Journal of the European Ceramic Society **15** (1995) 89–94

0955-2219/95/$9.50

Computer Simulation of β'-Sialon Synthesis

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(Received 24 January 1994; accepted 10 May 1994)

Abstract

Thermodynamic calculations in the system Si–Al–O–N were used to assess the capabilities of SiO_2 and Al_2O_3 mixtures to synthesise β'-sialon powders by reduction–nitridation. The Thermo-Calc databank, a sophisticated computer software together with assessed thermodynamic data, has been applied to calculate not just traditional phase diagrams but also various sections, isopleths, activity plots and property diagrams such as phase fraction diagrams. By controlling the temperature, the partial pressures of oxygen and nitrogen and the Si : Al ratio in the precursor mixtures the experimental work can be reduced to a minimum, based on the calculations. β'-Sialon was found to be stable only within a small region of oxygen and nitrogen partial pressures.

1 Introduction

The good mechanical and thermal properties of sialon ceramics make them useful as structural materials. To minimize the variation of the strength values, the fabrication of materials with uniform microstructure is required. When β'-sialon ceramics are formed from mixed powders such as silicon nitride, aluminum nitride and alumina,[1] the homogeneity is reduced and the microstructural control is difficult due to the complex mechanism of the preparation. The microstructure is more uniform and the densification temperature for synthesized sialon powders is 50–100°C lower when high-purity pre-prepared β'-sialon is used instead.[2] The production of nitrogen ceramics by simultaneous reduction and nitridation of oxides is of interest both because of the versatility of the process and the current availability of potential raw materials.[3]

To determine optimal values for the parameters that are necessary for the synthesis of β'-sialon powders, and thus minimize expensive and time-consuming experimental work, thermodynamic calculations have become important. Thermodynamic calculations have been used for many years to obtain information on the possible reactions in chemical and metallurgical systems.[4,5] In recent years thermodynamic software has been used not only for traditional equilibrium and phase diagram calculations but also for material development,[6] solidification simulations,[7] etc. Heterogeneous reactions make up the most significant group of interactions of interest in ceramics. In particular, those reactions involving gases and solids are of prime importance, e.g. reduction of solid oxides and chemical vapor deposition. Above 1000°C one can often use equilibrium thermodynamics together with simple kinetic estimations to understand the possible results of an experiment even if full equilibrium will not be established in the experiment. A thermodynamical description is always needed to simulate transformations as it is otherwise impossible to know the final state the system tries to reach.

Materials processes can often be described as a sequence of steps where the system is in equilibrium 'locally'. Combining extensive thermodynamic calculations in such a local equilibria simulation of a process was first done by Eriksson & Johansson[8] in the so-called SOLGAS-reactor. In a following paper a similar method will be used for the silicon nitride powder synthesis with a generic reactor module connected to Thermo-Calc.[9]

There are two requirements for the successful application of thermodynamic calculations to understand a chemical problem. One is a flexible and general software like Thermo-Calc and the other is a carefully assessed thermodynamic database for the system of interest. Such a database does not only contain data for the compounds and gases but also descriptions of the solid solution phases using sophisticated models[10] which can take into account the various types of crystalline

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structures of the condensed phases and how the components mix on different sublattices. Databases with thermodynamical parameters describing mixtures make it possible to predict the equilibrium state of very complex systems of non-ideal phases.

In this paper a thermodynamic database for the Si–Al–O–N system[11] was used to assess the capabilities of mixtures of SiO_2 and Al_2O_3 to produce β'-sialon by reduction–nitridation. Attention was focused on important factors in the synthesis process such as the temperature, the partial pressures of oxygen and nitrogen and the Si : Al ratio in the starting oxides mixture. The calculations are a powerful tool for planning experimental work as one may eliminate a large amount of experiments that are unlikely to give useful results.

2 The SiAlON System

A system formed by four elements can always be represented by a tetrahedron. In the SiAlON system the elements form two oxides and two nitrides, and take only one valency state in these condensed compounds. The plane generated by connecting the points representing these four compounds becomes an irregular four-cornered plane. Representing such an irregular quadrangle in atom % is not very practical. Instead Gauckler & Petzow[12] suggested a representation for the silicon nitride based systems using equivalent % of one cation and one anion, which transform the irregular quadrangle into a square. The system Si_3N_4–AlN–Al_2O_3–SiO_2 represented in this way is generally called the SiAlON system in the literature.

For the SiAlON system some isothermal experimental studies are known.[13,14] Gauckler *et al.*[13] indicate the existence of an homogeneous single-phase material with an expanded lattice, isostructural with β-Si_3N_4, which was termed β'-sialon. Solubility occurs only with a constant cation : anion ratio of 3 : 4 according to an atomic formula $Si_{6-z}Al_zO_zN_{8-z}$ within a solubility range of $0 < z < 4$. Compositional variation with this ratio does not require vacancies or interstitial atoms in the β-Si_3N_4 lattice. Other important phases in the system are the Si_2N_2O solid solution (O'), the X_l phase and the polytypes in the AlN corner.

A database for the SiAlON system has been assessed thermodynamically by Dorner *et al.*[15] and more recently by Hillert & Jonsson.[11] In such a database each phase is described by a model giving the variation of the Gibbs energy with temperature, pressure and composition. A number of model parameters must be assessed to give a good description of the experimental information. This technique has been used successfully in many metallic systems[16] and is often referred to as the 'Calphad technique'. Due to the lack of experimental information at the time when the SiAlON system was assessed some simplifications were introduced, for example only one polytype phase, 27R, is considered and it is restricted to the AlN–Al_2O_3 quasi-binary section.

Three of the phases in the SiAlON system, β'-sialon, O' and mullite have significant variations in composition and reciprocal models with ionic constituents have been selected by Hillert & Jonsson to describe this. For the β'-sialon phase the model has Si^{+4} and Al^{+3} on one sublattice with 3 sites and N^{-3} and O^{-2} on a sublattice with 4 sites, and this can be written as $(Si^{+4}, Al^{+3})_3(N^{-3}, O^{-2})_4$. Figure 1 shows the constitutional square of this reciprocal model. It has four corners and only one of these represent a real neutral compound, $(Si^{+4})_3(N^{-3})_4$, the others have a net charge and are thus unphysical. The line in Fig. 1 represents the neutral combinations of Al^{+3} and O^{-2} additions. The line goes from the Si_3N_4 corner to a composition Al_3O_3N on the opposite side.

For the O' phase the model selected by Hillert & Jonsson is a slightly modified reciprocal model. In this case there are three sublattices and the model can be written $(Si^{+4}, Al^{+3})_2(N^{-3}, O^{-2})_2(O^{-2})_1$. In the third sublattice there is only one constituent and thus the model is actually equivalent to a reciprocal one.

The mullite phase was modeled with three sublattices and the model can be written $(Al^{+3})_2 \cdot (Al^{+3}, Si^{+4})_1(O^{-2}, Va)_5$. As the first sublattice has only one constituent this is also a reciprocal model.

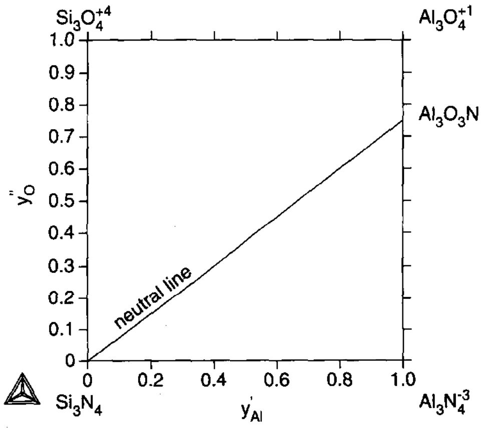


Fig. 1. The constitutional square for the β'-sialon model. The square represents a reciprocal model but only one corner is an electrically neutral compound. The axes represent the variation of Al^{+3} in sublattice 1 and O^{-2} in sublattice 2. The line drawn in the square represents the electrically neutral ratio of Al^{+3} and O^{-2} additions to Si_3N_4.

All other phases are treated as stoichiometric compounds. For X_1 the composition was selected to be $Si_{12}Al_{18}O_{39}N_8$ and $Al_9N_7O_3$ for R27.

In the development of a database it is important to be compatible with assessments of other oxide, nitride and metallic systems in order to make it possible to combine and extrapolate from different assessments. Some parameters for the spinel phase, stable at higher temperatures in the Al_2O_3 system, were thus taken from an assessment of the MgO–Al_2O_3 system by Hallstedt.[17]

Figure 2 is one example of the use of the SiAlON system assessed by Hillert & Jonsson, and shows the isothermal phase equilibrium at 1400°C without including the gas phase. Any phase or combination of phases, contained in Fig. 2, can be obtained by controlling the Si : Al ratio in the precursor and the oxygen and nitrogen partial pressures.

3 Calculated Diagrams in the SiAlON System

The database can be used to calculate any equilibrium state in the system using, for example, the Thermo-Calc software system.[18] This system uses the Gibbs energy minimization method[19] where the total free energy of the system is minimized with respect to the prescribed conditions. In Thermo-Calc a very flexible set of conditions can be used, not just the overall composition, temperature and pressure but also activities, the set of stable phases, composition of a phase, volumes, enthalpies, etc. The use of generally applicable software for thermodynamic calculations makes it possible to obtain diagrams that could not be perceived without this software. It is a useful tool for understanding how the system behaves under varying conditions and for testing the effect of different experimental techniques for controlling the system.

In this paper the calculations made to simulate the synthesis of two β'-sialon compositions, by reduction–nitridation of two silica : alumina mixture precursors with the ratio 2 : 1, composition A in Fig. 2, and 1 : 1, composition B in Fig. 2, respectively, are presented. The dotted lines into the diagram show the path of the reduction–nitridation process giving the final β'-sialon single-phase product.

Figure 3 describes the synthesis process better and shows the stable phase regions versus equivalent fraction aluminum and oxygen partial pressure in the system, at 1400°C. Reduction and nitridation of precursor mixture A shows that, as the reaction proceeds, first tridymite + mullite then tridymite + X_1, X_1 + O', β'-sialon + O' and β'-sialon are formed. For precursor mixture B first tridymite + mullite are formed as in the case of mixture A but then X_1 + mullite, X_1 + corundum, corundum + β'-sialon and β'-sialon are the phase fields through which the process progresses. The diagram was calculated at a constant activity of nitrogen equal to unity. Figure 3 emphasizes the importance of controlling the oxygen activity for the process and thus further calculations concerning that have been done.

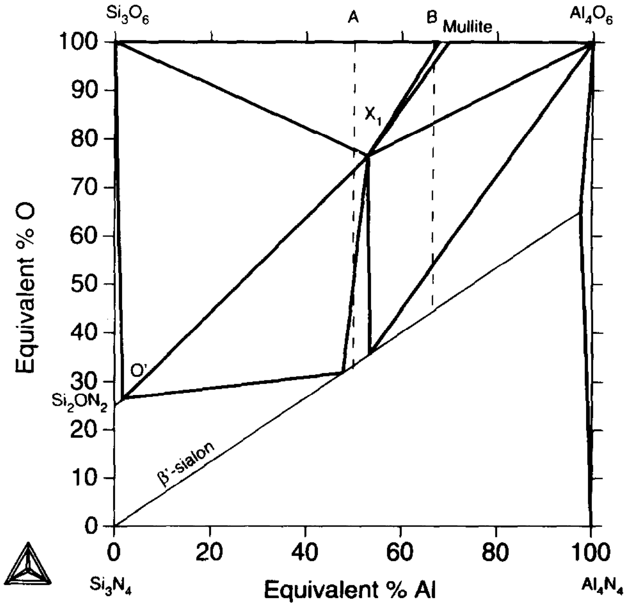


Fig. 2. Calculated isothermal section at 1400°C of the SiAlON system based on the database by Hillert & Jonsson.[11] The gas phase has been excluded. The mullite, O' and β'-sialon phases are treated with reciprocal solution models. The equivalent fraction of O and Al are used as axes. The dashed lines represent the precursor mixture A and B respectively.

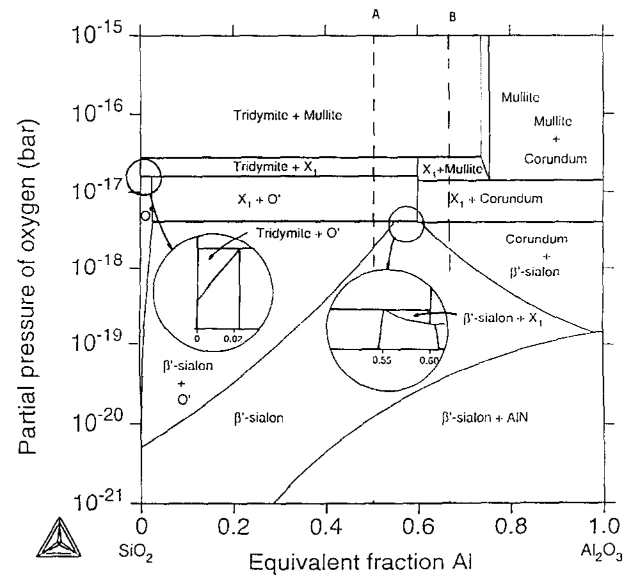
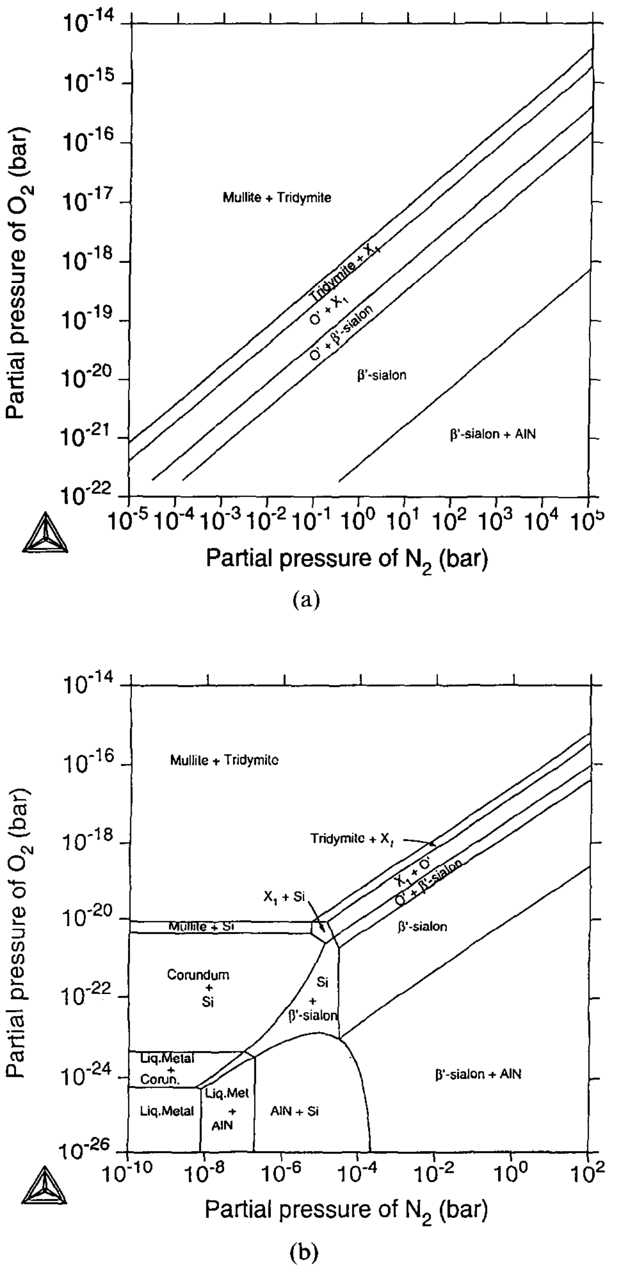


Fig. 3. The same diagram as in Fig. 2 but plotted with the variation in oxygen partial pressure instead of the equivalent % of oxygen on the vertical axis. The β'-sialon single-phase region is now an area and the three-phase regions are horizontal lines. The dashed lines represent the precursor mixture A and B respectively.

The stability regions for the phases in equilibrium at various nitrogen and oxygen partial pressures were calculated at 1250 and 1350°C for the precursor mixture A. Figure 4 shows the result. For the onset of β'-sialon formation the increase of oxygen partial pressure requires the nitrogen partial pressure to increase. This effect is more pronounced at lower temperatures. For a given nitrogen partial pressure the β'-sialon single-phase region has a width of about two orders of magnitude in oxygen partial pressure. For example at 1 bar nitrogen partial pressure Fig. 4(a) shows that the single β'-sialon region falls between 5×10^{-20} bar and 5×10^{-22} bar oxygen partial pressure. In Fig. 4(b) the phases appearing at very low oxygen and nitrogen partial pressures are shown. The left hand corner is liquid metal. Most of these phase regions are out of the experimental setup for β'-sialon synthesis.

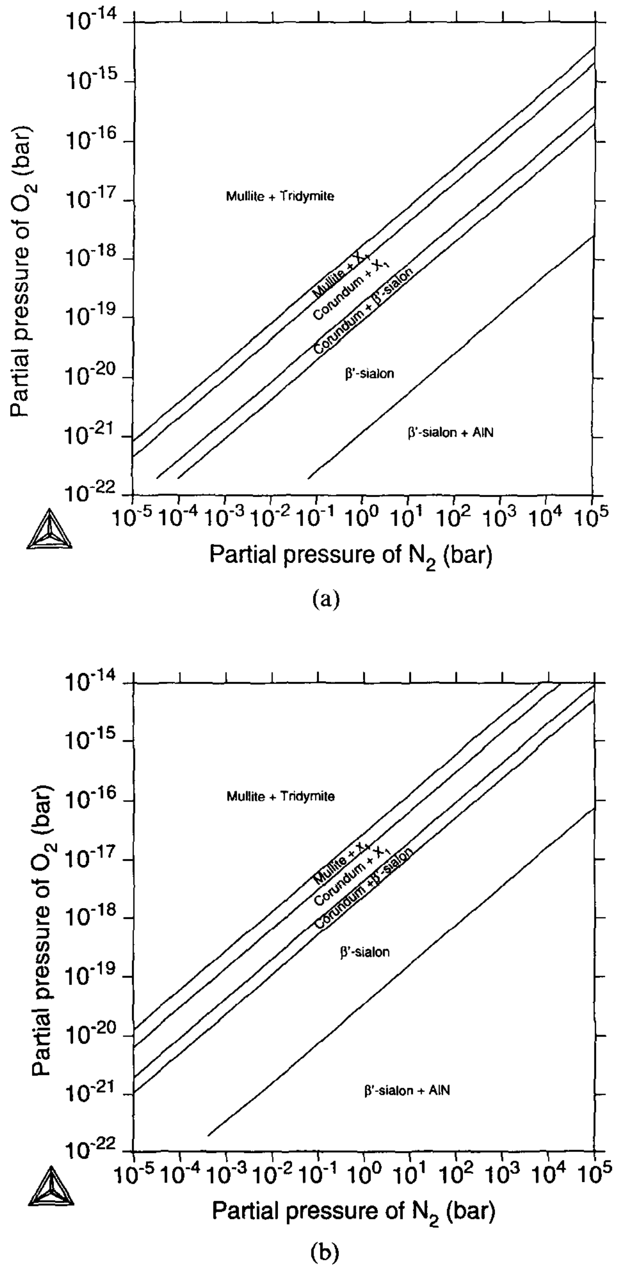
The same tendency to displace the β'-sialon stable region toward higher nitrogen partial pressures with increasing oxygen partial pressure is also observed for precursor mixture B. Figure 5(a) and (b) show the result of calculations for this mixture at 1250 and 1350°C respectively. The difference between mixtures A and B at 1250 or 1350°C is the β'-sialon stability region which is narrower for precursor B than for A. This means that the precursor B is less suitable for preparation of β'-sialon as the oxygen partial pressure must be kept in a smaller range. Experimentally this is much more difficult.



(a)

(b)

Fig. 4. The stability regions for the phases in equilibrium at various nitrogen and oxygen partial pressures. The ratio SiO_2 : Al_2O_3 is 2 : 1. (a) Calculated at 1250°C; (b) calculated at 1350°C.



(a)

(b)

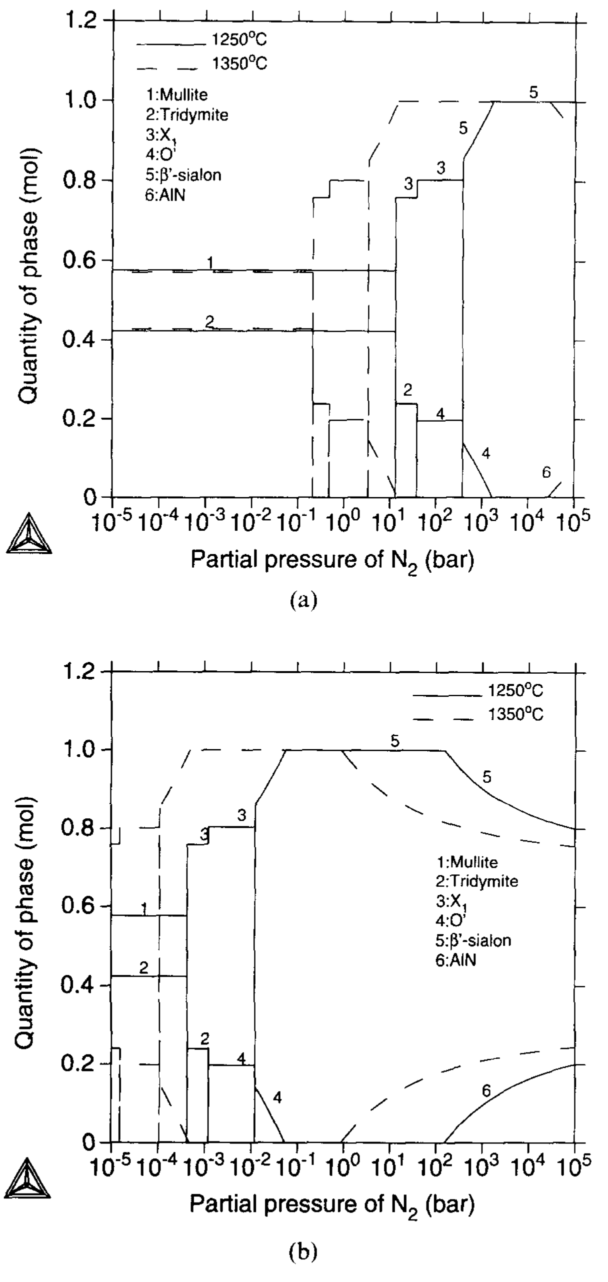
Fig. 5. The stability regions for the phases in equilibrium at various nitrogen and oxygen partial pressures. The ratio SiO_2 : Al_2O_3 is 1 : 1. (a) Calculated at 1250°C; (b) calculated at 1350°C.

A more suggestive way to present the result of the calculations and to see the influence of temperature, partial pressures of oxygen and nitrogen on the β'-sialon synthesis is to plot the quantity of phase as a function of partial pressure of nitrogen at different fixed temperatures, partial pressures of oxygen and silica : alumina ratios.

Figures 6 and 7 show the quantity of phase for a system with one mole of components, for the precursor mixture A and B respectively, as a function of partial pressure of nitrogen. The calculations were made for a partial pressure of oxygen equal to 10^{-17} bar, Figs 6(a) and 7(a), and 10^{-20} bar, Figs 6(b) and 7(b). Each figure shows calculations at two temperatures, 1250 and 1350°C, using solid and dashed lines respectively.

The experimental facilities to obtain β'-sialon powders can provide a partial pressure of nitrogen between 1 and 5 bar. The calculated diagrams, Figs 6(a) and 7(a), show that if the partial pressure of oxygen is 10^{-17} bar, it will be impossible to produce β'-sialon.

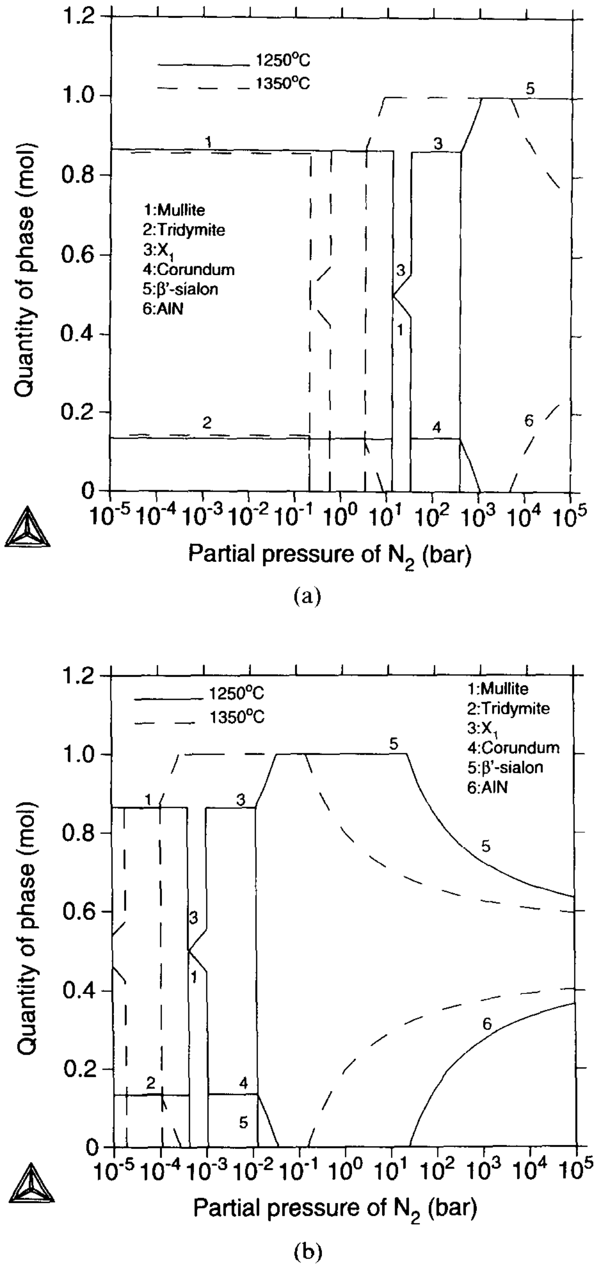
When the partial pressure of oxygen is 10^{-20} bar the synthesis of single-phase β'-sialon is experimentally possible at the lower temperature 1250°C, for both precursor mixtures A and B, Figs 6(b) and 7(b). Experiments to synthesize β'-sialon based on these thermodynamic calculations for the precursor mixture A were presented by Teoreanu *et al.*[20]



(a)

(b)

Fig. 6. Quantity of phase for a system with one mole of components as a function of nitrogen partial pressure. Calculations at 1250 and 1350°C are shown with solid and dashed lines respectively. The ratio $SiO_2 : Al_2O_3$ is 2 : 1. In (a) the oxygen partial pressure is 10^{-17} bar. In (b) the oxygen partial pressure is 10^{-20} bar.



(a)

(b)

Fig. 7. Quantity of phase for a system with one mole of components as a function of nitrogen partial pressure. Calculations at 1250 and 1350°C are shown with solid and dashed lines respectively. The ratio $SiO_2 : Al_2O_3$ is 1 : 1. In (a) the oxygen partial pressure is 10^{-17} bar. In (b) the oxygen partial pressure is 10^{-20} bar.

4 Conclusions

This paper sets out the thermodynamic basis for β'-sialon powder synthesis and describes the variables which must be controlled to obtain materials of desired phase composition, chemistry and morphology.

The most important variables in the β'-sialon synthesis are partial pressures of oxygen and nitrogen, Si : Al ratio in the precursor mixture and the temperature. The β'-sialon single-phase region exists only within a small region of oxygen and nitrogen partial pressures.

Thermodynamic calculations in the SiAlON system help to screen the most effective β'-sialon synthesis conditions and give guidelines for experimental work.

Acknowledgment

One of the authors (L. Dumitrescu) is grateful to the Swedish Institute for financial support.

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