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ScienceDirect
Journal of the European Ceramic Society 34 (2014) 4053–4058
www.elsevier.com/locate/jeurceramsoc

Phase equilibria study of K–O–Si system in equilibrium with air

G. Akdogan[a,b], H. Johto[b,1], P. Taskinen[b,*]

[a] *University of Stellenbosch, Department of Process Engineering, Private Bag X1, Matieland 7602, South Africa*
[b] *Aalto University, School of Chemical Technology, Metallurgical Thermodynamics and Modelling Research Group, Espoo, Finland*

Received 21 February 2014; received in revised form 30 April 2014; accepted 5 May 2014
Available online 13 June 2014

Abstract

The binary phase diagram in the silica rich corner of K–O–Si system in equilibrium with air has been studied at temperatures between 770 °C and 1500 °C. Equilibration at high temperature in an appropriate containment material of pure silica, followed by rapid quenching and measurement of phase structures and assemblages using SEM-EDS confirmed by an electron probe X-ray microanalysis technique, was carried out to obtain the phase composition data at equilibrium. The results are in good agreement with previous experimental data and close to the earlier assessed phase equilibria at silica saturation.

Keywords: Thermodynamics; Slag; Melting point; Solubility

1. Introduction

Reliable thermodynamic descriptions for important systems, such as K_2O–SiO_2, can contribute to a better understanding of the chemical reactions taking place during the processes in glass, ceramic technology and extractive metallurgy. The binary sub-systems are also the key to computational multi-component phase diagrams.

In copper smelting silica sand is added as flux and this contains sodium and potassium oxides as impurities. During smelting these impurities are believed to play important role in viscosity and liquidus temperature variations. In property assessments the low-order system properties, typically binaries, are derived by extrapolation from high-order systems and may be very far from their true nature, due to lack of data from the binary and ternary systems of industrial importance. This highlights the need for modelling of slag equilibria and its properties in the copper smelting and refining conditions. The thermodynamics of selected copper smelting slags with impurity components, i.e. K, and Na, becomes vital. Therefore, as an important part of the copper smelting slags, silica rich side of the K_2O–SiO_2 binary is of particular interest.

This binary system also has applications in combustion of biomass fuels in particular; the concentrations of potassium in some agricultural fuels considerably exceed those in coal and other more traditional fuels. Potassium catalysed pyrolysis has a profound influence on the char formation stage; generally increasing the char yields. The presence of potassium has a significant influence on the rates and profiles of evolution of gas components generated during the pyrolysis processes.[1]

According to Nordin,[2] high potassium contents can have the effect of lowering the melting point of the ash or bed material, thereby enhancing the ability of deposit formation and bed sintering. In view of the fact that the bed material is composed mainly of quartz particles, the formation of phases rich in potassium silicates is likely to play an important role in bed sintering when combusting agricultural biomass fuels.

The equilibrium diagram in the composition range from K_2SiO_3 to SiO_2 was first measured by Kracek et al.[3,4] by quenching techniques. Melting points of K_2SiO_3, $K_2Si_2O_5$ and $K_2Si_4O_9$ were reported as 976, 1045, and 770 °C, respectively. Four eutectics were reported at 780, 742, 769 and 767 °C at 45.5, 67.6, 72.5 and 73.6 wt% SiO_2 for K_2SiO_3–$K_2Si_2O_5$,

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[*] Corresponding author. P.O. Box 16200, FI-00076 Aalto, Finland. Tel.: +358 40 501 7411.
E-mail address: pekka.taskinen@aalto.fi (P. Taskinen).
[1] Present address: Boliden Harjavalta Oy, FI-29200 Harjavalta, Finland.

http://dx.doi.org/10.1016/j.jeurceramsoc.2014.05.007

$K_2Si_4O_9$–$K_2Si_2O_5$, Quartz-$K_2Si_4O_9$, and Tridymite–$K_2Si_4O_9$, respectively.

The K_2O–SiO_2 system has also been thermodynamically analysed by Eliezer et al.[5] who used $KO_{0.5}$ and SiO_2 as the species and a Redlich–Kister polynomial for representing the thermodynamic excess properties of the liquid phase. Their description does not extend to solutions richer in potassium oxide than 55 mol% K_2O, and a phase diagram is given for the section SiO_2–$K_2Si_2O_5$. Kim and Sanders[6] used a sub-regular model with K_2O and SiO_2 as components to describe the excess Gibbs energy of the liquid phase. The interaction parameters of the liquid phase were obtained solely from the liquidus curve of silica and estimates of the critical temperature and composition of the metastable liquid–liquid miscibility gap. The phase diagram was roughly outlined and thermodynamic properties of solid compounds used in the calculations were not given. This makes comparisons with experimental data difficult.

The thermodynamic data for the binary system, including its liquid and solid phases, were assessed and optimised by a CALPHAD-type thermodynamic fitting of the binary data in the K_2O–SiO_2 system by Allendorf and Spear[7]. The basic data on phase formation, melting point, eutectic compositions, and liquidus curves were obtained primarily from earlier work,[8,9] and an associate model with four associates as species was used for the liquid silicate phase. The predicted melting points and eutectic compositions are given in the paper along with the values reported by Wu et al.[9] While the liquidus temperatures were in exact agreement, the eutectic temperatures showed appreciable differences when compared with the assessed values obtained by Wu et al.[9]

Zaitsev et al.[10,11] constructed the equilibrium diagram for the K_2O–SiO_2 system based on the activities of SiO_2 and K_2O in K_2O–SiO_2 melts as calculated from a thermodynamic model of silicate melts. The model was developed from the theory of associated solutions[12]. An assumption of formation of Si–O cluster groups of arbitrary sizes and spatial configurations was presumed. Thermodynamic functions of formation of solid compounds and phase equilibria data were taken from 11 and 3, respectively. The model approximates the concentration and temperature dependencies of thermodynamic properties of the K_2O–SiO_2 melts as well as phase equilibria. In addition, this model takes into account the structure of melts and changes caused by variation of the concentrations of the components. Melting of the intermediate compounds $K_2O{\cdot}SiO_2$ and $K_2O{\cdot}2SiO_2$ is congruent, but incongruent in the case of $K_2O{\cdot}4SiO_2$. Correspondingly, two eutectic and the peritectic ($K_2O{\cdot}4SiO_2$, SiO_2, and liquid) points were presented in the join.

Forsberg[13] on the other hand developed a new thermodynamic description of the K_2O–SiO_2 system using $KSi_{0.25}O$ ($1/4K_4SiO_4$) and SiO_2 as species for the liquid phase. With respect to these components, the highly non-ideal interactions of potassium oxide and silica could be described by using only three temperature-independent Redlich–Kister coefficients for the excess Gibbs energy of the liquid phase. This treatment allowed appropriate choice of species with respect to the variation of thermodynamic properties with composition, thus the excess Gibbs energy of the liquid phase was described with a small number of parameters. In alkali silicate systems, this approach was further justified by the lack of experimental phase diagram and thermochemical information at high alkali oxide contents. The calculated phase diagram was in good agreement with the experimental liquidus data points from Kracek et al.[3]

Wu et al.[9] reported an optimisation of the system using the modified quasichemical model (MQSM)[14] for the liquid phase based upon the phase diagram studies of Kracek et al.[3,4] Their melting points of the compounds are close to the measured values but the eutectic temperatures as well as enthalpies of the compounds are different. According to Saulov[15], the most difficult liquid binary oxide solutions to optimise are those, in which one mixed component is a basic oxide, while the other is an acidic oxide. Liquids in such systems are usually characterised by very strong short-range ordering. One of the binary system with very strong short-range ordering is the system K_2O–SiO_2[1]. Large negative values of the Gibbs energy of the quasichemical reaction are usually required to fit available experimental data in such systems. Furthermore, strong compositional dependencies of the Gibbs energy of the quasichemical reactions are usually used.

The feature was originated from the described non-smoothness of the Gibbs energy of mixing expressed by the MQSM at the composition of maximum ordering. Previously suggested values[9] of the parameters of the MQSM were adjusted[15] to maintain acceptable fit of the experimental liquidus data reported by Kracek et al.[3] and the activities of K_2O measured by Zaitsev et al.[11], Frohberg et al.[16], Ravaine et al.[17], and Steiler[18]. Saulov demonstrated that the compound whose composition coincides with that of maximum ordering in the liquid phase was required for reasonable representation of phase equilibria in the vicinity of this composition. Limiting slopes of the liquidus curve of the compound were also calculated. The thermodynamic model for the system K_2O–SiO_2 was re-optimised. The new parameters of the model by Saulov[15] were found to fit the available experimental data and represent reasonably the phase relations for the entire compositional range.

Romero-Serrano et al.[19] employed the structural model by Lin and Pelton[20,21] for the liquid. The thermodynamic description of the system was optimised by Yazhenskikh et al.[22] with the modified associate species model[23]. Yazhenskikh et al.[22] reported the set of model parameters that reproduce the available experimental data and enable representing reasonable phase relations for the entire phase diagram. In the model they used three associates for describing the molten oxide phase. The most recent assessment extending over the whole compositional range has been made by Zhang et al.[24], using a two-sublattice model[25] with SiO_4^{4-} and SiO_2 associates in the anion sublattice.

Wu et al.[9], Zaitsev et al.[12] as well as Romero-Serrano et al.[19] supplied the calculated phase diagram only for the compositional range with high silica content.

In the present study, the phase equilibria of the K–O–Si system in equilibrium with air have been investigated to revisit the results reported by previous researchers as well as to confirm the positions of Quartz, Tridymite and Cristobalite liquidus. This work is part of the efforts to consolidate experimental phase equilibria data from K_2O–SiO_2 towards characterisation