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A Thermodynamic Reassessment of the Si–Al–O–N System

Lucia Dumitrescu* & Bo Sundman

Department of Materials Science and Engineering, Royal Institute of Technology, 100 44 Stockholm, Sweden

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Abstract

The Si–Al–O–N system has been thermodynamically reassessed due to the new model used for liquid in the Al_2O_3*–*SiO_2 *binary system and new experimental data in the* Al_2O_3*–AlN system. The* β*'-sialon phase is described by a new model,* $(Al^{3+},Si^{4+})_3(O^{2-},N^{3-})_3(N^{3-})_1$*, and a set of new parameters was found to describe better the experimental behaviour phase diagram and the* β*'-sialon stability in the system even at reasonably low temperatures. Phase diagrams calculated using the new assessment are presented.*

1 Introduction

A thermodynamic assessment of the Al–Si–O–N system was recently presented by Hillert and Jonsson.[1] Later Hallstedt *et al.*[2] proposed changes in the model for the liquid phase in the binary subsystem Al_2O_3–SiO_2 in order to extrapolate this system into the ternary CaO–Al_2O_3–SiO_2. There is also new experimental information on the Al_2O_3–AlN system given by Willems *et al.*[3,4] This requires a revaluation of the SiO_2–Al_2O_3 and Al_2O_3–AlN systems and subsequently of the Si_3N_4–AlN–Al_2O_3-SiO_2 system. The results of this reevaluation will be presented here. A second reason for the reevaluation is that it was discovered that the parameter values presented by Hillert and Jonsson predict that the β'-sialon phase is stable in the AlN–Al_2O_3 system below a certain temperature. There is no experimental support for such a result.

2 The Al_2O_3–SiO_2 System

The amphoteric nature of Al_2O_3 causes problems when this compound is mixed with either a strong acid like SiO_2 or a strong base like CaO. Previously,[5] Al_2O_3 was treated as a basic oxide, assuming that it would easily give away its oxygen. In the ternary system Al_2O_3–CaO–SiO_2 such an assumption would give, using the ionic liquid model,[6] the following model for the liquid phase

$$(Al^{3+},Ca^{2+})_p(O^{2-},SiO_4^{4-},SiO_2)_q$$

The site ratios, p and q, are set equal to the average charge on the other sublattice in order to maintain electroneutrality:

$$p = 2y_{O^{2-}} + 4y_{SiO_4^{4-}}$$

$$q = 3y_{Al^{3+}} + 2y_{Ca^{2+}}$$

Although each binary system could be described satisfactorily with this model it was impossible to obtain a reasonable extrapolation into the ternary system. As described by Hallstedt *et al.*[2] a better extrapolation could be obtained using the neutral species $AlO_{1.5}$ which would yield the following model for the liquid phase

$$(Ca^{2+})_p(O^{2-},SiO_4^{4-},SiO_2,AlO_{1.5})_q$$

The choice of $AlO_{1.5}$ rather than Al_2O_3 may be justified by the assumption that a network of triangles of O with an Al in the middle[7] forms in the liquid. As each O is shared between two Al, the basic unit is $AlO_{1.5}$. The reason for having SiO_2 as a constituent is similar because in SiO_2, which forms tetrahedra of four O with an Si in the middle, each O is shared between two Si. For the Al_2O_3–SiO_2 system this model reduces to $(AlO_{1.5},SiO_2)$, a simple associated solution model and this system was assessed in such a way by Hillert *et al.*[8]

3 The Al_2O_3–AlN System

McCauley and Corbin[9] published a phase diagram

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*On leave from Matpur SA, Sos. Garii Catelu nr. 5, Bucharest 3, Romania.

for the Al_2O_3–AlN system and they listed seven phases, AlN (with a wurtzite structure); $Al_9O_3N_7$ (with a 27R AlN polytype structure); $Al_7O_3N_5$ (with a 21R AlN polytype structure); $Al_6O_3N_4$ (with a 12H AlN polytype structure); $Al_{23}O_{27}N_5$ (with an AlON spinel structure); $Al_{22}O_{33}N_2$ (with a ϕ-spinel structure); and Al_2O_3 (with a corundum structure).

In the present work all phases, except $Al_{22}O_{33}N_2$ (ϕ-spinel structure), were taken into account. The new experimental information concerning the extention of the spinel phase in the quasibinary system Al_2O_3–AlN was also included.

The width of the homogeneity of the spinel phase varies with temperature: at 1850°C spinel is the stable phase between 66 mol% Al_2O_3 and 81 mol% Al_2O_3.[4] This region becomes smaller at lower temperatures. Below 1640°C[3] spinel is not stable.

Hillert and Jonsson[1] described the liquid phase in this quasibinary system with the model $(Al^{3+})_p(N^{3-},O^{2-})_q$. However, in line with the choice of $AlO_{1.5}$ as a species the present work will use the substitutional model ($AlO_{1.5}$,AlN).

4 The Si–Al–O–N System

The Si–Al–O–N system has four components and should be represented by a regular tetrahedron (Fig. 1). If the elements have their normal valencies (Si^{IV}, Al^{III}, O^{II}, and N^{III}) then all possible solid compounds lie on an irregular quadrilateral plane, and if the concentrations are expressed in equivalents, i.e. the corners of the tetrahedron are respectively $3Si^{12+}$, $4Al^{12+}$, $6O^{12-}$ and $4N^{12-}$, then these solid compounds all lie on a square plane in which any point represents a combination of 12 positive and 12 negative valencies (Fig. 2). Conventionally, Si_3N_4 is placed at the bottom left-hand corner of the square diagram and distances from left to right represent replacement of silicon by its equivalent of aluminium and distances from bottom to top the replacement of nitrogen by oxygen.[10]

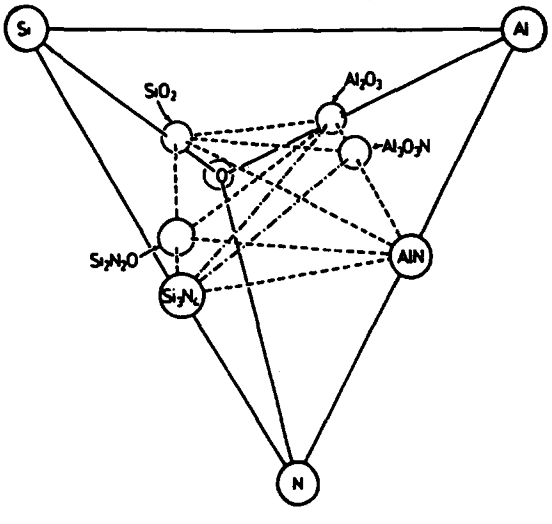

Fig. 1. The tetrahedral representation of the Si–Al–O–N system. Possible compositions are on the neutral plane indicated by the shared area.

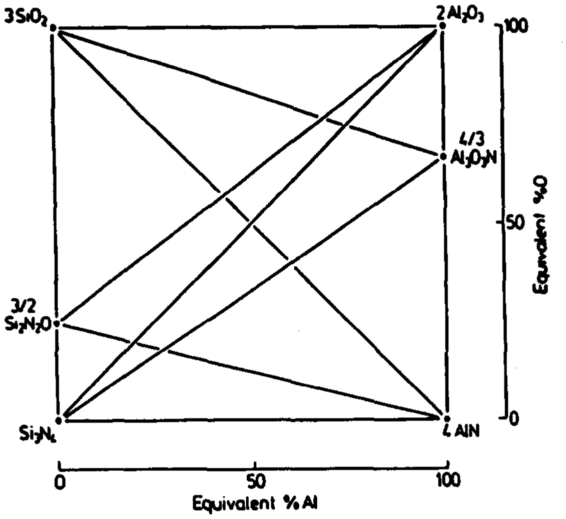

Fig. 2. The square representation of the Si–Al–O–N system using equivalent concentration.

The experimental work on the phase relations in the quasi-ternary system Si_3N_4–AlN–Al_2O_3–SiO_2

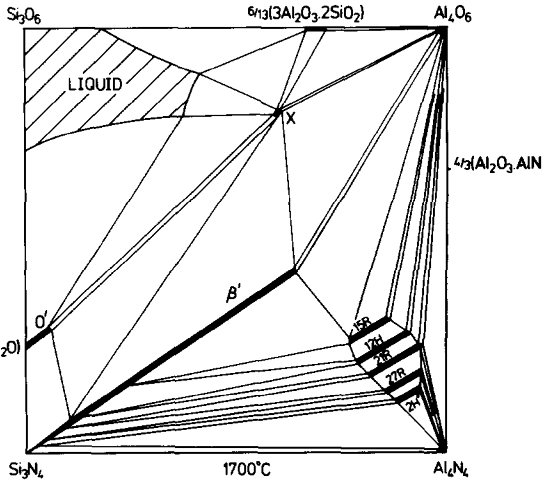

Fig. 3. The Si–Al–O–N behaviour diagram based on experimental data at 1700°C.[13]

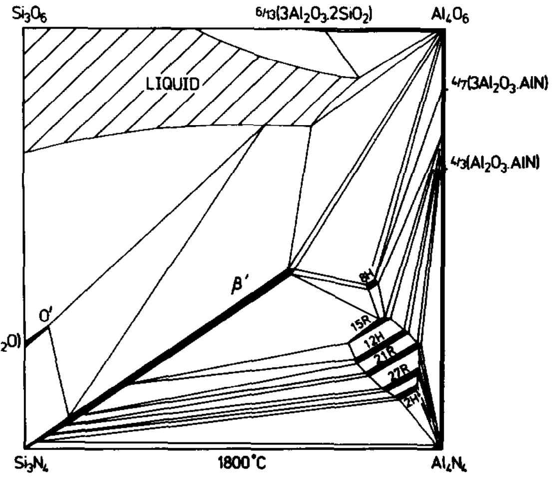

Fig. 4. The Si–Al–O–N behaviour diagram based on experimental data at 1800°C.[13]

was carried out mainly for the Si_3N_4–Al_2O_3–SiO_2 region of the diagram. The thermodynamic assessment of the SiAlON system is based on the experimental work of Naik *et al.*,[11] Bergman *et al.*[12] and on the most recent behaviour diagrams by Jack[13] for the Si_3N_4–Al_4N_4–Al_4O_6–Si_3O_6 system at 1700 and 1800°C (Figs 3 and 4). These two behaviour diagrams represent a summation of experimental observations. Jack did not claim that it is an equilibrium phase diagram in a thermodynamic sense due to the following difficulties and uncertainties of the experimental observations:

- weight losses due to evaporation, which change the overall composition;
- in the absence of liquid phase, the reaction between nitrides is very slow;
- in most experiments, the gaseous environment is ill-defined and many species are present in trace amounts (SiO(G), Si(G), Al_2O(G) etc.) and play a part depending on both thermodynamics and kinetics, and they affect the final phase assemblage.

Each phase in the system extends in a direction of constant metal: non-metal atom ratio (M:X) along which Si+N is replaced gradually by Al+O. The homogeneity ranges perpendicular to this are quite small.

The Si_3N_4 phase can dissolve a large amount of Al_2O_3 + AlN and forms β'-sialon. This phase extends essentially along the 3M:4X line with a homogeneity range described by $Si_{6-z}Al_zO_zN_{8-z}$, where z reaches a maximum of about 4 at 1700°C but decreases with decreasing temperature.

The Si_2N_2O phase can dissolve Al_2O_3 and forms O'-phase. This phase extends with a limited composition range along the 2M:3X line toward Al_2O_3.

The X-phase present in the system has a small range of homogeneity but, as in the previous assessment work by Hillert and Jonsson, it will be treated as a phase of fixed composition, $Si_{12}Al_{18}O_{39}N_8$. This composition is further supported by recent work by Anya and Hendry.[14]

Near the AlN corner of the diagram, six phases have been interpreted in terms of AlN-polytypes containing excess non-metal atoms. Their structures are directly related to their compositions M_mX_{m+1} and are described by the Ramsdell symbols 8H, 15R, 12H, 21R, 27R, and 2H.[15] In the strictest sense, polytypes are layer structures which, within very narrow limits, preserve a constant chemical composition and differ only in the way the layers are stacked together. In the sialon 'polytypes', both the composition and the unit cell dimensions show a systematic variation with structure type and the International Union of Crystallography has assigned the name 'polytypoids' to such series.[16]

For the β'-sialon phase a slightly modified model compared to that of Hillert and Jonsson will be adopted as there are two distinctly different sites for nitrogen.[17] It will be assumed that O^{2-} can enter only into one of the N^{3-} sublattices, leaving the other sublattice with one site always filled with N^{3-}. The new model would thus be

$$(Al^{3+},Si^{4+})_3(O^{2-},N^{3-})_3(N^{3-})_1$$

The maximum theoretical amount of Al to dissolve in β'-sialon would thus be Al_3O_3N.

At reasonably low temperatures the liquid phase exists mainly in the quasi-binary Al_2O_3–SiO_2 and it extends at higher temperatures considerably into the square towards the AlN corner of the diagram. It will be described with an associated solution model based on the species $SiN_{4/3}$ in addition to those already mentioned:

$$(AlN,\ AlO_{1.5},\ SiO_2,\ SiN_{4/3})$$

5 Optimization

The optimization was made using a computer program called Parrot,[18] which allows the simultaneous consideration of different types of thermodynamic and phase diagram data. First, models that depict different phases in the system were selected. A number of parameters for each phase were then optimized in order to describe the experimental information as well as possible. The program works by minimizing an error sum by varying selected model parameters. The sum of errors is calculated from the experimental information where each piece of information used is given an experimental uncertainty and also a weight according to its estimated accuracy and relative importance. In this system the available experimental information is not enough to allow the optimizing program to determine the model parameters without manual interaction.The weights were changed by trial and error and the model parameters were optimized until most of the information could be satisfactorily described. As input, selected experimental data together with known thermodynamical data for the solids and liquids were used.

The binary assessment of SiO_2–Si_3N_4 from Hillert and Jonsson[19] was accepted and together with the two new assessments of the quasibinaries, AlN–Al_2O_3 and SiO_2–Al_2O_3, a new thermodynamic assessment of the SiAlON system was attempted. There is no experimental information in the quasibinary system AlN–Si_3N_4.

The final thermodynamic description of the system, including the values of the assessed parameters, is given in Appendix 1.

The heat capacities for the crystalline phases were assumed to follow a Neuman–Kopp relation using linear combinations of the four stable compounds SiO_2, Al_2O_3, AlN and Si_3N_4.

Two interaction parameters were optimized for the liquid phase, one for the diagonal ($SiN_{4/3}$–$AlO_{1.5}$) and one for the ternary ($SiN_{4/3}$–SiO_2–$AlO_{1.5}$). Both parameters were assumed to be temperature independent.

For the β'-sialon phase two of the corner compounds were optimized, the neutral compound Al_3O_3N and for the charged compound $Al_3N_3^{4-}$. The parameter for the neutral compound was assumed to be linearly temperature dependant. In addition, the model has a reciprocal parameter, representing the simultaneous exchange of Al^{3+} with Si^{4+} and O^{2-} with N^{3-}. It was found that this parameter was necessary in order to keep the low solubility of Al_2O_3 in β'-sialon in the three-phase equilibrium liquid+O'+β'-sialon.

The solubility of Al_2O_3 in the O' phase was optimized using the fictitious corner compound $Si_2O_3^{2-}$ only. A linear temperature dependence for this parameter was required to describe the solubility for the whole temperature range. The model for the O' phase extends all the way to the composition Al_2O_3 but the parameter for this metastable compound was kept fixed to the same value as estimated by Hillert and Jonsson.

The melting temperature of the X phase was fitted to 1727°C using a single parameter representing the enthalpy of formation of X.

In the present work, the polytypes were only considered in the assessment of the AlN–Al_2O_3 system due to the very meagre information on their extension into the square diagram. They were thus treated as stoichiometric Al_2O_3–AlN phases. 21R, 27R and 12H were considered and only a single enthalpy value was fitted to describe the experimental sublimation or melting temperature. In the cases when the phases had a lower temperature limit an entropy of formation was also fitted.

6 Results

The new calculated phase diagram for the quasibinary AlN – Al_2O_3 is given in Fig. 5. Selected experimental data are included in Fig. 6 to give a comparison of the calculated diagram with the experimental data.

Figures 7–10 give a series of isothermal sections of the Si_3N_4–Al_4N_4–Al_4O_6–Si_3O_6 system. The comparison with experimental data shows good agreement. Figure 11 shows an extrapolation to higher temperature, 1900°C.

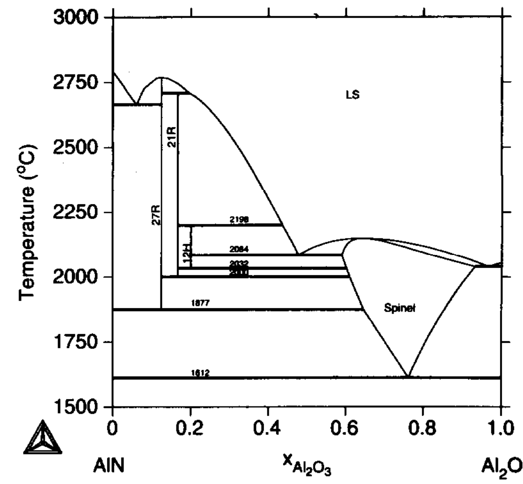

Fig. 5. The AlN–Al_2O_3 phase diagram at 1 bar, according to the present optimization, calculated without including the gas phase. The calculation includes one spinel phase and 27R, 21R, and 12H AlN-polytype phases.

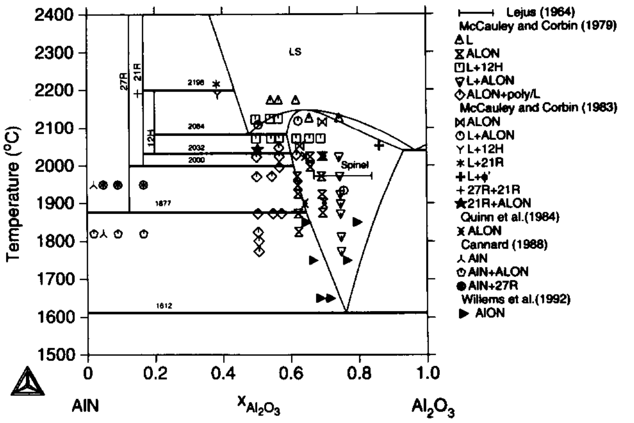

Fig. 6. Comparison of the calculated AlN–Al_2O_3 phase diagram with experimental data from several sources.

The calculated diagram at 1400°C is given in Fig. 12. Figure 13 shows an alternative presentation of this diagram using the oxygen potential as one of the axes. In this representation, the diagram is useful for determining the optimal values for the partial pressures of oxygen, an important

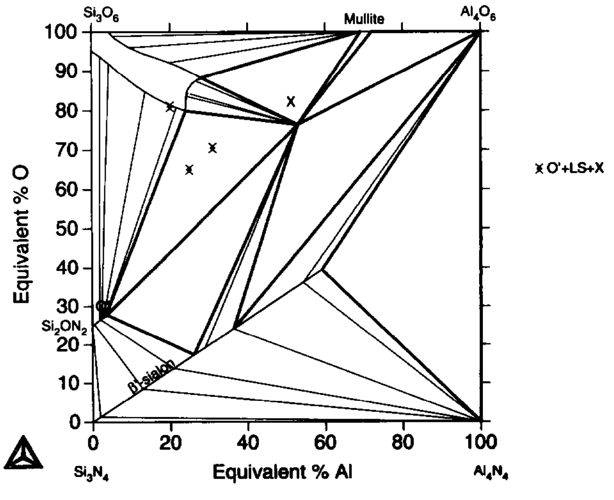

Fig. 7. Calculated section at 1600°C, in comparison with experimental data from Naik *et al.*[11]

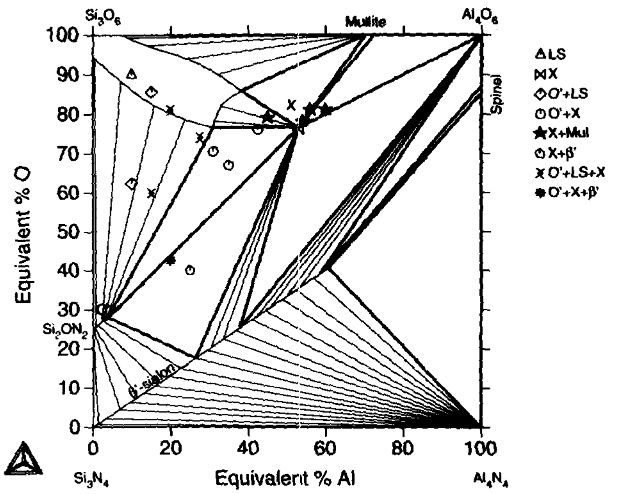

Fig. 8. Calculated section at 1650°C, in comparison with experimental data from Naik *et al.*[11]

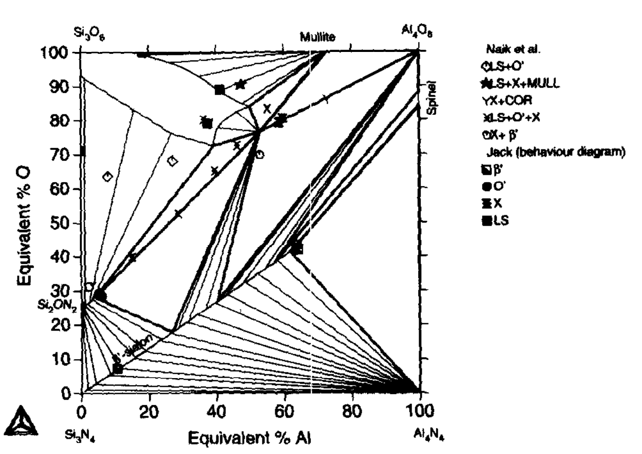

Fig. 9. Calculated section at 1700°C, in comparison with experimental data from Jack[13] and Bergman *et al.*[12]

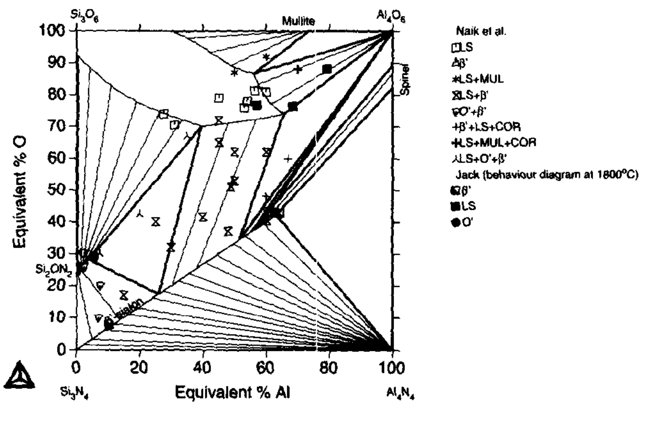

Fig. 10. Calculated section at 1750°C, in comparison with experimental data from Naik *et al.*[11] Good fit to experimental data has been obtained.

parameter for synthesis of different materials in the system, β'-sialon for example.

Generally there is good agreement between experimental and calculated data both for the $AlN–Al_2O_3$ and $Si_3N_4–Al_4N_4–Al_4O_6–Si_3O_6$ system.

In the $AlN–Al_2O_3$ diagram the spinel phase extends closer to the Al_2O_3 composition than

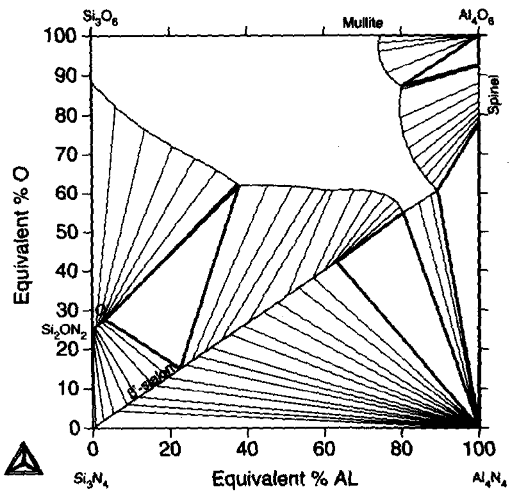

Fig. 11. Calculated section at 1900°C according to the present optimization.

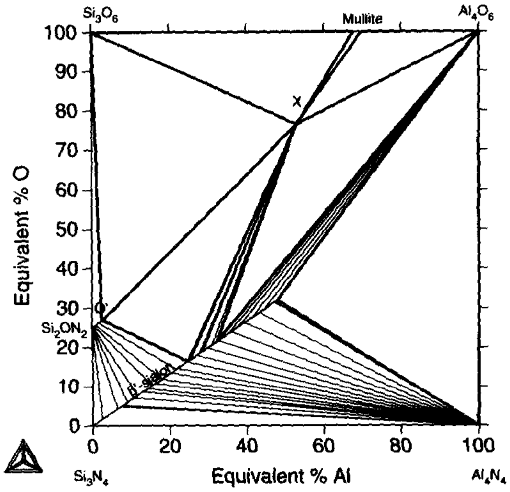

Fig. 12. Calculated section at 1400°C according to the present optimization.

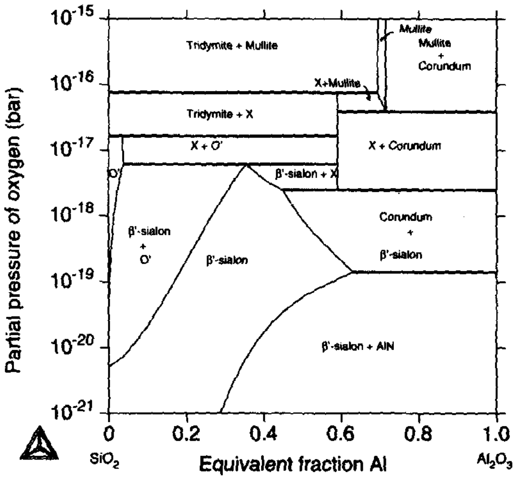

Fig. 13. The same calculation as for the diagram in Fig. 12 but using oxygen potential as an alternative presentation of the result.

experimental data can support. However, the description of the spinel phase must agree with the estimated stability of γ-alumina for pure Al_2O_3 as given by Hallstedt.[20] This restricts the possibilities to vary its composition. The experimental phase diagram in this range has several impossible features and the current fit is acceptable until better experimental data are available. The 27R, 21R, and 12H AlN-polytypes have been considered and the assessment give a good fit of their stability temperature range. Hillert and Jonsson only considered the 27R polytype but, otherwise, the present diagram is very similar to theirs. However, it should again be emphasized that their parameter values for β'-sialon make it stable in the AlN–Al_2O_3 diagram, a fact which was not noticed by them. This has now been avoided by the new assessment of the β'-sialon.

Figure 14 is a reproduction of the Si_3N_4–Al_4N_4–Al_4O_6–Si_3O_6 system at 1750°C calculated by Hillert and Jonsson and it may be compared with Fig. 10 from the present assessment. The most striking difference is that the β'-sialon phase does not extend as close to the AlN–Al_2O_3 side as before. This is a result of the new model for β'-sialon and of the set of new parameters. This has also resulted in the β'-sialon corners of three-phase triangles moving closer to the Si_3N_4 corner. This has resulted in a better agreement with the experimental points for LS + β' but some of those points still fall outside the calculated two-phase field.

Another improvement can be seen in Fig. 9 where an experimental point for X+corundum falls on the calculated two-phase field. According to Hillert and Jonsson, this two-phase field only exists at considerably lower temperatures. The parameter values given by Hillert and Jonsson predict that the X phase should melt at 1721°C. This is only 1°C different from the experimental value of Naik *et al.*[11] The present assessment predicts a melting point of 1727°.

Another difference between the two assessments concerns the liquid phase field which is wider and extents deeper into the diagram according to the present assessment. This has resulted in three experimental points for O'+LS+X at 1650°C, now falling outside the calculated three-phase triangle.

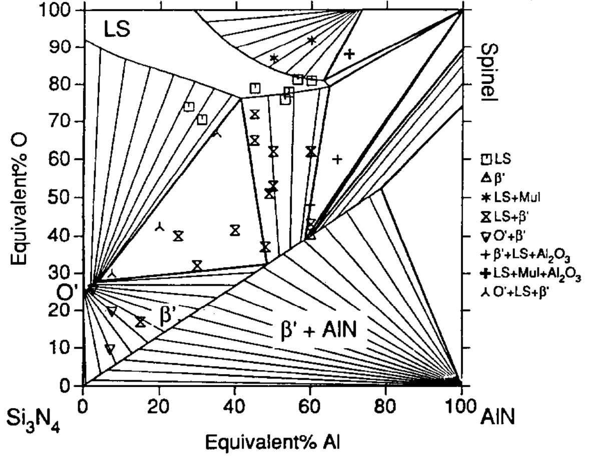

Fig. 14. Phase diagram at 1750°C calculated by Hillert and Jonsson using a different model for the liquid and β' phases.

It should again be emphasized that the ternary polytypes in the AlN-rich part of the diagram remain unassessed as there is no thermodynamical information available to evaluate them. Calorimetric measurements of the enthalpy of formation or the enthalpy of transformation are needed and their extension into the square diagram should be studied in more detail.

Acknowledgements

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Appendix 1. Thermodynamic Description of the Si–Al–O–N System

All parameter values are given in SI units (joules, moles, kelvin); $R = 8.31451$ J/(mol K).

Liquid slag (LS), (AlN,AlO$_{1\cdot5}$,SiN$_{1\cdot3}$,SiO$_2$)

$${}^0G^{\mathrm{LS}}_{\mathrm{AlN}} = {}^0G^{\mathrm{liq}}_{\mathrm{AlN}} = {}^0G_{\mathrm{AlN}} + 70541 - 23T$$

$${}^0G^{\mathrm{LS}}_{\mathrm{AlO1\cdot5}} = 0{\cdot}5\,{}^0G^{\mathrm{liq}}_{\mathrm{Al_2O_3}}$$

$${}^0G^{\mathrm{LS}}_{\mathrm{SiN_{4/3}}} = 1/3\,{}^0G^{\mathrm{liq}}_{\mathrm{Si_3N_4}} = 1/3({}^0G_{\mathrm{Si_3N_4}} + 209300 - 80.5T$$

$${}^0G^{\mathrm{LS}}_{\mathrm{SiO_2}} = {}^0G^{\mathrm{liq}}_{\mathrm{SiO_2}}$$

$${}^0L^{\mathrm{LS}}_{\mathrm{AlO1\cdot5,SiO2}} = 80121 - 30T$$

$${}^1L^{\mathrm{LS}}_{\mathrm{AlO1\cdot5,SiO2}} = 96000 + 44T$$

$${}^0L^{\mathrm{LS}}_{\mathrm{AlO1\cdot5,SiN4/3}} = -\ 15000$$

$${}^0L^{\mathrm{LS}}_{\mathrm{AlO1\cdot5,SiN4/3,SiO2}} = -\ 134000$$

AlN, (Al)$_1$(N)$_1$

$${}^{\circ}G^{\mathrm{AlN}}_{\mathrm{Al:N}} - H^{\mathrm{SER}} = {}^{\circ}G_{\mathrm{AlN}} - H^{\mathrm{SER}} = -345837.2$$
$$+ 359.86191T - 54.308659T\ln T + 8.5550404\cdot10^{-4}T^2$$
$$+ 2326379.8\ /\ T - 1.2556503\cdot10^{8}T^{-2}$$

β', (Al^{3+},Si^{4+})$_3$(N^{3-},O^{2-})$_3$(N^{3-})$_1$

$${}^{\circ}G^{\beta'}_{\mathrm{Al^{+3}:N^{-3}}} - H^{\mathrm{SER}} = {}^{\circ}4G_{\mathrm{AlN}} - 2340925$$

$${}^{\circ}G^{\beta'}_{\mathrm{Si^{+4}:N^{-3}:N^{-3}}} - H^{\mathrm{SER}} = {}^{\circ}G_{\mathrm{Si_3N_4}}$$

$${}^{\circ}G^{\beta'}_{\mathrm{Al^{+3}:O^{-3}:N^{-3}}} - H^{\mathrm{SER}} = {}^{\circ}G_{\mathrm{Al_2O_3}} + {}^{\circ}G_{\mathrm{AlN}}$$
$$+ 250300 - 92.3T$$

$${}^{\circ}G^{\beta'}_{\mathrm{Si^{+4}:O^{-2}:N^{-3}}} = {}^{\circ}G_{\mathrm{Si_3N_4}} + 100000$$

$${}^0L^{\beta'}_{\mathrm{Al^{+3}:Si^{+4}:N^{-3},O^{-2}:N^{-3}}} = 893000$$

Al$_2$O$_3$ (corundum), (Al)$_2$(O)$_3$

$298 < T < 600$ K

$${}^{\circ}G^{\mathrm{Al_2O_3}}_{\mathrm{Al:O}} - H^{\mathrm{SER}} = {}^{\circ}G_{\mathrm{Al_2O_3}} - H^{\mathrm{SER}} = -\ 1707351.3$$
$$+ 448.021092T - 67.4804T\ln T$$
$$- 0.06747T^2 + 1.4205433\cdot10^{-5}T^3 + 938780\ /\ T$$

$600 < T < 1500$ K

$${}^{\circ}G^{\mathrm{Al_2O_3}}_{\mathrm{Al:O}} - H^{\mathrm{SER}} = {}^{\circ}G_{\mathrm{Al_2O_3}} - H^{\mathrm{SER}} = -\ 1724886.06$$
$$+ 754.856573T - 116.258T\ln T$$
$$- 0.0072257T^2 + 2.78532\cdot10^{-7}T^3 + 2120700\ /\ T$$

$1500 < T < 3000$ K

$${}^{\circ}G^{\mathrm{Al_2O_3}}_{\mathrm{Al:O}} - H^{\mathrm{SER}} = {}^{\circ}G_{\mathrm{Al_2O_3}} - H^{\mathrm{SER}} = -\ 1772163.19$$
$$+ 1053.4548T - 156.058T\ln T$$
$$+ 0.00709105T^2 - 6.29402\cdot10^{-7}T^3 + 12366650\ /\ T$$

SiO$_2$ (cristobalite) (Si O$_2$)$_1$

$298 < T < 373$ K

$${}^{\circ}G_{\mathrm{SiO_2}} - H^{\mathrm{SER}} = -\ 601467.73 - 8140.2255T$$
$$+ 1399.8908T\ln T - 2.8579085T^2$$
$$+ 0.0010408145T^3 - 13144016\ /\ T$$

$373 < T < 453$ K

$${}^{\circ}G_{\mathrm{SiO_2}} - H^{\mathrm{SER}} = -\ 1498711.3 + 13075.913T$$
$$- 2178.3561T\ln T + 3.493609T^2$$
$$- 0.0010762132T^3 + 29100273\ /\ T$$

$453 < T < 543$ K

$${}^{\circ}G_{\mathrm{SiO_2}} - H^{\mathrm{SER}} = -\ 3224538.7 + 47854.938T$$
$$- 7860.2125T\ln T + 11.817149T^2$$
$$- 0.0033651832T^3 + 1.2750272\cdot10^{8}\ /\ T$$

$543 < T < 3300$ K

$${}^{\circ}G_{\mathrm{SiO_2}} - H^{\mathrm{SER}} = -\ 943127.51 + 493.26056T$$
$$- 77.5875T\ln T + 0.0030402\,45T^2$$
$$- 4.63118\cdot10^{-7}T^3 + 2227125\ /\ T$$

$3300 < T < 4000$ K

$${}^{\circ}G_{\mathrm{SiO_2}} - H^{\mathrm{SER}} = -\ 973891.99 + 587.05606T$$
$$- 87.373T\ln T$$

Mullite, $(Al^{3+})_1(Al^{3+})_1(Al^{3+},Si^{4+})_1(O^{2-},Va)_5$

$${}^{\circ}G^{\mathrm{Mullite}}_{\mathrm{Al^{+3}:Al^{+3}:Al^{+3}:O^{-2}}} - H^{\mathrm{SER}} = -2808415.35 + 13484407.2 / T + 1600.541T - 246.032747T\ln T + 0.0138772261T^2 - 8.37441995\cdot 10^8 / T^2$$

$${}^{\circ}G^{\mathrm{Mullite}}_{\mathrm{Al^{+3}:Al^{+3}:Si^{+4}:O^{-2}}} - H^{\mathrm{SER}} = -2649812 + 2348905.07 / T + 1050.05906T - 165.804515T\ln T - 0.0160571905T^2$$

$${}^{\circ}G^{\mathrm{Mullite}}_{\mathrm{Al^{+3}:Al^{+3}:Al^{+3}:VA}} - H^{\mathrm{SER}} = 0$$

$${}^{0}G^{\mathrm{Mullite}}_{\mathrm{Al^{+3}:Al^{+3}:Si^{+4}:VA}} - H^{\mathrm{SER}} = 3894128.51 + 2348905.07 / T + 1050.05906T - 165.804515T\ln T - 0.0160571905T^2$$

$${}^{\circ}L^{\mathrm{Mullite}}_{\mathrm{Al^{+3}:Al^{+3}:Al^{+3}:Si^{+4}:O^{-2}}} = -498147.243 + 64.0830461\,T$$

O', $(Al^{3+},Si^{4+})_2(N^{3-},O^{2-})_2(O^{2-})_1$

$${}^{\circ}G^{\mathrm{O'}}_{\mathrm{Al^{+3}:N^{-3}:O^{-2}}} - H^{\mathrm{SER}} = 0$$

$${}^{\circ}G^{\mathrm{O'}}_{\mathrm{Si^{+4}:N^{-3}:O^{-2}}} - H^{\mathrm{SER}} = {}^{\circ}G_{\mathrm{Si_2N_2O}} - H^{\mathrm{SER}} - 966831.914 + 731.008345T - 111.723752T\ln T - 0.00587194833T^2 + 2184668.61 / T$$

$${}^{\circ}G^{\mathrm{O'}}_{\mathrm{Al^{+3}:O^{-2}:O^{-2}}} = 2{}^{\circ}G_{\gamma\text{-}\mathrm{Al_2O_3}} - {}^{\circ}G_{\mathrm{Al_2O_3}}$$

$${}^{\circ}G^{\mathrm{O'}}_{\mathrm{Si^{+4}:O^{-2}:O^{-2}}} = {}^{\circ}G_{\mathrm{Si_2N_2O}} + 2{}^{\circ}G_{\gamma\text{-}\mathrm{Al_2O_3}} - {}^{\circ}G_{\mathrm{Al_2O_3}} + 10000 + 90T$$

27R, $(Al)_9(N)_7(O)_3$

$${}^{\circ}G^{\mathrm{27R}}_{\mathrm{Al:N:O}} = 7\,{}^{\circ}G_{\mathrm{AlN}} + {}^{\circ}G_{\mathrm{Al_2O_3}} + 340000 - 163T$$

21R, $(Al)_7(N)_5(O)_3$

$${}^{\circ}G^{\mathrm{21R}}_{\mathrm{Al:N:O}} = 5\,{}^{\circ}G_{\mathrm{AlN}} + {}^{\circ}G_{\mathrm{Al_2O_3}} + 308000 - 147T$$

12H, $(Al)_6(N)_4(O)_3$

$${}^{\circ}G^{\mathrm{12H}}_{\mathrm{Al:N:O}} = 4\,{}^{\circ}G_{\mathrm{AlN}} + {}^{\circ}G_{\mathrm{Al_2O_3}} + 274000 - 131T$$

Spinel, $(Al^{3+})_1(Al^{3+},Va)_2(N^{3-},O^{2-})_4$

$${}^{\circ}G^{\mathrm{Spinel}}_{\mathrm{Al^{+3}:Al^{+3}:N^{-3}}} = 4\,{}^{\circ}G_{\mathrm{AlN}} + 4\,{}^{\circ}G_{\mathrm{Al_2O_3}} + 617000 - 220T$$

$${}^{\circ}G^{\mathrm{Spinel}}_{\mathrm{Al^{+3}:Va:N^{-3}}} = 4\,{}^{\circ}G_{\mathrm{AlN}} + 12\,{}^{\circ}G_{\mathrm{Al_2O_3}} + 7632.4319 - 41.8012T$$

$${}^{\circ}G^{\mathrm{Spinel}}_{\mathrm{Al^{+3}:Al^{+3}:O^{-2}}} - H^{\mathrm{SER}} = 0$$

$${}^{\circ}G^{\mathrm{Spinel}}_{\mathrm{Al^{+3}:Va:O^{-2}}} = 8{}^{\circ}G_{\gamma\text{-}\mathrm{Al_2O_3}} + 44.9543T$$

X, $(Si)_{12}(Al)_{18}(O)_{39}(N)_8$

$${}^{\circ}G^{\mathrm{X}}_{\mathrm{Si:Al:O:N}} - H^{\mathrm{SER}} = 2\,{}^{\circ}G_{\mathrm{Si_3N_4}} + 6\,{}^{\circ}G_{\mathrm{SiO_2}} + 9\,{}^{\circ}G_{\mathrm{Al_2O_3}} - 350000$$

Parameters

$298 < T < 600$ K

$${}^{\circ}G^{\mathrm{liq}}_{\mathrm{Al_2O_3}} - H^{\mathrm{SER}} = -1607850.8 + 405.559491T - 67.4804T\ln T - 0.06747T^2 + 1.4205433\cdot 10^{-5}T^3 + 938780 / T$$

$600 < T < 1500$ K

$${}^{\circ}G^{\mathrm{liq}}_{\mathrm{Al_2O_3}} - H^{\mathrm{SER}} = -1625385.57 + 712.394972T - 116.258T\ln T - 0.0072257T^2 + 2.78532\cdot 10^{-7}T^3 + 2120700 / T$$

$1500 < T < 1912$ K

$${}^{\circ}G^{\mathrm{Liq}}_{\mathrm{Al_2O_3}} - H^{\mathrm{SER}} = -1672662.69 + 1010.9932T - 156.058T\ln T + 0.00709105T^2 - 6.29402\cdot 10^{-7}T^3 + 12366650 / T$$

1912 K $< T <$ 2327 K

$${}^{\circ}G^{\mathrm{Liq}}_{\mathrm{Al_2O_3}} - H^{\mathrm{SER}} = 29178041.6 - 168360.926T + 21987.1791T\ln T - 6.99552951T^2 + 4.10226192\cdot 10^{-4}T^3 - 7.98843618\cdot 10^9 / T$$

$2327 < T < 4000$ K

$${}^{\circ}G^{\mathrm{Liq}}_{\mathrm{Al_2O_3}} - H^{\mathrm{SER}} = -1757702.05 + 1344.84833T - 192.464T\ln T$$

$298 < T < 2980$ K

$${}^{\circ}G^{\mathrm{Liq}}_{\mathrm{SiO_2}} - H^{\mathrm{SER}} = -923689.98 + 316.24766T - 52.17T\ln T - 0.012002T^2 + 6.78\cdot 10^{-7}T^3 + 665550 / T$$

$2980 < T < 4000$ K

$${}^{\circ}G^{\mathrm{Liq}}_{\mathrm{SiO_2}} - H^{\mathrm{SER}} = -957614.21 + 580.01419T - 87.428T\ln T$$

$298 < T < 700$ K

$${}^{\circ}G_{\mathrm{Al}} - H^{\mathrm{SER}} = -7976.15 + 137.071542T - 24.3671976T\ln T - 0.001884662T^2 - 8.77664\cdot 10^{-7}T^3 + 74092 / T$$

$700 < T < 933.6$ K

$${}^{\circ}G_{\mathrm{Al}} - H^{\mathrm{SER}} = -11276.24 + 223.02695T - 38.5844296T\ln T + 0.018531982T^2 - 5.764227\cdot 10^{-6}T^3 + 74092 / T$$

$933.6 < T < 6000$ K

$${}^{\circ}G_{\mathrm{Al}} - H^{\mathrm{SER}} = -11277.683 + 188.661987T - 31.748192T\ln T - 1.234264\cdot 10^{28}T^{-9}$$

$298 < T < 1687$ K

$${}^{\circ}G_{\mathrm{Si}} - H^{\mathrm{SER}} = -8162.609 + 137.227259T - 22.8317533T\ln T - 0.001912904T^2 - 3.552\cdot 10^{-9}T^3 + 176667 / T$$

1687 < T < 6000 K

$$^{o}G_{\mathrm{Si}} - H^{\mathrm{SER}} = -9457.642 + 167.271767T - 27.196T\ln T - 4.20369\cdot 10^{30}T^{-9}$$

298 < T < 600 K

$$^{o}G_{\gamma\text{-}\mathrm{Al_2O_3}} - H^{\mathrm{SER}} = -1689977.34 + 469.458181T - 70.5452T\ln T - 0.070794T^{2} + 1.491345\cdot 10^{-5}T^{3} + 981165 / T$$

600 < T < 1500 K

$$^{o}G_{\gamma\text{-}\mathrm{Al_2O_3}} - H^{\mathrm{SER}} = -1708389.72 + 791.591946T - 121.754T\ln T - 0.0075467T^{2} + 2.89573\cdot 10^{-7}T^{3} + 2222750 / T$$

1500 < T < 3000 K

$$^{o}G_{\gamma\text{-}\mathrm{Al_2O_3}} - H^{\mathrm{SER}} = -1758861.75 + 1110.41976T - 164.253T\ln T + 0.00775305T^{2} - 6.8247\cdot 10^{-7}T^{3} + 13162750 / T$$

H^{SER} represents the sum of the enthalpies of the stable forms of the elements at 298 K and 1 bar.