Liquid Immiscibility and Thermodynamic Assessment of the Al_2O_3 – TiO_2 – SiO_2 System

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Abstract Phase equilibria in the TiO_2 – SiO_2 system have been studied experimentally using DTA and SEM/EDX. The thermodynamic parameters for the TiO_2 – SiO_2 system have been assessed considering new experimental data of the present work and from the literature. Moreover, the miscibility of the liquid in the Al_2O_3 – TiO_2 – SiO_2 system has been studied at 2013 K in air and shrinkage of the miscibility gap at 3.8 mol% Al_2O_3 has been demonstrated. The experimental data obtained in the present work and literature as well as the thermodynamic databases for the binary Al_2O_3 – TiO_2 , TiO_2 – SiO_2 , and Al_2O_3 – SiO_2 systems have been used to derive the thermodynamic description of the Al_2O_3 – TiO_2 – SiO_2 system using the CALPHAD approach. Solid phases have been modeled using the compound energy formalism. The liquid phase has been described by the two-sublattice partially ionic liquid model. A set of self-consistent parameters have been proposed, which resulted in a reasonably good agreement between the calculated and experimental data on the phase equilibria, liquid immiscibility, and thermodynamic properties in the Al_2O_3 – TiO_2 – SiO_2 system.

Keywords Ternary system · Al_2O_3 – TiO_2 – SiO_2 · Spinel · Pseudobrookite · CALPHAD · Thermodynamic assessment

1 Introduction

Alumina-based materials are widely used as refractory and filter materials in metal production. Research and development of ceramic filter materials for metal melt filtration need availability of thermodynamic databases to model the interactions of a liquid metal alloy containing oxide inclusions with a filter that can be coated with various ceramic coatings. Moreover, possible interactions of ceramic filters with coatings can be modeled to improve efficiency of the complex ceramic filter system. In practice, Al_2O_3 -based filter systems are currently being developed for aluminum-based melt filtration.^[1,2] Oxide films and Al_2O_3 particles formed during melting and alloying can be present as a suspension on the surface of the melt or inside the melt because of flow turbulence. Spinel inclusions appear due to the presence of magnesium ions in the aluminum melt, mainly coming from the refractories of the furnace. Magnesium entering the molten aluminum also leads to the formation of non-metallic inclusions other than spinel. TiO_2 coating deposited on corundum is supposed to filter actively spinel MgAl_2O_4 from Al-based molten alloy. The reduction of TiO_2 can then lead to the formation of Al_3Ti or $(\text{Al},\text{Si})_3\text{Ti}$.^[3] Therefore, to model Al melt filtration process, one should consider the Al–Mg–Ti–Si–O system. As a part of the mentioned complex system, the Al_2O_3 – TiO_2 – SiO_2 sub-system was recently investigated experimentally.^[4] Being a continuation of the study of the oxide system, the aim of the present work is a critical evaluation of available data on phase relations as well as thermodynamic modeling of the ternary system and assessment of thermodynamic parameters in the Al_2O_3 – TiO_2 – SiO_2 system to derive a self-consistent thermodynamic database using the CALPHAD approach by applying the Thermo-Calc software.^[5]

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2 Literature Review

2.1 Binary Al_2O_3 – TiO_2 System

The Al_2O_3 – TiO_2 system is characterized by the formation of an intermediate compound Al_2TiO_5 , also known as tialite, which has a pseudobrookite-type Fe_2TiO_5 structure with the lattice parameters of $a = 0.3605$, $b = 0.9445$, and $c = 0.9653$ nm.^[6] According to the authors own experimental data,^[7] the Al_2TiO_5 phase forms by the peritectic reaction $\text{L} + \text{Al}_2\text{O}_3 \leftrightarrow \text{Al}_2\text{TiO}_5$ at 2112 K and decomposes into Al_2O_3 and TiO_2 at temperature of 1552 K, and also participates in a eutectic reaction $\text{L} \leftrightarrow \text{TiO}_2 + \text{Al}_2\text{TiO}_5$ at 1999 K and 14.9 mol% of alumina. Al_2TiO_5 is nearly stoichiometric compound with a negligible homogeneity range. The mutual solubility of Al_2O_3 and TiO_2 is negligible too. A recent thermodynamic assessment of the Al_2O_3 – TiO_2 system^[8] was accepted in the present work. The calculated phase diagram agrees well with the experimental data.^[7] Considering the disordering of Al^{+3} and Ti^{+4} cations between the octahedral sites M1 and M2, the Al_2TiO_5 phase was modeled using the model $(\text{Al}^{+3}, \text{Ti}^{+4})_1 \text{M1} (\text{Al}^{+3}, \text{Ti}^{+4})_2 \text{M2} (\text{O}^{-2})_5$.

2.2 Binary Al_2O_3 – SiO_2 System

Mullite $\text{Al}_6\text{Si}_2\text{O}_{13}$ is the only stable crystalline phase in the Al_2O_3 – SiO_2 system at atmospheric pressure. The character of mullite melting as congruent or peritectic is under discussion in the literature. However, the data from Fabrichnaya et al.^[9] showing the peritectic reaction $\text{L} + \text{Al}_2\text{O}_3 \leftrightarrow \text{Al}_6\text{Si}_2\text{O}_{13}$ at 2166 K and a eutectic reaction $\text{L} + \text{SiO}_2 \leftrightarrow \text{Al}_6\text{Si}_2\text{O}_{13}$ at 1855 K and 97.64 mol% of SiO_2 were accepted in this work. The compound $\text{Al}_6\text{Si}_2\text{O}_{13}$ has a mullite-type structure with $a = 0.7452$, $b = 0.7581$, and $c = 0.2851$ nm.^[10] The solid solution homogeneity range of mullite bends towards higher Al_2O_3 contents with temperature increase. The mutual solubility of Al_2O_3 and SiO_2 is negligible. The thermodynamic assessment of the Al_2O_3 – SiO_2 system presented by Dumitrescu and Sundman^[11] was accepted in the present work after verification by Fabrichnaya et al.^[9]

2.3 Binary TiO_2 – SiO_2 System

First studies^[12–14] were carried out in a reducing atmosphere, which caused the formation of Ti_2O_3 and Ti_3O_5 in addition to TiO_2 . Nevertheless, Umezu and Kakiuchi^[12] detected the formation of immiscible liquids in melts (35.7–75.1 mol% TiO_2 at 1853 K) and determined a eutectic reaction at 15.0 mol% TiO_2 and 1773 K. In air, Bunting^[15] observed the eutectic at 8.0 mol% TiO_2 and

1813 K and did not report liquid immiscibility since the study was limited to 15.8 mol% TiO_2 . Rickers and Hummel^[16] reported a solid solution of $(\text{SiO}_2 + \text{TiO}_2)$ and relocated the eutectic to 17.0 mol% TiO_2 and 1813 K. Agamawi and White^[17] confirmed the eutectic at 8.0 mol% TiO_2 ^[15] but at 1843 K. Later, DeVries et al.^[18] specified the eutectic point (8.1 mol% TiO_2 and 1823 ± 4 K) previously determined by Bunting,^[15] and also confirmed the presence of stable immiscibility in the liquid phase extending from 15.0 to 90.8 mol% TiO_2 at 2053 K. McTaggart and Andrews^[19] reported the presence of two liquids existing between 15.9 and 92.2 mol% TiO_2 above 2038 K. The presence of the two-liquid region was subsequently confirmed,^[20,21] but without experimental details. Kirschen et al.^[22] and Kirillova et al.^[23] carried out the high temperature investigations (up to 2533 K), however contradictory data on the boundaries of the miscibility gap were reported. Despite a number of studies of the phase equilibria in the TiO_2 – SiO_2 system, it was concluded that there are still several inconsistencies in the description of this system, and a new experimental study is necessary.

Taking into account the miscibility gap data, the TiO_2 – SiO_2 system was first assessed by Kaufman^[24] using the CALPHAD method. Next thermodynamic assessments were performed by DeCapitani and Kirschen^[25] and Kirschen et al.^[22] using the Margules-type excess polynomial model and assuming the interaction parameters to be either temperature independent or dependent. An optimized phase diagram using a sub-regular solution model was recently proposed.^[23] Based on their own experimental data, the critical point of the miscibility gap (2416 K at 58.9 mol% TiO_2) was calculated as the lowest in comparison with other calculations.^[22,24,25] Since these assessments are incompatible with the ionic two-sublattice liquid model, a new thermodynamic description of the system needs to be developed. Using all up-to-date experimental data, the TiO_2 – SiO_2 system was newly assessed by Boulay et al.^[26] using the partially ionic model to describe the liquid phase. However, the Ti^{+4} cations introduced on the first sublattice were only considered in^[26] rather than the mixing of Ti^{+2} and Ti^{+3} on the cationic sublattice and Ti^{+4} as a neutral TiO_2 species on the anionic sublattice as accepted in the present work regarding the Ti–O system.^[7,27] Therefore, their assessment^[26] is not accepted in the present work.

2.4 Ternary Al_2O_3 – TiO_2 – SiO_2 System

A literature review and an extensive experimental study of solid–liquid phase equilibria in the Al_2O_3 – TiO_2 – SiO_2 system in air were carried out by the present authors.^[4] The phase equilibria in the Al_2O_3 – TiO_2 – SiO_2 system were investigated in the temperature range from 1486 K to melting by energy-dispersive X-ray spectroscopy (EDX)

and X-ray diffraction (XRD) to confirm phase assemblages in the annealed samples. The solid-state invariant reaction $\text{SiO}_2 + \text{Al}_2\text{TiO}_5 \leftrightarrow \text{Al}_6\text{Si}_2\text{O}_{13} + \text{TiO}_2$ was found at 1743 K. On the liquidus projection, three invariant reactions were observed: eutectic $\text{L} \leftrightarrow \text{TiO}_2 + \text{SiO}_2 + \text{Al}_2\text{TiO}_5$ at 1750 K and transitional type reactions $\text{L} + \text{Al}_6\text{Si}_2\text{O}_{13} \leftrightarrow \text{SiO}_2 + \text{Al}_2\text{TiO}_5$ at 1779 K and $\text{L} + \text{Al}_2\text{O}_3 \leftrightarrow \text{Al}_6\text{Si}_2\text{O}_{13} + \text{Al}_2\text{TiO}_5$ at 2007 K. No ternary phases were observed in the system.^[4] Data on the crystal structures of all solid phases in the Al_2O_3 – TiO_2 – SiO_2 system are given in Table 1. Experimental investigation of the miscibility gap extending into the ternary system from the TiO_2 – SiO_2 side was carried out by Kirschen et al.^[22] A substantial contraction of the miscibility gap was found at an Al_2O_3 content of 4.0 mol% at 2073 K and a single-phase liquid at 10 mol% above 1970 K.

The thermodynamic description of the Al_2O_3 – TiO_2 – SiO_2 system was first undertaken by Kaufman^[24] using the CALPHAD approach. The calculated isothermal sections in the temperature range of 1000–2800 K indicated extended miscibility gap in the liquid (up to about 25% Al_2O_3). Kaufman also indicated the tie-lines change at low temperatures resulting in a reaction at 1707 K: $\text{Al}_6\text{Si}_2\text{O}_{13} + \text{TiO}_2 \leftrightarrow \text{SiO}_2 + \text{Al}_2\text{TiO}_5$. Wherein, three-phase equilibria ($\text{SiO}_2 + \text{TiO}_2 + \text{Al}_6\text{Si}_2\text{O}_{13}$) and ($\text{Al}_6\text{Si}_2\text{O}_{13} + \text{TiO}_2 + \text{Al}_2\text{TiO}_5$) are stable above 1707 K, and ($\text{SiO}_2 + \text{Al}_6\text{Si}_2\text{O}_{13} + \text{Al}_2\text{TiO}_5$) and ($\text{SiO}_2 + \text{Al}_2\text{TiO}_5 + \text{TiO}_2$) are stable below this temperature. However, these data contradict the experimental ones^[4,33] at which the opposite stable equilibria were found above and below the reaction temperature. The liquidus projection of the Al_2O_3 – TiO_2 – SiO_2 system was also calculated^[22] with emphasis on the immiscibility in the liquid using the thermodynamic description derived on the basis of their own experimental data.

Germany). Three samples of the Al_2O_3 – TiO_2 – SiO_2 system were prepared by co-hydrolysis followed by thermal decomposition of aqueous solutions.^[33] The initial solutions were aluminium tri-sec-butoxide $\text{C}_{12}\text{H}_{27}\text{AlO}_3$ ($M = 246.32 \text{ g mol}^{-1}$, $\rho = 0.967 \text{ g cm}^{-3}$, 97%), titanium(IV) isopropoxide $\text{C}_{12}\text{H}_{28}\text{TiO}_4$ ($M = 284.23 \text{ g mol}^{-1}$, $\rho = 0.955 \text{ g cm}^{-3}$, 97%), and tetraethoxysilane $\text{C}_8\text{H}_{20}\text{SiO}_4$ ($M = 208.33 \text{ g mol}^{-1}$, $\rho = 0.934 \text{ g cm}^{-3}$, 98%) produced by Alfa Aesar, Germany. Details of the sample preparation routine can be found elsewhere.^[4,33] The samples were heat treated at targeted temperatures in a muffle furnace (NABERTHERM, Germany) in order to achieve a pseudo-equilibrium state of the samples followed by furnace-cooling, and then examined.

X-ray diffraction study was carried out using an URD63 X-ray diffractometer (Seifert, FPM, Freiberg, Germany) with $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). ICSD (Inorganic Crystal Structure Database, 2017, Karlsruhe, Germany)^[34] was used for interpretation of the powder diffraction patterns. Qualitative and quantitative analyses of the XRD patterns were performed by Rietveld analysis using MAUD software.^[35,36] Microstructure examination was done using LEO 1530 Gemini (Zeiss, Germany) equipped with an EDX detector (Bruker AXS Mikroanalysis GmbH, Germany). DTA measurements were performed on (i) TG-DTA SETSYS Evolution-1750 (SETARAM Instrumentation, France) in air using B-type tri-couple DTA rod (Pt/PtRh10% thermocouple) and open Pt crucibles and (ii) TG-DTA SETSYS Evolution-2400 (SETARAM Instrumentation, France) using tungsten DTA rod and open W crucibles and employing a permanent inert He flow. The heating and cooling curves were recorded at the rates of 10 and 30 K min^{-1} , respectively. Temperature calibration of SETSYS Evolution-2400 was done using melting points of Al, Al_2O_3 , and temperature of solid-state transformation in LaYO_3 ^[37]

3 Experimental Part

Two samples of the TiO_2 – SiO_2 system were prepared by solid-state reaction from high-purity oxide powders (TiO_2 99.990% and SiO_2 99.995%, ~ 40 mesh, Alfa Aesar,

Table 1 Data on the crystal structures of the solid phases of the Al_2O_3 – TiO_2 – SiO_2 system

Phase	Crystal system	Space group	Pearson symbol	Structure type	References
Al_2O_3	Trigonal	$R\bar{3}cH$	hR10	Corundum- Al_2O_3	28
TiO_2	Tetragonal	$P4_2/nmc$	tP6	Rutile	29
Q- SiO_2	Trigonal	$P3_221$	hP9	Quartz, low- SiO_2	30
C- SiO_2	Tetragonal	$P4_12_12$	tP12	Cristobalite(alpha)	31
T- SiO_2	Hexagonal	$P63/mmc$	hP12	Tridymite	32
Al_2TiO_5	Orthorhombic	$Cmcm$	oS32	Pseudobrookite- Fe_2TiO_5	6
$\text{Al}_6\text{Si}_2\text{O}_{13}$	Orthorhombic	$Pbam$	oP16	Mullite	10

4 Thermodynamic Models

4.1 Liquid

The ionic two-sublattice model^[38,39] is applied to the $\text{Al}_2\text{O}_3\text{--TiO}_2\text{--SiO}_2$ system, using the formula $(\text{Al}^{+3}, \text{Ti}^{+2}, \text{Ti}^{+3})_P(\text{O}^{-2}, \text{Va}, \text{AlO}_{3/2}, \text{O}, \text{SiO}_4^{-4}, \text{SiO}_2, \text{TiO}_2)_Q$. P and Q are the number of sites on each sublattice that vary depending on the composition to keep electroneutrality. The same model can be used for both metallic and oxide melts. At a low oxygen content, the model becomes equivalent to the substitutional solution model considering interactions between metallic atoms. The liquid phase in the $\text{Al}_2\text{O}_3\text{--TiO}_2$ system was reassessed in the previous work^[7] using the formula $(\text{Al}^{+3}, \text{Ti}^{+2}, \text{Ti}^{+3})_P(\text{O}^{-2}, \text{Va}, \text{AlO}_{3/2}, \text{O}, \text{TiO}_2)_Q$. Even as phase interactions with the metal were not considered in that study, the species Ti^{+2} , Ti^{+3} , Va , and O originated from the description of the Ti--O system. Since there is a continuous liquid solution in the Ti--O system from Ti to TiO_2 , vacancies are necessary to have consistent description of this binary system. The description of the liquid phase in the $\text{Al}_2\text{O}_3\text{--SiO}_2$ system is accepted from the works of Dumitrescu and Sundman^[11] and Fabrichnaya et al.^[9] They both used a simple associated solution model considering interactions only between neutral species: $(\text{AlO}_{3/2}, \text{SiO}_2)$. For the $\text{TiO}_2\text{--SiO}_2$ system, the ionic two-sublattice model is applied using the formula $(\text{Ti}^{+2}, \text{Ti}^{+3})_P(\text{O}^{-2}, \text{Va}, \text{SiO}_4^{-4}, \text{SiO}_2, \text{TiO}_2)_Q$. However, the species SiO_4^{-4} cannot be formed in the $\text{TiO}_2\text{--SiO}_2$ system due to a wide liquid immiscibility, i.e. TiO_2 does not participate in either destroying or sharing network of SiO_2 . In this case, the liquid TiO_2 is described by the neutral species TiO_2 and the liquid SiO_2 by neutral SiO_2 . Thus, this model can be reduced to the $(\text{SiO}_2, \text{TiO}_2)$ substitutional model and the corresponding interactions parameters were only assessed in this work.

The ionic two-sublattice model was developed within the framework of the compound energy formalism (CEF)^[40] widely used in CALPHAD assessments. CEF is proposed to describe thermodynamic models of phases with two or more sublattices that exhibit a variation in composition. For a two-sublattice model, the Gibbs energy is defined as

$$\Delta G^\varphi = \sum_i \sum_j y_i^s \cdot y_j^t \cdot G_{ij}^s + R \cdot T \cdot \sum_s \alpha_s \sum_i y_i^s \cdot \ln(y_i^s) + \Delta G^{ex}, \quad (\text{Eq 1})$$

where y_i^s and y_j^t are the mole fractions of constituents i and j on the sublattices s and t , respectively; α_s is the number of sites on sublattice s per mole of formula unit of a phase.

The excess Gibbs energy term associated with the different sublattices is described with Redlich–Kister equation as

$$\Delta G^{ex} = \sum_s y_i^s \sum_t y_j^t L_{j,m}^t + \sum_t y_j^t \sum_s y_i^s L_{i,k}^s. \quad (\text{Eq 2})$$

The binary interaction parameters $L_{i,k}^s$ between i and k species on the sublattice s are signified as

$$L_{i,k}^s = \sum_n {}^n L_{i,k} (y_i^s - y_k^s)^n. \quad (\text{Eq 3})$$

Hereinafter, a colon is used to separate species on different sublattices, and a comma is used to separate the species on the same sublattice.

4.2 Mullite

Mullite is a part of the orthorhombic aluminosilicates system of general composition $\text{Al}_2(\text{Al}_{2+2x}\text{Si}_{2-2x})\text{O}_{10-x}$. The structure of mullite (space group: $Pbam$) can be derived from the closely related but structurally simpler sillimanite (Al_2SiO_5 , with $x = 0$; space group: $Pbnm$). In sillimanite, edge-connected AlO_6 octahedra form chains running parallel to the crystallographic c -axis and are cross-linked by double chains with alternating AlO_4 and SiO_4 tetrahedra. In mullite, part of Si^{+4} is replaced by Al^{+3} , which also leads to the formation of oxygen vacancies. The formation of O vacancies is accompanied by a displacement of the tetrahedral positions next to the bridging O atoms to new distorted tetrahedral positions that form triclusters. Thus, three different Al sites were described in mullite: one octahedral (O), one tetrahedral (T) as in sillimanite, and a distorted tetrahedral (T^*) site assigned to Al in the tetrahedral triclusters.^[41,42] Considering this, mullite phase was modeled on the basis of a sublattice description within CEF using the formula $(\text{Al}^{+3})_1^O (\text{Al}^{+3})_1^{T^*} (\text{Al}^{+3}, \text{Si}^{+4})_1^T (\text{O}^{-2}, \text{Va})_5$.^[9,11] The description is accepted in this work.

According to Schneider,^[43–45] Ti^{+4} is incorporated into the mullite structure at the Al^{+3} positions in the AlO_6 octahedra. The resulting model for mullite in the $\text{Al}_2\text{O}_3\text{--TiO}_2\text{--SiO}_2$ system is then $(\text{Al}^{+3}, \text{Ti}^{+4})_1^O (\text{Al}^{+3})_1^{T^*} (\text{Al}^{+3}, \text{Si}^{+4})_1^T (\text{O}^{-2}, \text{Va})_5$.

This model gives a new neutral end-member $(\text{Ti}^{+4})_1^O (\text{Al}^{+3})_1^{T^*} (\text{Al}^{+3})_1^T (\text{O}^{-2})_5$, a hypothetical Al_2TiO_5 with the mullite-type structure. The Gibbs energy of this end-member is adjusted as

$${}^\circ G_{\text{Ti}^{+4}; \text{Al}^{+3}; \text{Al}^{+3}; \text{O}^{-2}} = {}^\circ G_{\text{CORUND}} + {}^\circ G_{\text{TiO}_2} + a_1 \quad (\text{Eq 4})$$

where ${}^\circ G_{\text{CORUND}}$ is the Gibbs energy of corundum Al_2O_3 ,^[46] ${}^\circ G_{\text{TiO}_2}$ is the Gibbs energy of rutile TiO_2 ,^[27] and a_1 is the optimized parameter.

The remaining three parameters in the mullite system (in bold) are evaluated using the reciprocal reactions (Eqs. (5) to (7)):

$$^{\circ}G_{\text{Al}^{+3}:\text{Al}^{+3}:\text{Al}^{+3}:\text{Va}} + ^{\circ}G_{\text{Ti}^{+4}:\text{Al}^{+3}:\text{Al}^{+3}:\text{O}^{-2}} = ^{\circ}G_{\text{Ti}^{+4}:\text{Al}^{+3}:\text{Al}^{+3}:\text{Va}} + ^{\circ}G_{\text{Al}^{+3}:\text{Al}^{+3}:\text{Al}^{+3}:\text{O}^{-2}} \quad (\text{Eq 5})$$

$$^{\circ}G_{\text{Al}^{+3}:\text{Al}^{+3}:\text{Si}^{+4}:\text{O}^{-2}} + ^{\circ}G_{\text{Ti}^{+4}:\text{Al}^{+3}:\text{Al}^{+3}:\text{O}^{-2}} = ^{\circ}G_{\text{Ti}^{+4}:\text{Al}^{+3}:\text{Si}^{+4}:\text{O}^{-2}} + ^{\circ}G_{\text{Al}^{+3}:\text{Al}^{+3}:\text{Al}^{+3}:\text{O}^{-2}} \quad (\text{Eq 6})$$

$$^{\circ}G_{\text{Ti}^{+4}:\text{Al}^{+3}:\text{Si}^{+4}:\text{O}^{-2}} + ^{\circ}G_{\text{Al}^{+3}:\text{Al}^{+3}:\text{Si}^{+4}:\text{Va}} = ^{\circ}G_{\text{Ti}^{+4}:\text{Al}^{+3}:\text{Si}^{+4}:\text{Va}} + ^{\circ}G_{\text{Al}^{+3}:\text{Al}^{+3}:\text{Si}^{+4}:\text{O}^{-2}} \quad (\text{Eq 7})$$

All these reactions are assumed to have $\Delta G = 0$.

4.3 Pseudobrookite

Aluminum titanate Al_2TiO_5 (tialite) has a pseudobrookite structure (space group: $Cmcm$). For the Al_2O_3 – TiO_2 system, the three-sublattice model for pseudobrookite Al_2TiO_5 was applied^[8] and the description is accepted in this work. In brief, the cation disordering in Al_2TiO_5 was described with the formula $(\text{Ti}^{+4}, \text{Al}^{+3})_1^{\text{M1}} (\text{Ti}^{+4}, \text{Al}^{+3})_2^{\text{M2}} \text{O}_5$. In normal pseudobrookite structure, the M1 sites are fully occupied by the Ti^{+4} cations and the M2 sites by Al^{+3} . The degree of inversion is then determined as occupancy of M1 by Al^{+3} . According to experimental data,^[6,47,48] the degree of cation disorder is close to 0.667, which corresponds to complete disorder. In the presence of SiO_2 , the substitution of the Al^{+3} cations by Si^{+4} in Al_2TiO_4 is expected,^[49,50] although no experimental details on the crystal structure were found. Also considering the ionic radii concept ($\text{Al}^{+3} = 0.054$ nm, $\text{Si}^{+4} = 0.041$ nm, and $\text{Ti}^{+4} = 0.061$ nm), the structural incorporation of Si^{+4} into both the M1 and M2 sublattices is proposed in this work. Thus, the formula for the pseudobrookite phase is extended accordingly $(\text{Ti}^{+4}, \text{Al}^{+3}, \text{Si}^{+4})_1^{\text{M1}} (\text{Ti}^{+4}, \text{Al}^{+3}, \text{Si}^{+4})_2^{\text{M2}} \text{O}_5$.

The Gibbs energy of normal pseudobrookite Al_2TiO_5 is described by the end-member $(\text{Ti}^{+4})_1^{\text{M1}} (\text{Al}^{+3})_2^{\text{M2}} \text{O}_5$ (or $^{\circ}G_{\text{Ti}^{+4}:\text{Al}^{+3}}$; here and further in the discussion of pseudobrookite, the oxygen index is omitted). To model the degree of inversion in Al_2TiO_5 , the end-member $(\text{Al}^{+3})_1^{\text{M1}} (\text{Ti}^{+4})_2^{\text{M2}} \text{O}_5$ (or $^{\circ}G_{\text{Al}^{+3}:\text{Ti}^{+4}}$) is used. The values for the $^{\circ}G_{\text{Ti}^{+4}:\text{Al}^{+3}}$, $^{\circ}G_{\text{Al}^{+3}:\text{Ti}^{+4}}$, $^{\circ}G_{\text{Al}^{+3}:\text{Al}^{+3}}$ (or $^{\circ}G_{\text{Al}_3\text{O}_5}^{\text{tialite}}$), and $^{\circ}G_{\text{Ti}^{+4}:\text{Ti}^{+4}}$ (or $^{\circ}G_{\text{Ti}_3\text{O}_5}^{\text{tialite}}$) were taken from the previous assessment.^[8]

A new neutral end-member $(\text{Si}^{+4})_1^{\text{M1}} (\text{Al}^{+3})_2^{\text{M2}} (\text{O}^{-2})_5$, a hypothetical Al_2SiO_5 with the pseudobrookite structure, is found in the pseudobrookite system. To define corresponding parameters, a simplified model $(\text{Al}^{+3}, \text{Si}^{+4})_1^{\text{M1}} (\text{Al}^{+3}, \text{Si}^{+4})_2^{\text{M2}} \text{O}_5$ can be considered in this case. Similarly to the description of Al_2TiO_5 , the four

thermodynamic parameters for new end-members can be expressed only by two independent parameters related to normal and inverse structures, respectively, $^{\circ}G_{\text{Si}^{+4}:\text{Al}^{+3}}$ and $^{\circ}G_{\text{Al}^{+3}:\text{Si}^{+4}}$:

$$^{\circ}G_{\text{Si}^{+4}:\text{Al}^{+3}} = ^{\circ}G_{\text{ANDAL}} + a_2, \quad (\text{Eq 8})$$

$$^{\circ}G_{\text{Al}^{+3}:\text{Si}^{+4}} = 2(^{\circ}G_{\text{ANDAL}} + a_2) + a_3 - ^{\circ}G_{\text{Al}_3\text{O}_5}^{\text{tialite}} - 4RT\ln 0.5, \quad (\text{Eq 9})$$

where $^{\circ}G_{\text{ANDAL}}$ is the Gibbs energy of andalusite,^[51] $^{\circ}G_{\text{Al}_3\text{O}_5}^{\text{tialite}}$ (or $^{\circ}G_{\text{Al}^{+3}:\text{Al}^{+3}}$) is the Gibbs energy of a fictive compound Al_3O_5 with the pseudobrookite structure,^[8] and a_2 and a_3 are the optimized parameters.

The fourth parameter $^{\circ}G_{\text{Si}^{+4}:\text{Si}^{+4}}$ (or $^{\circ}G_{\text{Si}_3\text{O}_5}$) is determined by the reciprocal reaction

$$^{\circ}G_{\text{Si}^{+4}:\text{Al}^{+3}} + ^{\circ}G_{\text{Al}^{+3}:\text{Si}^{+4}} - ^{\circ}G_{\text{Al}^{+3}:\text{Al}^{+3}} - ^{\circ}G_{\text{Si}^{+4}:\text{Si}^{+4}} = \Delta G_1, \quad (\text{Eq 10})$$

where $\Delta G_1 = 0$.

The remaining two parameters in pseudobrookite model, $^{\circ}G_{\text{Ti}^{+4}:\text{Si}^{+4}}$ and $^{\circ}G_{\text{Si}^{+4}:\text{Ti}^{+4}}$, are related to the mentioned parameters by the following reciprocal reaction

$$^{\circ}G_{\text{Si}^{+4}:\text{Si}^{+4}} + ^{\circ}G_{\text{Ti}^{+4}:\text{Ti}^{+4}} - ^{\circ}G_{\text{Ti}^{+4}:\text{Si}^{+4}} - ^{\circ}G_{\text{Si}^{+4}:\text{Ti}^{+4}} = \Delta G_2, \quad (\text{Eq 11})$$

where ΔG_2 is the non-zero value optimized in this work ($\Delta G_2 = \Delta G_3 + \Delta G_4$), which could be defined by Eqs. (12) and (13):

$$^{\circ}G_{\text{Ti}^{+4}:\text{Si}^{+4}} = 1/3^{\circ}G_{\text{Ti}_3\text{O}_5}^{\text{tialite}} + 2/3^{\circ}G_{\text{Si}_3\text{O}_5} + \Delta G_3, \quad (\text{Eq 12})$$

$$^{\circ}G_{\text{Si}^{+4}:\text{Ti}^{+4}} = 2/3^{\circ}G_{\text{Ti}_3\text{O}_5}^{\text{tialite}} + 1/3^{\circ}G_{\text{Si}_3\text{O}_5} + \Delta G_4. \quad (\text{Eq 13})$$

4.4 Rutile, Corundum and SiO_2 -Based Phases

The corundum phase is the Al_2O_3 -rich solid solution, which crystallizes with trigonal symmetry in the space group $R\bar{3}c$. Since no reliable information on any solubility in rutile, corundum, and SiO_2 -based phases is reported, these phases are described as stoichiometric. The description of corundum is taken from Hallstedt,^[46] the description of rutile is from Hampl and Schmid-Fetzer,^[27] and the descriptions of Q- SiO_2 , C- SiO_2 , and T- SiO_2 are all from Hillert et al.^[51]

5 Results and Discussion

5.1 The Binary TiO_2 – SiO_2 System

According to DTA measurements up to 1923 K in air, the eutectic temperature in the SiO_2 -rich side of the TiO_2 – SiO_2 system was determined to be 1818 K (Fig. 1a). The non-

intensive and long-drawn-out thermal effect observed for the sample TS-2 can probably be explained by the viscosity of the sample. The temperature obtained in air is in a good agreement with most published data, however this value is more than 60 K higher than that reported by Kirillova et al.^[23] although the experimental conditions were similar. DTA measurement of the sample TS-1 in He indicated a decrease in the temperature of eutectic (1798 K; Fig. 1a). In Fig. 2a, SEM/EDX revealed the eutectic composition measured for the sample TS-2 after melting in DTA, which was equal to 8.7 mol% TiO_2 . The microstructure examination of the sample TS-1 after DTA melting (up to 1923 K) in air did not reveal the eutectic formation, probably due to the glass formation. However, a SiO_2 enriched matrix containing 7.0 mol% of TiO_2 and practically pure TiO_2 grains were observed, which indicates the presence of a two-phase field ($\text{L1-SiO}_2 + \text{TiO}_2$) discussed below. The temperature and composition of the eutectic reaction are summarized along with the literature data in Table 2.

To study liquid immiscibility in the TiO_2 – SiO_2 system, the sample TS-1 was heated up both in air and in an He atmosphere. The sample exhibiting the miscibility gap resulted in the separation of the melt into two liquids: one rich in SiO_2 called L1 and the other rich in TiO_2 called L2 (including the TiO_2 grains and the surrounding matrix). Merely on visual examination, the sample TS-1 heat treated at 2013 K in air followed by furnace-cooling was partially melted, however the temperature of the monotectic reaction $\text{L1} \leftrightarrow \text{L2} + \text{TiO}_2$ was not reached, revealing the presence of the two-phase field ($\text{L1-SiO}_2 + \text{TiO}_2$). As supporting evidence, no certain L2 spherulites were observed for the sample TS-1 melted in air (Fig. 2c), while the grains of practically pure TiO_2 and SiO_2 -rich L1 were only detected (Table 3). The experiments in air above 2023

K are not possible in the current work. Therefore, the sample TS-1 was also heated up to 2273 K in a He atmosphere using DTA. In this case, the solidified microstructure of the sample is characterized by the appearance of TiO_2 -rich spheres (L2) embedded in the SiO_2 -rich matrix (L1) as illustrated in Fig. 2b, which indicates that the monotectic temperature was reached. Considering these data and literature data, this indicates a decrease in temperature of equilibria in the He atmosphere as compared to air. A similar behavior was observed for the MnO -containing system.^[52] When compared with the literature data, a decrease in the temperature of a monotectic reaction to 1962 K was found (Fig. 1b; Table 2). DeVries et al.^[18] discussed the effect of the atmosphere on the results of phase equilibria in the TiO_2 – SiO_2 system: Umezu and Kakiuchi^[12] got substantially lower temperatures of eutectic and monotectic reactions in a strongly reducing atmosphere than DeVries et al. in air. However, the temperature of the monotectic reaction obtained by Kirillova et al.^[23] in a protective gas atmosphere (He) was not substantially different from the results^[18,19] obtained in air. Possible reasons for the fact that the equilibria temperatures in this work were lower than those reported in the literature could be both the effect of the oxygen partial pressure and the accuracy of the temperature measurement. Since faster diffusion occurs in the liquid state than in solid, it can be assumed that the compositions L1 and L2 correspond to the temperature of the monotectic equilibrium. However, the samples were heated to higher temperatures, and therefore the compositions of the two liquids could correspond to the temperatures higher than the monotectic temperature. Thus, there is uncertainty in indicated liquid compositions, since the temperature corresponding to the measured compositions L1 and L2 is not

Fig. 1 DTA heating curves of the samples (a) TS-1 and TS-2 related to eutectic (in air and in He), and (b) TS-1 related to monotectic reaction (in He). No undercooling effects were observed

Fig. 2 Microstructures of the samples (a) TS-2 after DTA heating up to 1973 K in air; (b) TS-1 after DTA heating up to 2273 K in He, fine TiO_2 solids are distributed in SiO_2 -rich L1; (c) TS-1 after heat

treatment at 1213 K in air; (d) ATS-3 after heat treatment at 1213 K in air; (e) ATS-7 after heat treatment at 1213 K in air; and (f) ATS-8 after heat treatment at 1213 K in air

Table 2 Invariant equilibria in the TiO_2 – SiO_2 system

Reaction	Temperature, K	Composition, mol% TiO_2	References
$\text{L} \leftrightarrow \text{SiO}_2 + \text{TiO}_2$	1773	15.0	12
	1813 $\pm$ 10	8.0	15
	1813	17.0	16
	1843	8.0	17
	1823 $\pm$ 4	8.1	18
	1755	22.4	23
	1818	8.7	Exp., this work (Air)
	1833	4.5	Calc., this work ($p(\text{O}_2) = 0.21$ bar)
	1810	4.8	Calc., this work ($p(\text{O}_2) = 1 \cdot 10^{-2.5}$ bar)
$\text{L1} \leftrightarrow \text{L2} + \text{TiO}_2$	1853	35.7–75.1	12
	2038	15.9–92.2	19
	2053 $\pm$ 10	15.0–90.8	18
	2046	27.4–85.4	23
	1962	19.3–92.3 ^a	Exp., this work (He)
	2085	18.6–84.1	Calc., this work ($p(\text{O}_2) = 0.21$ bar)
	2050	22.6–83.8	Calc., this work ($p(\text{O}_2) = 1 \cdot 10^{-2.5}$ bar)

^aThe compositions L1 and L2 for the sample TS-1 heated up to 2123 K in He were attributed to the temperature of monotectic equilibrium of 1962 K. Since the sample was heated to higher temperatures than monotectic, the compositions of the two liquids could correspond to the temperature higher than monotectic; see details in text.

exactly known. On the other hand, the compositions L1 and L2 observed for the samples melted in a He atmosphere may differ from those obtained under air conditions. Since the experimental study of the sample in air at a higher temperature (above 2023 K) was not possible in the current

work, the temperature of the monotectic reaction of 2053 K available from the literature^[18,23] is accepted. The compositions of the coexisting liquids L1 and L2 measured by EDX are given in Table 3.

Table 3 Sample compositions in the TiO₂–SiO₂ and Al₂O₃–TiO₂–SiO₂ systems along with SEM/EDX and XRD results

Sample	Nominal sample composition and composition by EDX* [†] , mole fraction			Annealing temperature, K/annealing time, days	Phases by XRD (Vol%)	Lattice parameters, Å		Phases by SEM/EDX	Phase composition by SEM/EDX [†] , mole fraction		
	Al ₂ O ₃	TiO ₂	SiO ₂			a	c		Al ₂ O ₃	TiO ₂	SiO ₂
TS-1	0.500	0.500		1683/5	TiO ₂ 36	4.594	2.959				
	0.545*	0.455			C-SiO ₂ 56	4.990	6.969				
					Q-SiO ₂ 8	4.912	5.401				
				1923 ^{a,b}				L1	0.070	0.930	
								TiO ₂	0.994	0.006	
				2013/12h ^a				L1	0.215	0.785	
								TiO ₂	0.988	0.012	
				2023 ^{a,c}				L1	0.200	0.800	
								TiO ₂	0.994	0.006	
				2123 ^c				L1	0.193	0.807	
								L2	0.923	0.077	
								TiO ₂	–	–	
TS-2	0.100	0.900		1683/7	TiO ₂ 7	4.601	2.964				
	0.123*	0.877			C-SiO ₂ 88	4.994	6.973				
					Q-SiO ₂ 5	4.913	5.405				
ATS-3	0.036	0.543	0.421	2013/12h				L ^d	0.052	0.437	0.511
	0.038*	0.534	0.428					TiO ₂	0.002	0.952	0.046
ATS-7	0.020	0.700	0.280	2013/12h				L1	–	–	–
	0.022*	0.744	0.233					L2	0.016	0.834	0.150
								TiO ₂	0.003	0.992	0.005
ATS-7a	0.020	0.700	0.280	2013/12h				L1	0.030	0.419	0.551
	0.021*	0.747	0.233					L2	0.014	0.804	0.182
								TiO ₂	0.003	0.991	0.006
ATS-8	0.080	0.550	0.370	2013/12h				L ^d	0.062	0.415	0.523
	0.049*	0.592	0.359					TiO ₂	0.003	0.990	0.007

*EDX measurement of the powdered samples before heat treatment

[†]The standard deviation is in most cases below 0.2 mol%^aMonotectic temperature is not reached, only the two-phase field (L1+TiO₂) is present^bHeated in DTA in air without holding at the reached temperature^cHeated in DTA in a He atmosphere without holding at the reached temperature. These data are only for comparison, see details in the text^dOne homogeneous liquid

5.2 Liquid Immiscibility in the Al₂O₃–TiO₂–SiO₂ System

The microstructures of the samples ATS-3, -7, and -8 heat treated at 2013 K in air are shown in Fig. 2. One should keep in mind that the bulk sample compositions differ slightly from the nominal ones, therefore, only the sample

compositions measured using EDX are considered (see Table 3). As discussed above, the temperature of the monotectic reaction in the TiO₂–SiO₂ boundary is about 2053 K. However, a tendency to the separation of the melt into two liquids was observed at 2013 K for the samples ATS-7 and -7a (Fig. 2e): the globular particles enriched in TiO₂ for the liquid rich in TiO₂ (L2) and the liquid rich in

SiO₂ (L1) with TiO₂-rich inclusions. The samples ATS-7 and -7a contain 2.1–2.2 mol% Al₂O₃. In contrast, typical dendritic microstructures without separation were observed for the samples ATS-3 and -8 (Fig. 2d, f), which contain a slightly higher amount of Al₂O₃, 3.8 and 4.9 mol% Al₂O₃, respectively. This suggests that the miscibility gap extends into the ternary system by no more than 3.8 mol% Al₂O₃. It can be assumed that a clearer separation of two liquids would be observed at high temperatures (above 2053), but this cannot be done in the present work. The compositions of the coexisting liquids L1 and L2 measured by EDX are given in Table 3. The results obtained are in a good agreement with those proposed by Kirschen et al.,^[22] Fig. 3.

Fig. 3 Experimental miscibility gap with data by Kirschen et al.^[22] Solid triangles and spheres point to the compositions of the quenched coexisting liquids, open symbols denote the quench of a homogeneous liquid

5.3 Thermodynamic Optimization and Calculations

The Thermo-Calc software^[5] was applied to optimize thermodynamic parameters using the PARROT module within the CALPHAD approach,^[53] and the further calculations of the phase diagram were carried out in the POLY-3 module. During optimization, individual weights were assigned to every type of experimental data considering uncertainties of each experimental method. Thermodynamic descriptions of the binary subsystems Al₂O₃–TiO₂ and Al₂O₃–SiO₂ were accepted from the works of Ilatovskaia et al.^[7,8] and Dumitrescu and Sundman,^[11] respectively. Thermodynamic data for the solid phases in the TiO₂–SiO₂ system originated from Hampl and Schmid-Fetzer^[27] and Hillert et al.^[51] were accepted, and the liquid phase of the system was only re-assessed in this work. The thermodynamic parameters for the Al₂O₃–TiO₂–SiO₂ system were assessed in this work based on the phase equilibria data obtained by XRD, SEM/EDX, and DTA in the previous work^[4] and available in the literature.^[17,22,54,55]

5.3.1 The Binary TiO₂–SiO₂ System

The calculated phase diagram of the TiO₂–SiO₂ system is shown in Fig. 4a. Due to the large uncertainties in the reported liquid immiscibility data, different weights were assigned to the corresponding data points during optimization. Since a critical assessment of the available data was provided and the modeling was amended by their own experimental measurements at high temperatures, larger weight was given to the data of Kirillova et al.^[23] The critical point of the miscibility gap calculated by Kirillova et al.^[23] is at 2416 K and 58.9 mol% TiO₂. In this work, it

Fig. 4 Calculated (a) phase diagram of the TiO₂–SiO₂ system at $p(\text{O}_2) = 0.21$ bar (black) and $p(\text{O}_2) = 1 \cdot 10^{-2.5}$ bar (red), and (b) activity of SiO₂ (in relation to the liquid state) in the TiO₂–SiO₂ system at 1800 and 1900 K and $p(\text{O}_2) = 0.21$ bar. Red marks are for He, see text for details

Table 4 Thermodynamic description for the $\text{Al}_2\text{O}_3\text{--TiO}_2\text{--SiO}_2$ system.

Phase	Sublattice model	Thermodynamic parameter
Ionic liquid	$(\text{Al}^{+3}, \text{Ti}^{+2}, \text{Ti}^{+3})_p(\text{O}^{-2}, \text{Va}, \text{AlO}_{3/2}, \text{O}, \text{SiO}_4^{-4}, \text{SiO}_2, \text{TiO}_2)_q$	${}^0G_{\text{Al}^{+3}, \text{O}^{-2}}^{\text{ionic}} = +\text{GAL2O3_L} + 1000000$
		${}^0G_{\text{Ti}^{+2}, \text{O}^{-2}}^{\text{ionic}} = +2 \cdot \text{GTiO1} + 141000 - 61.4 \cdot T$
		${}^0G_{\text{Ti}^{+3}, \text{O}^{-2}}^{\text{ionic}} = +2 \cdot \text{GTi2O3} + 114147.4 - 45.6 \cdot T$
		${}^0G_{\text{Al}^{+3}, \text{Va}}^{\text{ionic}} = +\text{GLIQA1}$
		${}^0G_{\text{Ti}^{+2}, \text{Va}}^{\text{ionic}} = +\text{GLIQT1}$
		${}^0G_{\text{Ti}^{+3}, \text{Va}}^{\text{ionic}} = +\text{GLIQT1} + 200000$
		${}^0G_{\text{AlO}_{3/2}}^{\text{ionic}} = +0.5 \cdot \text{GAL2O3_L}$
		${}^0G_{\text{O}}^{\text{ionic}} = +2648.9 + 31.44 \cdot T + \text{GHSEROO}$
		${}^0G_{\text{SiO}_2}^{\text{ionic}} = +\text{GSIO2LIQ}$
		${}^0G_{\text{TiO}_2}^{\text{ionic}} = +\text{GTiO2L}$
		${}^0L_{\text{Al}^{+3}, \text{O}^{-2}, \text{Va}}^{\text{ionic}} = -829000 + 106 \cdot T$
		${}^0L_{\text{Al}^{+3}, \text{Va}, \text{AlO}_{3/2}}^{\text{ionic}} = +110000 + 46 \cdot T$
		${}^0L_{\text{Ti}^{+2}, \text{Ti}^{+3}, \text{O}^{-2}}^{\text{ionic}} = +19431.27$
		${}^0L_{\text{Ti}^{+2}, \text{O}^{-2}, \text{Va}}^{\text{ionic}} = +168314.44 - 100 \cdot T$
		${}^1L_{\text{Ti}^{+2}, \text{O}^{-2}, \text{Va}}^{\text{ionic}} = +190655.57 - 95 \cdot T$
		${}^0L_{\text{Ti}^{+3}, \text{O}^{-2}, \text{TiO}_2}^{\text{ionic}} = -36682.45$
		${}^1L_{\text{Ti}^{+3}, \text{O}^{-2}, \text{TiO}_2}^{\text{ionic}} = +2382.5262$
		${}^0L_{\text{AlO}_{3/2}, \text{SiO}_2}^{\text{ionic}} = +80121 - 30 \cdot T$
		${}^1L_{\text{AlO}_{3/2}, \text{SiO}_2}^{\text{ionic}} = -96000 + 44 \cdot T$
		${}^0L_{\text{AlO}_{3/2}, \text{SiO}_2, \text{TiO}_2}^{\text{ionic}} = 243290.93 + 101.960677 \cdot T^*$
		${}^1L_{\text{AlO}_{3/2}, \text{SiO}_2, \text{TiO}_2}^{\text{ionic}} = -171852.904^*$
		${}^2L_{\text{AlO}_{3/2}, \text{SiO}_2, \text{TiO}_2}^{\text{ionic}} = -39633.9976^*$
		${}^0L_{\text{AlO}_{3/2}, \text{TiO}_2}^{\text{ionic}} = -38740.379 + 30.0537421 \cdot T$
		${}^1L_{\text{AlO}_{3/2}, \text{TiO}_2}^{\text{ionic}} = -34495.5858 + 19.6769796 \cdot T$
		${}^2L_{\text{AlO}_{3/2}, \text{TiO}_2}^{\text{ionic}} = -9914.83619$
		${}^0L_{\text{AlO}_{3/2}, \text{O}}^{\text{ionic}} = +50000 + 50 \cdot T$
		${}^0L_{\text{SiO}_2, \text{O}}^{\text{ionic}} = +50000^*$
		${}^0L_{\text{SiO}_2, \text{TiO}_2}^{\text{ionic}} = +54860.4 - 4.927958 \cdot T^*$
		${}^1L_{\text{SiO}_2, \text{TiO}_2}^{\text{ionic}} = -26345.39 + 12.837078 \cdot T^*$
		${}^0G_{\text{Al}^{+3}, \text{Al}^{+3}, \text{O}^{-2}}^{\text{Mullite}} = +\text{GAAOMULL}$
Mullite	$(\text{Al}^{+3}, \text{Ti}^{+4})_1^{\text{O}}(\text{Al}^{+3})_1^{\text{T}}(\text{Al}^{+3}, \text{Si}^{+4})_1(\text{O}^{-2}, \text{Va})_5$	

Table 4 continued

Phase	Sublattice model	Thermodynamic parameter
Pseudobrookite	$(\text{Ti}^{+4}, \text{Al}^{+3}, \text{Si}^{+4})_{\text{I}}^{\text{M1}} (\text{Ti}^{+4}, \text{Al}^{+3}, \text{Si}^{+4})_{\text{II}}^{\text{M2}} (\text{O}^{2-})_5$	${}^0G_{\text{Al}^{+3};\text{Al}^{+3};\text{Si}^{+4};\text{O}^{2-}}^{\text{Mullite}} = +\text{GASOMULL}$
		${}^0G_{\text{Al}^{+3};\text{Al}^{+3};\text{Al}^{+3};\text{Al}^{+3};\text{Va}}^{\text{Mullite}} = 0$
		${}^0G_{\text{Al}^{+3};\text{Al}^{+3};\text{Si}^{+4};\text{Va}}^{\text{Mullite}} = +\text{GASOMULL} + \text{BASOMULL}$
		${}^0L_{\text{Al}^{+3};\text{Al}^{+3};\text{Al}^{+3};\text{Al}^{+3};\text{Si}^{+4};\text{O}^{2-}}^{\text{Mullite}} = -498147 + 64.083 \cdot T$
		${}^0G_{\text{Ti}^{+4};\text{Al}^{+3};\text{Al}^{+3};\text{Al}^{+3};\text{O}^{2-}}^{\text{Mullite}} = +\text{GCRUND} + \text{GTIO2} + 350000$ *
		${}^0G_{\text{Ti}^{+4};\text{Al}^{+3};\text{Si}^{+4};\text{O}^{2-}}^{\text{Mullite}} = +\text{GCRUND} + \text{GTIO2} + 350000 + \text{GASOMULL} - \text{GAAOMULL}^*$
		${}^0G_{\text{Ti}^{+4};\text{Al}^{+3};\text{Si}^{+4};\text{Va}}^{\text{Mullite}} = +\text{GCRUND} + \text{GTIO2} + 350000 - \text{GAAOMULL}^*$
		${}^0G_{\text{Ti}^{+4};\text{Al}^{+3};\text{Si}^{+4};\text{Va}}^{\text{Mullite}} = +\text{GCRUND} + \text{GTIO2} + 350000 + \text{GASOMULL} - \text{GAAOMULL}^*$
		${}^0G_{\text{Al}^{+3};\text{Al}^{+3};\text{Si}^{+4};\text{O}^{2-}}^{\text{Psbk}} = +\text{GAL3O5}$
		${}^0G_{\text{Ti}^{+4};\text{Al}^{+3};\text{O}^{2-}}^{\text{Psbk}} = +\text{GTIAL_NO}$
		${}^0G_{\text{Al}^{+3};\text{Ti}^{+4};\text{O}^{2-}}^{\text{Psbk}} = +2 \cdot \text{GTIAL_IN} - \text{GAL3O5} + 23.05244 \cdot T$
		${}^0G_{\text{Ti}^{+4};\text{Ti}^{+4};\text{O}^{2-}}^{\text{Psbk}} = +\text{GTI3O5}$
		${}^0G_{\text{Si}^{+4};\text{Al}^{+3};\text{O}^{2-}}^{\text{Psbk}} = +\text{GANDAL} + 1810 + 5.288 \cdot T^*$
		${}^0G_{\text{Al}^{+3};\text{Si}^{+4};\text{O}^{2-}}^{\text{Psbk}} = +2 \cdot \text{GANDAL} + 3665.42 + 23.816 \cdot T - \text{GAL3O5} + 23.05244 \cdot T^*$
		${}^0G_{\text{Si}^{+4};\text{Si}^{+4};\text{O}^{2-}}^{\text{Psbk}} = +\text{GSI3O5}^*$
GHSEROO	(298.15–1000)	${}^0G_{\text{Ti}^{+4};\text{Si}^{+4};\text{O}^{2-}}^{\text{Psbk}} = +0.3333 \cdot \text{GTI3O5} + 0.6667 \cdot \text{GSI3O5} + 10195^*$
		${}^0G_{\text{Si}^{+4};\text{Ti}^{+4};\text{O}^{2-}}^{\text{Psbk}} = +0.6667 \cdot \text{GTI3O5} + 0.3333 \cdot \text{GSI3O5} + 45975^*$
GHSERAL	(298.15–700)	$-3480.87 - 25.503038 \cdot T - 11.1355 \cdot T \cdot \ln T - 0.005098875 \cdot T^2 + 6.61845833 \cdot 10^{-7} \cdot T^3 - 38365 \cdot T^{-1}$
		$-6568.763 + 12.659879 \cdot T - 16.8138 \cdot T \cdot \ln T - 5.957975 \cdot 10^{-4} \cdot T^2 + 6.781 \cdot 10^{-9} \cdot T^3 + 262905 \cdot T^{-1}$
		$-13986.728 + 31.259624 \cdot T - 18.9536 \cdot T \cdot \ln T - 0.000425243 \cdot T^2 + 1.0721 \cdot 10^{-8} \cdot T^3 + 4383200 \cdot T^{-1}$
		$-7976.15 + 137.071542 \cdot T - 24.3671976 \cdot T \cdot \ln T - 0.001884662 \cdot T^2 - 8.77664 \cdot 10^{-7} \cdot T^3 + 74092 \cdot T^{-1}$
		$-11276.24 + 223.02695 \cdot T - 38.5844296 \cdot T \cdot \ln T + 0.018531982 \cdot T^2 - 5.764227 \cdot 10^{-6} \cdot T^3 + 74092 \cdot T^{-1}$
GHSERTI	(933.6–2900)	$-11277.683 + 188.661987 \cdot T - 31.748192 \cdot T \cdot \ln T - 1.234264 \cdot 10^{28} \cdot T^{-9}$
		$-8059.921 + 133.615208 \cdot T - 23.9933 \cdot T \cdot \ln T - 0.004777975 \cdot T^2 + 1.06716 \cdot 10^{-7} \cdot T^3 + 72636 \cdot T^{-1}$
		$-7811.815 + 132.988068 \cdot T - 23.9887 \cdot T \cdot \ln T - 0.0042033 \cdot T^2 - 9.0876 \cdot 10^{-8} \cdot T^3 + 42680 \cdot T^{-1}$
		$+908.837 + 66.976538 \cdot T - 14.9466 \cdot T \cdot \ln T - 0.0081465 \cdot T^2 + 2.02715 \cdot 10^{-7} \cdot T^3 - 1477660 \cdot T^{-1}$
		$-124526.786 + 638.806871 \cdot T - 87.2182461 \cdot T \cdot \ln T + 0.008204849 \cdot T^2 - 3.04747 \cdot 10^{-7} \cdot T^3 + 36699805 \cdot T^{-1}$
GCRUND	(298.15–600)	$-1707351.3 + 448.021092 \cdot T - 67.4804 \cdot T \cdot \ln T - 0.06747 \cdot T^2 + 1.4205433 \cdot 10^{-5} \cdot T^3 + 1683920 \cdot T^{-1}$

Table 4 continued

Function	Temperature range	
GAL203_L	(600–1500)	$-1724886.06 + 754.856573 \cdot T - 116.258 \cdot T \cdot \ln T - 0.0072257 \cdot T^2 + 2.78532 \cdot 10^{-7} \cdot T^3 + 2120700 \cdot T^{-1}$
	(1500–3000)	$-1772163.19 + 1053.4548 \cdot T - 156.058 \cdot T \cdot \ln T + 0.00709105 \cdot T^2 - 6.29402 \cdot 10^{-7} \cdot T^3 + 12366650 \cdot T^{-1}$
	(298.15–600)	$-1607850.8 + 405.559491 \cdot T - 67.4804 \cdot T \cdot \ln T - 0.06747 \cdot T^2 + 1.4205433 \cdot 10^{-5} \cdot T^3 + 938780 \cdot T^{-1}$
	(600–1500)	$-1625385.57 + 712.394972 \cdot T - 116.258 \cdot T \cdot \ln T - 0.0072257 \cdot T^2 + 2.78532 \cdot 10^{-7} \cdot T^3 + 2120700 \cdot T^{-1}$
	(1500–1912)	$-1672662.69 + 1010.9932 \cdot T - 156.058 \cdot T \cdot \ln T + 0.00709105 \cdot T^2 - 6.29402 \cdot 10^{-7} \cdot T^3 + 12366650 \cdot T^{-1}$
	(1912–2327)	$+29178041.6 - 168360.926 \cdot T + 21987.1791 \cdot T \cdot \ln T - 6.99552951 \cdot T^2 + 4.10226192 \cdot 10^{-4} \cdot T^3 - 7.98843618 \cdot 10^9 \cdot T^{-1}$
GLIQUAL	(2327–4000)	$-1757702.05 + 1344.84833 \cdot T - 192.464 \cdot T \cdot \ln T$
	(298.15–933.59)	$+11005.029 - 11.841867 \cdot T + 7.934 \cdot 10^{-20} \cdot T^7 + \text{GHSERAL}$
	(933.59–6000)	$+10482.282 - 11.253974 \cdot T + 1.231 \cdot 10^{38} \cdot T^{-9} + \text{GHSERAL}$
GLIQTl	(298.15–1300)	$+12194.415 - 6.980938 \cdot T + \text{GHSERTl}$
	(1300–1940.99)	$+368610.36 - 2620.99904 \cdot T + 357.005867 \cdot T \cdot \ln T - 0.15526855 \cdot T^2 + 1.2254402 \cdot 10^{-5} \cdot T^3 - 65556856 \cdot T^{-1} + \text{GHSERTl}$
	(1940.99–6000)	$+104639.72 - 340.070171 \cdot T + 40.9282461 \cdot T \cdot \ln T - 0.008204849 \cdot T^2 + 3.04747 \cdot 10^{-7} \cdot T^3 - 36699805 \cdot T^{-1} + \text{GHSERTl}$
GTIO2L	(298.15–6000)	$+ \text{GTIO2} + 62222.4 - 28.2 \cdot T$
GTlIO1	(298.15–2500)	$-551056.766 + 252.1669378 \cdot T - 41.994808 \cdot T \cdot \ln T - 0.00889792452 \cdot T^2 + 1.0970448 \cdot 10^{-8} \cdot T^3 + 327015.164 \cdot T^{-1}$
GTIO2	(298.15–4000)	$-976986.6 + 484.74037 \cdot T - 77.76175 \cdot T \cdot \ln T - 67156800 \cdot T^{-2} + 1683920 \cdot T^{-1}$
GTlIO3	(298.15–470)	$-1545045.78 + 185.96227 \cdot T - 30.3934128 \cdot T \cdot \ln T - 0.099958898 \cdot T^2 - 5.93279345 \cdot 10^{-6} \cdot T^3 - 117799.056 \cdot T^{-1}$
	(470–2115)	$-1586585.8 + 937.087 \cdot T - 147.673862 \cdot T \cdot \ln T - 0.0017371312 \cdot T^2 - 1.53383348 \cdot 10^{-10} \cdot T^3 + 2395423.68 \cdot T^{-1}$
GSIO2LIQ	(298.15–2980)	$-923689.98 + 316.24766 \cdot T - 52.17 \cdot T \cdot \ln T - 0.012002 \cdot T^2 + 6.78 \cdot 10^{-7} \cdot T^3 + 665550 \cdot T^{-1}$
	(2980–4000)	$-957614.21 + 580.01419 \cdot T - 87.428 \cdot T \cdot \ln T$
GANDAL	(298.15–6000)	$-2656008.38 + 1091.19544 \cdot T - 171.253095 \cdot T \cdot \ln T - 0.0136670814 \cdot T^2 + 2523931.61 \cdot T^{-1}$
GAAOMULL	(298.15–6000)	$-2808415.35 + 1600.541 \cdot T - 246.032747 \cdot T \cdot \ln T + 0.0138772261 \cdot T^2 + 13484407.2 \cdot T^{-1} - 8.37441995 \cdot 10^8 \cdot T^{-2}$
GASOMULL	(298.15–6000)	$-2649812 + 1050.05906 \cdot T - 165.804515 \cdot T \cdot \ln T - 0.0160571905 \cdot T^2 + 2348905.07 \cdot T^{-1}$
BASOMULL	(298.15–6000)	$+6543940.51$
GTlIAL_NO	(298.15–6000)	$-2676129.071049 + 1162.4925771 \cdot T - 182.6374 \cdot T \cdot \ln T - 0.011098 \cdot T^2 + 2346281 \cdot T^{-1}$
GTlIAL_IN	(298.15–6000)	$+ \text{GTlIAL_IN} + 4.44159874 - 11.5312421 \cdot T$

Table 4 continued

Function	Temperature range
GAL3O5	(298.15–6000)
GTI3O5	(298.15–6000)
GSI3O5	(298.15–6000)

$$\begin{aligned}
 &+1.5 \cdot \text{GTIAL_NO} - 0.5 \cdot \text{GTI3O5} + 4.44159874 - 0.0050421 \cdot T \\
 &+3 \cdot \text{GTIO2} - \text{GHSEROO} \\
 &+3 \cdot \text{GANDAL} + 5475.42 + 29.104 \cdot T - 2 \cdot \text{GAL3O5} + 23.05244 \cdot T *
 \end{aligned}$$

All values are in SI units: J, mol, K.

*Parameters assessed in this work

is calculated to be at 2325 K and 46.25 mol% TiO_2 . The eutectic point calculated in this work is at 1833 K and 4.0 mol% TiO_2 . These results are compared with the experimental data in Table 2, showing reasonable agreement.

It should be noted that the data of Kirschen et al.^[22] are shown in Fig. 4a for comparison, but they were not accounted quantitatively in this work. Although Kirschen et al. performed very good levitation-quenching experiments for the TiO_2 – SiO_2 binary system, the experimental temperatures were probably chosen too high (one should keep in mind that the uncertainty of the temperature measurement by optical pyrometer used in^[22] is about ± 50 K) as evidenced by the microstructure provided in their work. When the molten sample is quenched from above the critical temperature of miscibility gap, the homogeneous melt could decompose into two separated liquid phases, resulting in an interconnected structure but not well-dispersed droplets. That, in turn, makes it more difficult to interpret the results obtained. Such a behavior was observed by Kirillova et al.^[23] for the sample containing 50 mol% TiO_2 quenched from 2458 to 2533 K.

As discussed above, the experiments in an He atmosphere revealed a decrease in temperatures. Thus, the calculations performed at $p(\text{O}_2) = 1 \cdot 10^{-2.5}$ bar are compared with the obtained experimental results in Fig. 4a. The selection of oxygen partial pressure for calculations is based on the results of Dilner et al.,^[52] where consistency between calculations and DTA measurements performed in the same device was found. According to the calculations, a decrease in the temperature of a monotectic reaction to 2025 K at $p(\text{O}_2) = 1 \cdot 10^{-2.5}$ bar was found. The eutectic temperature calculated at $p(\text{O}_2) = 1 \cdot 10^{-2.5}$ bar is also 23 K lower than that calculated in air. A similar temperature shift (20 K) for heating in air and in He was observed experimentally (see Fig. 1a). The agreement between calculations and the DTA results in this case is good.

Stolyarova and Lopatin^[56] measured the activity of SiO_2 in the BaO – TiO_2 – SiO_2 system at 1900 K using high-temperature differential mass spectrometry. The activity of SiO_2 in the TiO_2 – SiO_2 system at 1900 K for TiO_2 – SiO_2 1:1 is only available. The calculated activity of SiO_2 (in relation to the liquid state) in the TiO_2 – SiO_2 system at 1800 and 1900 K at $p(\text{O}_2) = 0.21$ bar is compared with the experimental data in Fig. 4b. The experimental activity at 1900 K is well reproduced in this work.

5.3.2 The Ternary Al_2O_3 – TiO_2 – SiO_2 System

Using the assessed thermodynamic parameters from the binary systems, an interpolation was first performed. However, the interaction parameters were introduced into the mullite, pseudobrookite, and liquid descriptions to fit

Fig. 5 Isothermal section of the Al_2O_3 – TiO_2 – SiO_2 system determined experimentally^[4](left) and calculated (right) at $p(\text{O}_2) = 0.21$ bar and **a** 1722 K, **b** 1747 K, and **c** 1792 K

experimental data.^[4,17,22,54,55] The derived database is presented in Table 4. Using the derived Al_2O_3 – TiO_2 – SiO_2 thermodynamic description, the calculated isothermal sections of the Al_2O_3 – TiO_2 – SiO_2 system at 1486, 1722, 1747, and 1792 K are shown in Fig. 5 along with the experimental results^[4] indicating a good consistency despite the below-mentioned shortcomings.

Data on the solid-state transformation and invariant equilibria on the liquidus of the Al_2O_3 – TiO_2 – SiO_2 system

measured by DTA and SEM/EDX^[4] were accounted. Assuming that there is no solubility of other components in corundum Al_2O_3 , the phase was modeled as stoichiometric. Limited solubilities in rutile TiO_2 and cristobalite SiO_2 were observed in the experimental work,^[4] however they were not modeled in this work due to the lack of reliable data. The evident solubility in C- SiO_2 may be explained by the experimental difficulty of reaching equilibrium in the SiO_2 -rich region of the ternary system caused by the high

viscosity. Parameters describing ternary extension of mullite and pseudobrookite were optimized based on the composition measurements^[4,55] However, an attempt to get a wider ternary extension of the homogeneity range of mullite leads to the solid-state reaction $\text{C-SiO}_2 + \text{Al}_2\text{TiO}_5 \leftrightarrow \text{Al}_6\text{Si}_2\text{O}_{13} + \text{TiO}_2$ becoming inconsistent with the experimental results.^[4] It should also be noted that even if the ternary extensions of mullite and pseudobrookite are not considered in the calculations, the solid-state reaction does not occur, and the low-temperature assemblages are stable up to the solidus temperatures that leads to invariant reactions on liquidus inconsistent with the experimental

Fig. 6 Calculated liquidus projection of the $\text{Al}_2\text{O}_3\text{--TiO}_2\text{--SiO}_2$ system at $p(\text{O}_2) = 0.21$ bar. The enlarged area schematically shows the position of the monovariant lines, since they are in fact very close to each other

data. Therefore, the Gibbs energy of the pseudobrookite phase was adjusted to be more stable than mullite to keep the solid-state reaction. This was the reason for the widespread extension of pseudobrookite into the ternary system and the negligible or even absent extension of mullite when pseudobrookite Al_2TiO_5 is thermally stable (above 1552 K^[7]). It should be noted that such discrepancy with the experimental data could be explained by the fact that the used thermodynamic descriptions of the binary Al_2O_3 – SiO_2 and Al_2O_3 – TiO_2 systems are not mutually consistent. Since some thermodynamic parameters describing the Al_2O_3 – SiO_2 and Al_2O_3 – TiO_2 systems were accepted unchanged, the conditions for optimization of newly obtained parameters were limited. In this case, a possible way to improve the reproduction of experimental data is to re-assess the parameters for the Al_2O_3 – SiO_2 and/or Al_2O_3 – TiO_2 systems. However, changing of these binary systems will most likely lead to inconsistencies in previous descriptions in which these systems have already been used. Therefore, the current thermodynamic description is used, however further re-optimization is considered to be necessary.

The complex description of the liquid phase was necessary to fit the parameters of melting relations determined recently.^[4] The results on the liquid immiscibility obtained in this work were also considered. Given the experimental data on liquidus, the ternary mixing parameters were optimized for the liquid phase (see Table 4). The calculated liquidus surface is presented in Fig. 6, whereas the calculated temperatures and compositions of invariant reactions are presented in Table 5 along with the experimental data. The agreement with the experimental data^[4] is relatively good and the calculations indicate the same character of the

Table 5 Invariant reactions in the Al_2O_3 – TiO_2 – SiO_2 system

Reaction	Type	Temperature, K	Composition, mol%			References
			Al ₂ O ₃	TiO ₂	SiO ₂	
SiO ₂ + Al ₂ TiO ₅ ↔ Al ₆ Si ₂ O ₁₃ + TiO ₂	<i>U</i> , transitional	1743				Exp., 4
		1743	35.9	27.8	36.3	Calc., this work
L ↔ TiO ₂ + SiO ₂ + Al ₂ TiO ₅	<i>E</i> , eutectic	1750	3.6	12.6	83.8	Exp., 4
		1761.6	7.86	14.74	77.38	Calc., this work
		1743	4.7	10.9	84.4	17
L + Al ₆ Si ₂ O ₁₃ ↔ SiO ₂ + Al ₂ TiO ₅	<i>U</i> ₁ , transitional	1779	8.9	14.1	77.0	Exp., 4
		1762.2	7.84	14.61	77.53	Calc., this work
		1753	5.2	10.0	84.8	17
L + Al ₂ O ₃ ↔ Al ₆ Si ₂ O ₁₃ + Al ₂ TiO ₅	<i>U</i> ₂ , transitional	2007				Exp., 4
		2006	39.5	27.2	33.9	Calc., this work
		1983	43.3	34.1	22.6	54
		2000				55

invariant reactions. The calculated critical point of the miscibility gap is at the composition $5.2\text{Al}_2\text{O}_3\text{--}62.1\text{TiO}_2\text{--}32.7\text{SiO}_2$ (in mol%), which reproduces well the experimentally observed value of 3.8 mol% Al_2O_3 discussed above.

6 Conclusion

Phase equilibria in the $\text{TiO}_2\text{--SiO}_2$ system were studied using DTA and SEM/EDX, and the miscibility gap in liquid was observed. Moreover, the miscibility of the liquid in the $\text{Al}_2\text{O}_3\text{--TiO}_2\text{--SiO}_2$ system was studied at 1013 K in air, which demonstrated shrinkage of the miscibility gap at 3.8 mol% Al_2O_3 .

The CALPHAD approach was applied to derive the thermodynamic descriptions of the $\text{TiO}_2\text{--SiO}_2$ and $\text{Al}_2\text{O}_3\text{--TiO}_2\text{--SiO}_2$ systems which are suitable for calculation of the phase diagrams in air conditions. However, including Ti^{+3} in the description of solid phases requires further experimental studies at low oxygen partial pressures, whereas Ti^{+3} was only considered in the liquid phase. The mullite and pseudobrookite phases were modeled within the compound energy formalism. For the liquid phase, the two-sublattice partially ionic model was applied. The present description reproduces the recent experimental data for the solid-state reaction $\text{C-SiO}_2 + \text{Al}_2\text{TiO}_5 \leftrightarrow \text{Al}_6\text{Si}_2\text{O}_{13} + \text{TiO}_2$ and liquid immiscibility, although reproducing of the solid-state reaction required the introduction of a rather extended ternary solubility in the Al_2TiO_5 phase which was not observed experimentally. The calculated isothermal sections and liquidus projection are reasonably consistent with the experimental data.

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