitrogen-rich phases in the SiAlON system.

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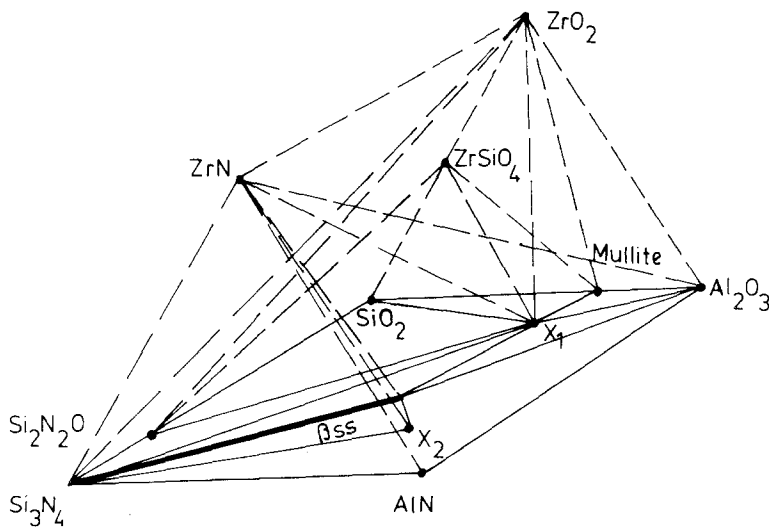


Figure 8 Proposed phase relations in the system Si₃N₄-AlN-ZrN-SiO₂-Al₂O₃-ZrO₂ after Layden and Holmquist [16].

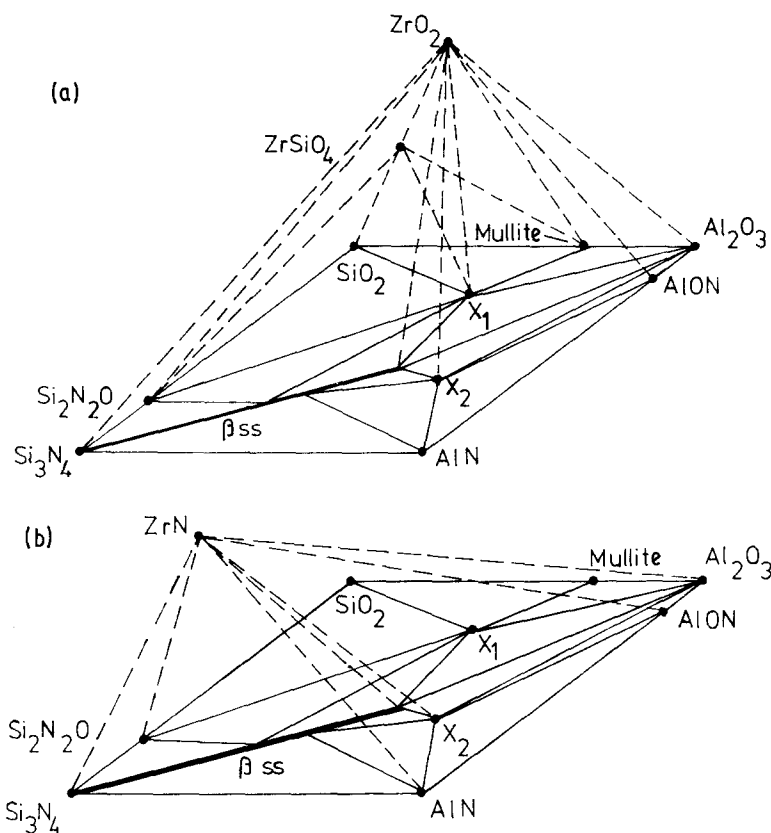


Figure 9 (a) Phase relations of the solid phases with ZrO_2 between 1800 and 1900 K found by calculation and experiment, (b) phase relations of the solid phases with ZrN between 1800 and 1900 K found by calculation and experiment.

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