Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 28 (2008) 643–647

www.elsevier.com/locate/jeurceramsoc

Thermodynamics of the Al_2O_3–Al_4C_3 system
II. Free energies of mixing, solid solubilities and activities

J.-M. Lihrmann [*]

LIMHP, UPR CNRS 1311, Avenue J.-B. Clément, 93430 Villetaneuse, France

Received 27 March 2006; received in revised form 24 June 2006; accepted 30 June 2006
Available online 8 November 2007

Abstract

The phase diagram of the Al_2O_3–Al_4C_3 system is now based on unit constituents 1/5 Al_2O_3 and 1/7 Al_4C_3, and the formation of intermediate compounds 1/9 Al_4O_4C and 1/4 Al_2OC below 2100 K is addressed in terms of free energies of mixing, with corresponding partial molar quantities. Some relations are derived involving extents of solid solubilities and activities, especially at the eutectoid temperature. It is shown that the positive excess amount, relative to the stoichiometric mole fraction, of 1/7 Al_4C_3 in the oxycarbide 1/9 Al_4O_4C, highest at that temperature, can be no greater than 3.98×10^{-10}, whereas, based on a reasonable assumption, the negative amount should not exceed 6.9319488×10^{-5}. Activities $a_{1/7\text{Al}_4\text{C}_3}$ and $a_{1/5\text{Al}_2\text{O}_3}$ calculated at the eutectoid temperature show that both 1/7 Al_4C_3 and 1/5 Al_2O_3 present remarkably large positive deviations from Raoultian behaviour, as attested by their activity coefficients at infinite dilution.

Keywords: Chemical properties; Al_2O_3; Carbides; Aluminium oxycarbides; Refractories; Al_4C_3; Thermodynamic data

1. Introduction

Mixing quantities are most convenient to describe alloy properties and phase equilibria; they are used here to clarify some thermodynamic characteristics of aluminium oxycarbides 1/9 Al_4O_4C and 1/4 Al_2OC. An ideal situation, where activities $a_{1/5\text{Al}_2\text{O}_3}$ and $a_{1/7\text{Al}_4\text{C}_3}$ would be known at all temperatures and compositions throughout the phase diagram, can be arrived at if Gibbs free energies of formation of all phases are known at each temperature as functions of composition, what occurs extremely seldom; all partial molar properties of all phases could then be obtained at any temperature and composition. Such a situation can be approached when Gibbs free energies of formation of all phases are accurately known at least at some compositions, and simultaneously, solubility extents are large enough to be accurately measured; models can then be sought to describe the behaviour of the various solutions at any given temperature. In the present case, typical for most ceramic phase diagrams, solid solubilities are extremely reduced, the very reason why no indication of measurement may be found; only limiting conditions on activities and solubility extents can then be determined. This is shown here, more especially at the temperature of the eutectoid decomposition of 1/4 Al_2OC, i.e. where the solubility extent of the other intermediate compound is expectedly the largest.

2. Rationale

Appropriate thermochemical functions of part 1 of this study are used to determine free energies of mixing for both intermediate compounds 1/9 Al_4O_4C and 1/4 Al_2OC at their stoichiometric compositions; partial molar quantities can then be derived from molar quantities by use of the well known common tangent rule.[1,2]

3. Results and discussion

The 1/5 Al_2O_3–1/7 Al_4C_3 phase diagram is presented on Fig. 1 with exaggerated solubilities for both end members and each of the intermediate oxycarbides; the loci of points A through F are the solubility limits of solid solutions α through γ, as temperature varies. The temperatures of invariant reactions are listed in Table 1 according to several references. In ref. 3, the würtzite-structure Al_2OC oxycarbide is considered a stable phase of the Al_2O_3–Al_4C_3 binary system, even if the

---

[*] Tel.: +33 1 49 40 34 23; fax: +33 1 49 40 34 14.
E-mail address: lihrmann@limhp.univ-paris13.fr.

0955-2219/$ – see front matter © 2007 Published by Elsevier Ltd.
doi:10.1016/j.jeurceramsoc.2006.06.010

authors acknowledge that the surrounding nitrogen may partly contribute to its stability; in contrast, in ref.4, the formation of this compound is entirely attributed to extrinsic agents and is thus not integrated to the Al_2O_3–Al_4C_3 system, in contradiction with high temperature isothermal experiments[5,6] performed with commercial powders of Al_2O_3 and Al_4C_3 in the absence of nitrogen, and involving the formation of Al_2OC, by solid state and/or liquid state reactions, above 1983 K. The same result can also be achieved at lower temperatures in the presence of stabilizing agents, either intentionally added as, for example, würtzite AlN powder,[8] or already present in naturally occurring minerals.[9]

From the thermochemical functions of part 1, the Gibbs free energies of formation of unit constituents are readily obtained in the temperature intervals (K) 298–933, 933–1500 and 1500–2100. Table 2 illustrates that in the entire range 1000–2100 K, the most stable of them is 1/5 Al_2O_3, followed by 1/9 Al_4O_4C and 1/7 Al_4C_3; in its domain of stability, 1/4 Al_2OC ranks between 1/9 Al_4O_4C and 1/7 Al_4C_3. The uncertainties on some values express continuity requirements between adjacent temperature intervals, otherwise strictly verified.

Table 3 contains the free energies of mixing for both oxycarbides as functions of temperature, with necessary continuity requirements, as well as the molar Gibbs free energy of the eutectoid decomposition of 1/4 Al_2OC; the calculated invariant temperature is $T' = 1983.05310490$ K. It is attested that except for the case of retrograde solubility,[10] out-ruled here, the maximum solubilities occur at invariant temperatures. In the interval 1000–2100 K of interest to us, this occurs for β compound at temperature T'; points D and E then become a single point, since γ-solubility is nil at that temperature.

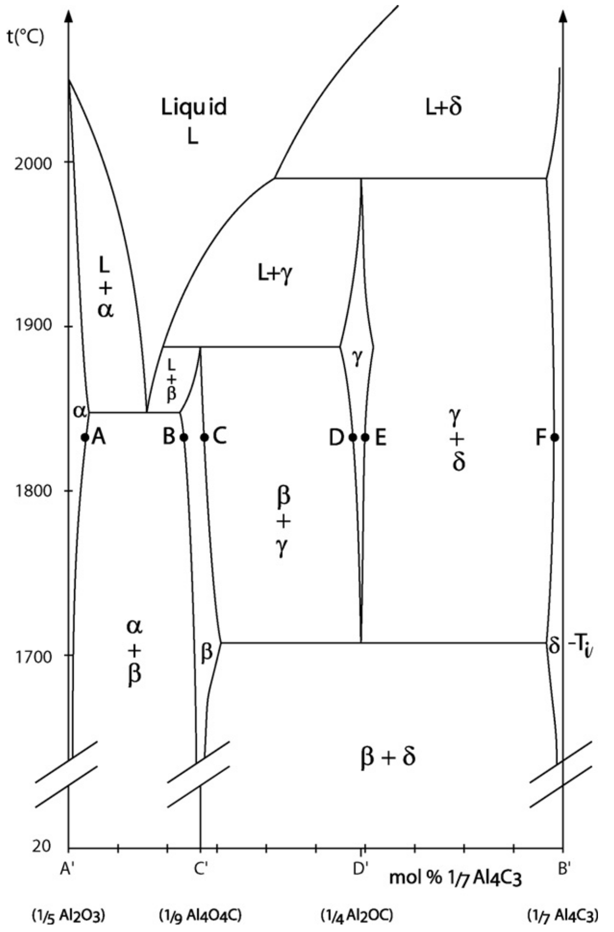

Fig. 1. 1/5 Al_2O_3–1/7 Al_4C_3 phase diagram with exaggerated solid solubilities.

Table 1
Temperatures (°C) of invariant reactions in the Al_2O_3–Al_4C_3 system, and compositions of equilibrium liquid phase, in mole fraction 1/7 Al_4C_3 (resp. Al_4C_3)

Eutectic	Al_4O_4C peritectic	Al_2OC peritectic	Al_2OC eutectoid	Reference
1840	1890	2000	–	3
0.135 (0.10)	0.20 (0.15)	0.43 (0.35)	–	
1905	1940	–	–	4
1850	1870	1990	1710	7
0.16 (0.12)	0.235 (0.180)	0.32 (0.28)		
1850	1890	1990	1710	Present
0.150 (0.113)	0.180 (0.135)	0.41 (0.33)		

Table 2
Gibbs free energies (J mol^{-1}) of formation of unit constituents

	298 K	933 K	1500 K
1/5 Al_2O_3	−316,492.986264	−276,745.297878	$-239{,}298.421614 \pm 3.02 \times 10^{-4}$
1/9 Al_4O_4C	−243,269.7845	−212,508.563091	$-182{,}658.532448 \pm 1.39 \times 10^{-4}$
1/4 Al_2OC	Unstable	Unstable	Unstable
1/7 Al_4C_3	−29,137.07375	$-24{,}217.89451435 \pm 5 \times 10^{-8}$	−16,073.1370984

	$T_1 = 1983.0531050$ K	2100 K
1/5 Al_2O_3	−207,862.332118	−200,311.591776
1/9 Al_4O_4C	−157,580.8843	−151,561.340238
1/4 Al_2OC	−92,647.8265882	−89,043.875595
1/7 Al_4C_3	−9,162.46667171	−7,517.76936886

Table 3
Free energies of reactions (i) through (iii) as functions of temperature, in S.I. units

Reaction	Temperature	$\Delta_r G^\circ$
$7/27\,(1/7\,Al_4C_3) + 20/27\,(1/5\,Al_2O_3) = 1/9\,Al_4O_4C$ (i)	$1000 \le T < 1500$	$\Delta G_m^{(i)} = -1\,233.3332963 + 17/27 \times 10^{-6}T + 1/27 \times 10^{-6}T \ln T - 3.1/9 \times 10^{-12}\,T^3 + 1/27 \times 10^{-3}/T$
	$1500 < T \le 2100$	$\Delta G_m^{(i)} = -1\,233.33325926 + 16/27 \times 10^{-6}T - 1/27 \times 10^{-13}T^3 + 2/27 \times 10^{-2}/T$
	$T = 1500\,K$	$\Delta G_m^{(i)} = -1\,233.33274521 \pm 3.6283 \times 10^{-4}$
$7/12\,(1/7\,Al_4C_3) + 5/12\,(1/5\,Al_2O_3) = 1/4\,Al_2OC$ (ii)	$T' \le T \le 2100$	$\Delta G_m^{(ii)} = -3\,512.49998333 + 43.5592003333T - 5.55T \ln T - 1/12 \times 10^{-13}T^3 + 1/6 \times 10^{-3}/T$
$1/4\,Al_2OC = 9/16\,(1/9\,Al_4O_4C) + 7/16\,(1/7\,Al_4C_3)$ (iii)	$T' \le T \le 2100$	$\Delta_r G^{(iii)} = 2\,818.750025 - 43.5592 \times 10^{-3}T + 5.55T \ln T + 1/16 \times 10^{-13}T^3 + 1/4 \times 10^{-3}/T$

Fig. 2, representing integral molar free energies of mixing of solid solutions α, β, γ, δ as functions of composition at any given temperature between T' and 2100 K, illustrates the common tangent rule for the three two-phase equilibrium systems occurring at such a temperature; this graphical construction is expressed into equations in the Appendix A.

For the $(\beta+\gamma)$ equilibrium system, defined by Eq. (1a) through (6a), $X_1 = \ln a_{1/7Al_4C_3}$ and $X_2 = \ln a_{1/5Al_2O_3}$, as given by Eqs. (7a) and (8a), are functions of the solid solubility range δ_C. At temperature T', in order to have $X_1 < 0$, it is requested that δ_C verify the condition

$$\delta_C < 3.98 \times 10^{-10} \tag{1}$$

It then appears from Table 4, which illustrates the dependence of X_1, X_2 and corresponding activities, on δ_C, that in this system at this temperature, the activities $a_1 = a_{1/7Al_4C_3}$ and $a_2 = a_{1/5Al_2O_3}$, are such that, using[11] $R = 8.314471\,J\,mol^{-1}\,K^{-1}$,

$$0.99999999999 \ge a_{1/7Al_4C_3} \ge 0.99999999997 \tag{2}$$

$$0.90394912039 \ge a_{1/5Al_2O_3} \ge 0.90394912036 \tag{3}$$

Furthermore, since at temperature T' the tangents S_2 and S_3 on Fig. 2A are rigorously equal, it follows that in the $(\beta+\gamma+\delta)$ equilibrium system, $X_1 = \ln(1-\delta_F) \cong -\delta_F$, whence a condition on δ_F at this temperature:

$$5 \times 10^{-14} (\equiv 0) < \delta_F < 2.6 \times 10^{-11} \tag{4}$$

If δ_F is nearly constant between the invariant plateaux of temperatures 1983 and 2263 K, the following condition applies on X_2 and δ_E in this temperature interval in addition to Eq. (9a):

$$\left(\frac{5}{12} - \frac{\delta_E}{2}\right) X_2 < \frac{\Delta G_m^{(ii)}}{RT} + \frac{7}{12} \times 1.08 \times 10^{-10} \tag{5}$$

More importantly, Eq. (10a) through (14a) describe the $(\alpha+\beta)$ equilibrium at a given temperature T. Solutions at the eutectoid temperature are listed in Table 5 for different values of δ_A; since no limiting condition exists on δ_A or δ_B it is deliberately assumed that δ_A should not exceed 10^{-5}. From Tables 4 and 5, activity coefficients at infinite dilution may be calculated, reaching $\gamma^\infty_{1/7Al_4C_3} >$

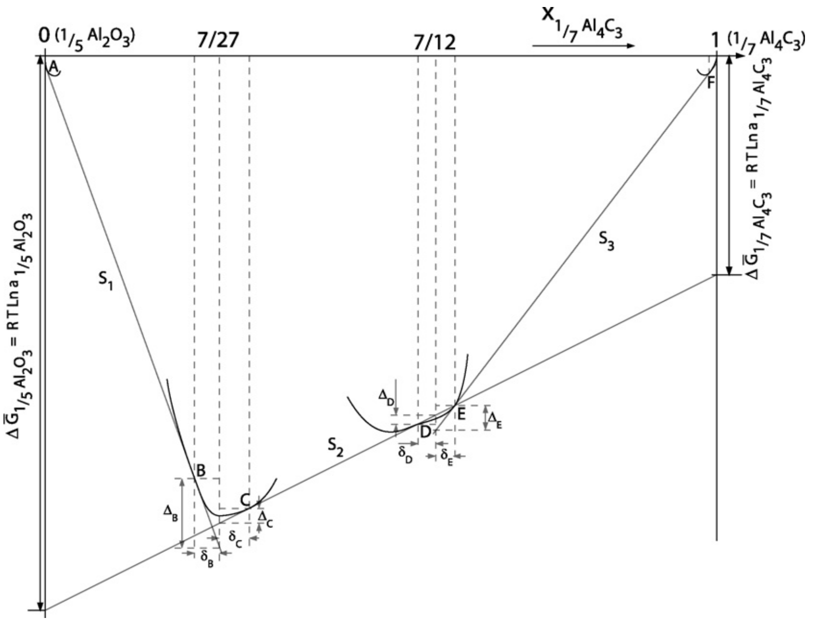

Fig. 2. Free energies of mixing of solutions α, β, γ and δ at the vicinity of $x_{1/7\,Al_4C_3} = \{0;7/27;7/12;1\}$; common tangent rule and vertical intercepts for the $(\alpha+\beta)$, $(\beta+\gamma)$ and $(\gamma+\delta)$ equilibrium systems between T' and 2100 K.

Table 4
X_1, X_2 and activities as functions of solubility extent δ_C (mole fraction) at temperature T'

δ_C	X_1	$a_1 = a_{1/7\,Al_4C_3}$	X_2	$a_2 = a_{1/5\,Al_2O_3}$
3.97×10^{-10}	-5×10^{-14} ($\equiv 0$)	0.99999999999	−0.10098220296	0.90394912036
2.00×10^{-10}	-1.3×10^{-12}	0.99999999998	−0.10098220294	0.90394912037
→ 0	$\rightarrow -2.6 \times 10^{-12}$	→ 0.99999999997	→ −0.10098220292	→ 0.90394912039

Table 5
X_1, X_2 and activities as functions of solubility extent δ_A (mole fraction) at temperature T'

δ_A	δ_B	X_1	$a_1 = a_{1/7\,Al_4C_3}$	X_2	$a_2 = a_{1/5\,Al_2O_3}$
10^{-5}	6.9319488×10^{-5}	−0.28853057985	0.74936388935	-1.000005×10^{-5}	0.99999
10^{-8}	6.9319×10^{-8}	−0.28852058981	0.74937137557	-1.0000×10^{-8}	0.99999999
10^{-10}	6.90×10^{-10}	−0.28852057991	0.74937138298	-1.00×10^{-10}	0.9999999999
→ 0	→ 0	→ −0.28852057981	→ 0.74937138306	→ 0	0.999999999. . .999

74936 and $35000814941.1 < \gamma^{\infty}_{1/5Al_2O_3} < 166119628290 \times 10^2$ and therefore showing important (1/7 Al_4C_3) and extremely large (1/5 Al_2O_3) positive deviations from Raoultian behaviour.

4. Conclusion

It is shown that, in the temperature interval 1000–2100 K, the positive excess amount of 1/7 Al_4C_3 in the oxycarbide 1/9 Al_4O_4C, relative to the stoichiometric molar fraction value, can be no greater than 3.98×10^{-10}, value determined at the eutectoid temperature. No such condition exists for the negative excess amount; however if we reasonably assume that the solubility of 1/7 Al_4C_3 in 1/5 Al_2O_3 should not exceed 10^{-5}, we have shown that this amount should be smaller than 6.9319488×10^{-5}. In terms of activities, both 1/7 Al_4C_3 and 1/5 Al_2O_3 present remarkably large positive deviations from Raoultian behaviour, as attested by their activity coefficients at infinite dilutions. Other limiting conditions on solubilities or activities are established.

Acknowledgements

Numerous previous or present colleagues are acknowledged for their interest in aluminium oxycarbides, including: B. de la Morinerie, European Patent Office, Den Haag (the Netherlands); Mrs R. Monteiro, University of Aveiro, Portugal; Mrs S. Boskovic and Mrs E. Kostic, B. Kidric Inst. of Nuclear Sciences, Belgrade (Serbia); J.S. Haggerty, Ceramics Processing Res. Laboratory, MIT, Cambridge, MA (USA); R. Pampuch, Inst. of Mining and Metallurgy, Cracow (Poland); C. Pommier and C. Petot, Université Paris-Nord, Villetaneuse (France); H. Schubert, Powder Metal. Laboratory, MPI, Stuttgart (Germany); Mrs A. Schneider and R. Schober, Fraunhofer Inst. of Ceramic Technol. and Sintered Materials, Dresden (Germany); Mrs R. Fischer and A. Goldstein, Israël Ceramic and Silicate Inst., Haïfa (Israël); V. Rosen-band and Y. Goldman, Combustion and Propulsion Laboratory, Technion, Haïfa.

Appendix A

Let us briefly remind that it follows from the phase rule that the chemical potential, μ_i, of component i be equal in all phases of an equilibrium system; the same becomes true for the activity a_i, and for the partial molar quantity $\Delta\overline{G}_i = RT \ln a_i$, of this component, when its chemical potential in all phases of the equilibrium system is referred to a common reference state (in the present case the pure solid state under unit pressure at the temperature of interest), whence the common tangents shown on Fig. 2A.

End-solutions α and δ obey Raoult's and Henry's laws, so that ΔG_m writes

$$\Delta G_m = RT[\times \ln(\gamma^{\infty} x) + (1-x)\ln(1-x)],$$

$$\text{with tangent} \frac{d\Delta G_m}{dx}(<0) = RT \ln \frac{\gamma^{\infty} x}{1-x};$$

x is the mole fraction of the solute and γ^{∞}, its activity coefficient, independent of composition; the product ($\gamma^{\infty} x$) represents the activity of the solute whereas $(1-x)$ is both the mole fraction and the activity of the solvent. For intermediate compounds β and γ, ΔG_m are unknown functions of composition; it is assumed that both compounds extend on each side of the stoichiometric values.

As shown on Fig. 2A, equilibrium between β and γ requires an inflexion point at D and leads to the following equations, with unknowns $X_1 = \ln a_{1/7Al_4C_3}$, $X_2 = \ln a_{1/5Al_2O_3}$, δ_C, Δ_C, δ_D, Δ_D (all four positive):

$$RT\,[(7/27 + \delta_C)\,X_1 + (20/27\; - \delta_C)X_2] = \Delta G_m^{(i)} + \Delta_C/2 \tag{1a}$$

$$RT[(7/12 - \delta_D)X_1 + (5/12 + \delta_D)X_2] = \Delta G_m^{(ii)} - \Delta_D/2 \tag{2a}$$

$$\frac{\Delta_C}{\delta_C} = \frac{\Delta_D}{\delta_D} \tag{3a}$$

$$\frac{\Delta_{\mathrm{C}}}{\delta_{\mathrm{C}}} = \frac{-\Delta G_{\mathrm{m}}^{(\mathrm{i})} + \Delta G_{\mathrm{m}}^{(\mathrm{ii})} + (\Delta_{\mathrm{C}} - \Delta_{\mathrm{D}})/2}{35/108 - \delta_{\mathrm{D}}} \tag{4a}$$

$$\frac{\Delta_{\mathrm{C}}}{\delta_{\mathrm{C}}} = \frac{-\Delta G_{\mathrm{m}}^{(\mathrm{i})} + \Delta G_{\mathrm{m}}^{(\mathrm{ii})} + (\Delta_{\mathrm{C}} + \Delta_{\mathrm{D}})/2}{35/108} \tag{5a}$$

$$\frac{\Delta_{\mathrm{C}}}{\delta_{\mathrm{C}}} = \frac{-\Delta G_{\mathrm{m}}^{(\mathrm{i})} + \Delta G_{\mathrm{m}}^{(\mathrm{ii})} - (\Delta_{\mathrm{C}} - \Delta_{\mathrm{D}})/2}{35/108 - \delta_{\mathrm{C}}} \tag{6a}$$

[It has to be realized that if $a_{1/7\mathrm{Al_4C_3}}$ and $a_{1/5\mathrm{Al_2O_3}}$ are indeed constant over the entire [CD] segment, the intercepts of the common tangent with vertical axes being respectively $\Delta\overline{G}_{1/5\mathrm{Al_2O_3}} = RT \ln a_{1/5\mathrm{Al_2O_3}}$ and $\Delta\overline{G}_{1/7\mathrm{Al_4C_3}} = RT \ln a_{1/7\mathrm{Al_4C_3}}$, they are however different from their values at the stoichiometric compositions, $x_{1/7\mathrm{Al_4C_3}} = 7/27$ and $x_{1/7\mathrm{Al_4C_3}} = 7/12$].

At the particular temperature T', corresponding to the highest value of δ_{C}, nil solubility of γ compound requests $\delta_{\mathrm{D}} = 0$. Thus (4a) becomes

$$\frac{\Delta_{\mathrm{C}}}{\delta_{\mathrm{C}}} = \frac{-\Delta G_{\mathrm{m}}^{(\mathrm{i})} + \Delta G_{\mathrm{m}}^{(\mathrm{ii})} + (\Delta_{\mathrm{C}} - \Delta_{\mathrm{D}})/2}{35/108} \tag{4$'$a}$$

(4′a) and (5a) yield $\Delta_{\mathrm{D}} = 0$, whence

$$RT' \, [7/12\, X_1 + 5/12\, X_2] = \Delta G_{\mathrm{m}}^{(\mathrm{ii})} \tag{2$'$a}$$

Eqs. (5a), (6a) and (1a) straightforwardly lead to

$$RT'[(7/27 + \delta_{\mathrm{C}})X_1 + (20/27 - \delta_{\mathrm{C}})X_2] = \frac{\Delta G_{\mathrm{m}}^{(\mathrm{i})} + (108/35)\delta_{\mathrm{C}}(\Delta G_{\mathrm{m}}^{(\mathrm{ii})}/2 - \Delta G_{\mathrm{m}}^{(\mathrm{i})})}{(1 - 54/35)\delta_{\mathrm{C}}} \tag{1$'$a}$$

Solutions of (1′a), (2′a) system at temperature T' are

$$X_1(\delta_{\mathrm{C}}) = \frac{(5/12\, \Delta G_{\mathrm{m}}^{(\mathrm{i})} - 20/27\, \Delta G_{\mathrm{m}}^{(\mathrm{ii})}) + \delta_{\mathrm{C}}(39/14\, \Delta G_{\mathrm{m}}^{(\mathrm{ii})} - 9/7\, \Delta G_{\mathrm{m}}^{(\mathrm{i})})}{RT'(1 - 54/35\, \delta_{\mathrm{C}})(-35/108 + \delta_{\mathrm{C}})} \tag{7a}$$

$$X_2(\delta_{\mathrm{C}}) = \frac{(7/27\, \Delta G_{\mathrm{m}}^{(\mathrm{ii})} - 7/12\, \Delta G_{\mathrm{m}}^{(\mathrm{i})}) + \delta_{\mathrm{C}}(9/5\, \Delta G_{\mathrm{m}}^{(\mathrm{i})} - 3/10\, \Delta G_{\mathrm{m}}^{(\mathrm{ii})})}{RT'(1 - 54/35\, \delta_{\mathrm{C}})(-35/108 + \delta_{\mathrm{C}})} \tag{8a}$$

Similarly, at any given temperature in the interval [T', 2100 K], activities $a_{1/7\mathrm{Al_4C_3}}$ and $a_{1/5\mathrm{Al_2O_3}}$ in the $(\gamma + \delta)$ equilibrium system verify the following equation:

$$RT[(7/12 + \delta_{\mathrm{E}}/2)\, X_1 + (5/12 - \delta_{\mathrm{E}}/2)\, X_2] = \Delta G_{\mathrm{m}}^{(\mathrm{ii})} \tag{9a}$$

The equations describing the $(\alpha + \beta)$ system at some equilibrium temperature are as follows:

$$RT(\delta_{\mathrm{A}}\, X_1 + (1 - \delta_{\mathrm{A}})\, X_2) = \Delta G_{\mathrm{m},\alpha} \tag{10a}$$

$$X_2 = \ln(1 - \delta_{\mathrm{A}}) \tag{11a}$$

$$RT[(7/27 - \delta_{\mathrm{B}}/2)X_1 + (20/27 + \delta_{\mathrm{B}}/2)X_2] = \Delta G_{\mathrm{m}}^{(\mathrm{i})} \tag{12a}$$

$$\frac{\Delta_{\mathrm{B}}}{\delta_{\mathrm{B}}} = RT(X_2 - X_1) \tag{13a}$$

$$\frac{\Delta_{\mathrm{B}}}{\delta_{\mathrm{B}}} = \frac{\Delta G_{\mathrm{m},\alpha} - \Delta G_{\mathrm{m}}^{(\mathrm{i})}}{7/27 - (\delta_{\mathrm{A}} + \delta_{\mathrm{B}}/2)} \tag{14a}$$

They can be easily solved as a function of δ_{A}, starting for example with the approximate relation $\Delta_{\mathrm{B}}/\delta_{\mathrm{B}} \cong -\Delta G_{\mathrm{m}}^{(\mathrm{i})}/(7/27)$ and using (13a) to get $(X_1)_{\mathrm{approx}}$; (12a) and (13a) combining into

$$\Delta_{\mathrm{B}} = 2[\Delta G_{\mathrm{m}}^{(\mathrm{i})} - RT(7/27\, X_1 + 20/27\, X_2)] \tag{15a}$$

lead to $(\Delta_{\mathrm{B}})_{\mathrm{approx}}$, whence $(\delta_{\mathrm{B}})_{\mathrm{approx}}$ from (13a) and $(\Delta G_{\mathrm{m},\alpha})_{\mathrm{approx}}$ from (10a). Extremely few iterations initiated with the improved value of $\Delta_{\mathrm{B}}/\delta_{\mathrm{B}}$ (14a) bring the final solution, for any given starting value of δ_{A}. In contrast with the three phase equilibrium, the condition for the (X_1, X_2) solution to be acceptable, namely $\delta_{\mathrm{A}}/(7/27 - \delta_{\mathrm{B}}/2) < (-\Delta G_{\mathrm{m},\alpha}/ - \Delta G_{\mathrm{m}}^{(\mathrm{i})})$, is much less severe and is always verified.

References

1. Gibbs, J. W., On the equilibrium of heterogeneous substances. *Trans. Connecticut. Acad.*, 1877, **108–248**, 343–524.
2. Roozeboom, H. W. B., *Die heterogenen Gleichgewichte vom Standpunkte der Phasenlehre*. F. Vieweg und Sohn, Braunschweig, 1904.
3. Foster, L. M., Long, G. and Hunter, M. S., Reactions between aluminium oxide and carbon. The $\mathrm{Al_2O_3}$–$\mathrm{Al_4C_3}$ phase diagram. *J. Am. Ceram. Soc.*, 1966, **39**(1), 1–11.
4. Motzfeldt, K. and Sandberg, B., Carbothermal reduction of aluminium oxide. In *Light Metals*, ed. S. Peterson. TMS-AIME, Warrendale, PA, 1979, pp. 411–428.
5. Lihrmann, J.-M., Nouvelles céramiques dans le système C-Al-O-N; étude de la résistance à l'usure. D. thesis, Université Louis Pasteur, Strasbourg (Fr), 1982.
6. Lihrmann, J.-M., Importance of the liquid phase for the processing of structural ceramics in the SiCAlON system. In *Structural ceramics: processing, microstructure and properties*, ed. J. J. Bentzen *et al.* Riso Natl Laboratory, Roskilde (Denmark), 1990, pp. 395–402.
7. Qiu, C. and Metselaar, R., Thermodynamic evaluation of the $\mathrm{Al_2O_3}$–$\mathrm{Al_4C_3}$ system and stability of Al-oxycarbides. *Z. Metallk.*, 1995, **86**, 198–205.
8. Lihrmann, J. M., Zambetakis, T. and Daire, M., High temperature behavior of the aluminum oxycarbide $\mathrm{Al_2OC}$ in the system $\mathrm{Al_2O_3}$–$\mathrm{Al_4C_3}$ and with additions of aluminum nitride. *J. Am. Ceram. Soc.*, 1989, **72**(9), 1704–1709.
9. Goldin, B. A., Ryabkov, Yu., Istomin, P. V. and Grass, V. E., *High temperature chemical reduction of natural oxide minerals*. Russian Academy of Sciences, Ekaterinburg, 2001.
10. Prince, A., *Alloy phase equilibria*. Elsevier, Amsterdam, 1966.
11. Moldover, M. R., Trustler, J. P. M., Edwards, T. J., Mehl, J. B. and Davis, R. S., Measurement of the universal gas constant R using a spherical acoustic resonator. *NIST Selected Abstracts (Metrology)*, 2005.