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STUDY OF PHASE EQUILIBRIA IN SALT AND OXIDE SYSTEMS BY THE OSCILLATION METHOD OF PHASE ANALYSIS

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The phase equilibria data are presented for two binary systems (LiCl–KCl and K_2O–Nb_2O_5) which are received by thermal and oscillation method of phase analysis.

Keywords: *liquidus, oxides, phase diagrams, phase equilibria, salts*

Introduction

Phase equilibria in binary systems are attracting attention for theoretical and experimental studies, because of their practical importance in technical applications and science. In the same time single oxide systems do not investigated well enough in comparison with well studied metal or salt systems. In this paper we are presenting our results for salt (LiCl–KCl) and oxide (K_2O–Nb_2O_5) binary systems. Developed by us [1] oscillation method of phase analysis (OPA) was used for measurements.

Experimental

Oscillation method of phase analysis scheme involves a thin plate which is placed on long rod dipped into the investigated medium. A process of plate oscillation in Newton liquid is studied. A harmonic driving force activates a plate in a frequency interval from 70 to 250 Hz. An equation solution for thin plate movement in viscous unbounded medium is analyzed in [1] in more detail. Solution variants which can be realized easier are chosen for study. Crucible with melt and heating furnace are movable relative the probe. It gives a set-up operational flexibility for experiment providing.

A scheme of the OPA cell is shown in Fig. 1. That construction can be used for measurement of the melt viscosity and phase equilibria study up to 2000°C under atmosphere of air, vacuum, or inert gases [1–6]. A tube for melt stirring by gas bubbling is dipped in a sample under investigation. It makes a uniform sample to measure melt parameters by the probe (thin plate) and thermocouple.

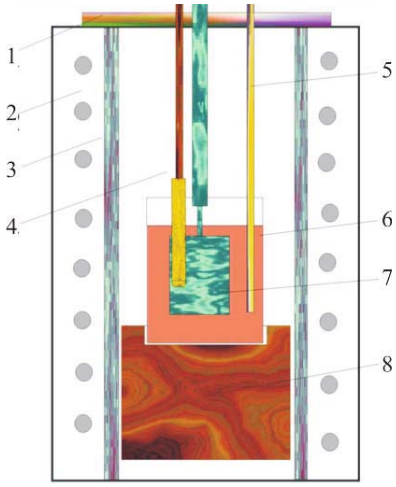

Fig. 1 Schematic diagram of the OPA measuring system: 1 – ceramic lid, 2 – furnace, 3 – ceramic tube, 4 – thermocouple in platinum jacket, 5 – platinum tube for air flow, 6 – the sample in platinum crucible, 7 – the probe (thin platinum plate), 8 – thick ceramic support

The idea of OPA method is as follows. The amplitude of the probe oscillation is usually considered as a measure of homogenous medium resistance. The resistance of melt rises sharply and the amplitude of the probe oscillation decreases (Fig. 2) due the different environmental influences (temperature, magnetic field, ultrasound, etc.) on the medium under study (for example, the solid phase is formed under cooling). An effect is more significant when the crystals appear on the probe surface. Obviously, the amplitude of the probe oscillation depends on quantity, size, and shape of the crystals that appear on the probe surface, which allows us to quantitatively estimate the crystallization rate.

Crystals are dissolving when the temperature of the sample increases. A melt resistance decreases and

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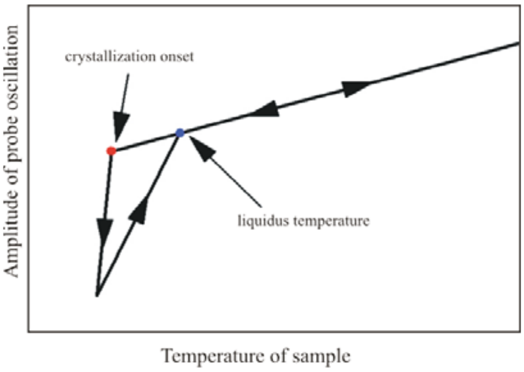

Fig. 2 Typical oscillogram (the oscillation amplitude of probe *vs.* temperature)

oscillation amplitude rises. However, if the heating rate is slow enough, the heating process can be considered as thermodynamically equilibrium. In some experiments when phase equilibria are studying for oxide systems, heating rate was less than 1°C h^{-1}. Amplitude of the probe oscillations can be restored to initial value for given temperature by heating which was before crystallization, when crystals formed on the oscillated plate are fully dissolved.

As it is shown in our analysis and experiments [2], the sensitivity of solid phase formation on the probe may be as much as 10^{-5} of a total sample volume which can be in from 30 to 50 cm^3 that is two-three orders more than sensitivity of the other analytical methods. Thermal analysis is carried out concurrently with OPA in one experiment because our set-up has thermocouple dipped in the melt.

A broad experience of OPA using for phase equilibria measurements when studying different systems (metal, oxide and salts) has revealed the essential advantages of OPA. Our studies revealed that 14 parameters of liquid phase and processes of crystallization and melting could be under quantitative monitoring. These parameters can be listed such as a melt viscosity; temperature of the stable and metastable liquidus, temperature of crystallization onset and super-cooling before crystallization onset, temperature of melting end (super-heating); type of melt solidification, i.e. crystallization or vitrification, type of liquefies of the solidified sample such as melting or glass softening, liquation effects due to gravitation and crystallization separation, effects of ‘memory’, when composition of the crystallized phase depends on thermal prehistory of sample both solid and liquid, relative crystallization and melting rate, time estimation to reach equilibrium between crystals and melt in the processes of crystallization and melting, time taken for spontaneous crystallization onset at given conditions, estimation of the crystallized mass, sampling for the determination of the composition and growth shape of the crystallized phases and compounds.

Crystallization and/or melting processes of a solid phase generate significant (up to some percent) composition heterogeneities ranged on a height and radius of the sample as it is shown in our experiments. These heterogeneities are appeared in result of gravity liquation and temperature gradient. Crystallization and liquation effects grow up as the melt viscosity decreases. Sample composition does not get equilibrium for a long time even sample overheating over melting temperature reached several hundreds degrees. The sample homogeneity can be readily obtained by stirring, for example, by gas (helium, nitrogen or air) bubbling (Fig. 1). OPA method is very powerful instrument for investigation of phase equilibria in multi-component systems and it can be useful both for study of liquidus [7] and processes of melting and thermal decomposition of solid [8] as it is following from our experiments.

Results and discussion

The system LiCl–KCl

The experiments are carried out on nitrogen atmosphere in the platinum crucible. The homogeneity was reached by bubbling of nitrogen via platinum pipe. The precise data on liquidus temperature is obtained by oscillation method of phase analysis (OPA) on 16 compositions from 0 to 100 mol% KCl (Fig. 3) and eutectic temperature was determined by thermal analysis (TA). The admissible error was not more than ±2°C. This system has a simple eutectic [9]. Our data illustrate eutectic point temperature of 352°C and composition of 41.8 mol% KCl. Melting temperature of components are very close to a literature data (see, for example [10]), i.e. 607°C for LiCl and 774°C for KCl.

The system K_2O – Nb_2O_5

The measurements were carried out on air in platinum crucible. The homogeneity was reached by bubbling of air via platinum pipe. There were investigated 35 compositions from 24.9 to 66.4 mol% Nb_2O_5 (Fig. 4). The admissible error was ±2°C.

Qualitatively, our phase diagram is well consistent with data [11]. However, the discrepancy in the congruent-melting temperature of $3K_2O{\cdot}Nb_2O_5$ is greater than 200°C. Other invariant equilibria and the congruent-melting temperatures of compounds differ less significantly. For the compounds formed in the region from 25 to 30 mol% Nb_2O_5 such significant discrepancy in the melting temperatures is likely

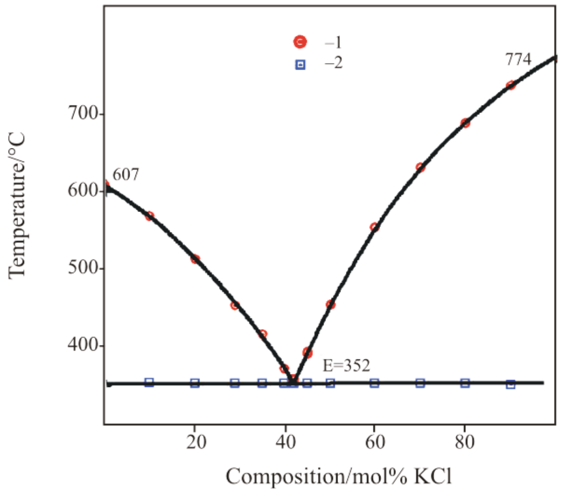

Fig. 3 Phase diagram of system LiCl–KCl. 1 – data obtained by OPA, 2 – data obtained by thermal analysis

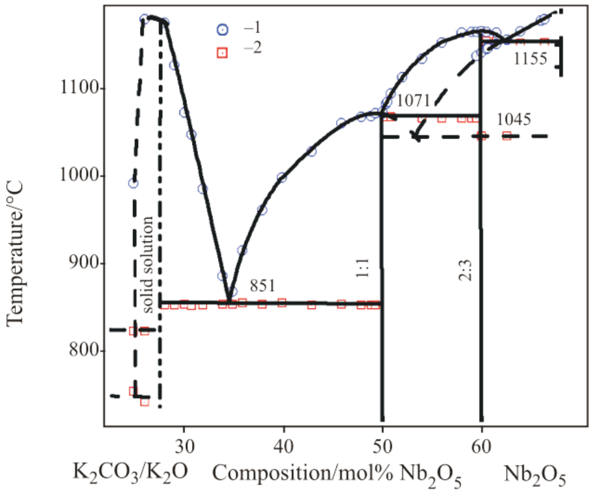

Fig. 4 Phase diagram of system $K_2O–Nb_2O_5$. 1 – data obtained by OPA (solid line is stabile liquidus and dash line is metastable liquidus), 2 – data obtained by thermal analysis

because the full elimination of carbon dioxide during the synthesis in this region of samples containing more than 28 mol% Nb_2O_5 occurred only after more than 2 h annealing at temperatures above 1000°C. If samples do not be heated above 950°C during preparation, potassium carbonate exists in the melted samples in the same fashion at temperatures from 900 to 950°C (the carbonate concentration in the melt based on CO_2 was about fifth part of initial concentration). The secondary crystallization of the sample started during subsequent heating or long exposure at 950–1000°C in process of carbon dioxide elimination from the melt. We would stress that in all our experiments the liquidus temperature are determined both OPA and TA methods usually.

In samples with high potassium oxide (carbonate) concentrations, CO_2 was not fully removed after one day exposure at 1200°C. Thus, the region with less than 28 mol% Nb_2O_5 is part of the $K_2O–K_2CO_3–Nb_2O_5$ system. Weighing the sample of composition $3K_2O{\cdot}Nb_2O_5$ after long annealing at 1200°C, we found that, while preparing this sample under the specified conditions, we have removed a three-fourths of carbon dioxide which was contained in the batch. Therefore, there is some uncertainty in the results obtained for the region bounded by vertical dashed lines in Fig. 4. Moreover, thermal effects at 820 and 760°C are related to the $K_2O–K_2CO_3–Nb_2O_5$ system, that is well agrees with research [11].

Carbon dioxide is fully eliminated during preparation from samples containing more than 28 mol% Nb_2O_5, as monitored by weighing; a well-defined TA thermal reaction at 851°C which is attributed to eutectic between $3K_2O{\cdot}Nb_2O_5$ and $K_2O{\cdot}Nb_2O_5$ (Fig. 4). This temperature well agrees with published result [11]. Nevertheless, this thermal effect is absent in samples with small quantities of niobium oxide (Fig. 4), that can be explained by existence of solid solution in this region of composition.

The peritectic temperature obtained for potassium metaniobate $K_2O{\cdot}Nb_2O_5$ in our experiments (1071°C) is higher than in [11] (1049°C) or [12] (1062°C). According to our data, the compound $2K_2O{\cdot}3Nb_2O_5$ melts congruently at 1166°C and forms the eutectic with the compound $K_2O{\cdot}3Nb_2O_5$ at 1155°C. The spontaneous crystallization of $2K_2O{\cdot}3Nb_2O_5$ is started usually when undercooling was more than 400°C. The primary crystallizing phase was identified as $K_2O{\cdot}3Nb_2O_5$ under the standard cooling conditions (5°C min^{-1}) in the region with more than 59 mol% Nb_2O_5 (Fig. 4). The compound $K_2O{\cdot}3Nb_2O_5$ crystallized under small undercooling (5°C) relative to the metastable extension of the liquidus line of this phase. A peak was observed at 1045°C in the DTA heating curves near the $2K_2O{\cdot}3Nb_2O_5$ composition in several experiments. That peak was likely due to the metastable eutectic between $K_2O{\cdot}Nb_2O_5$ and $K_2O{\cdot}3Nb_2O_5$ (Fig. 4). The temperature of this eutectic reaction is close to the peritectic decomposition temperature of potassium metaniobate (1049°C) given in [11].

It was necessary either to keep the sample above the metastable liquidus temperature of $K_2O{\cdot}3Nb_2O_5$ for about 20 till 30 min in order to crystallize $2K_2O{\cdot}3Nb_2O_5$ melted samples containing more than 59 mol% Nb_2O_5. The primary crystallizing phase is $K_2O{\cdot}3Nb_2O_5$ if the samples are cooled at the standard rate (5°C min^{-1}).

Conclusions

The oscillation method of phase analysis designed by us makes it possible to obtain the extensive reliable precise data on phase transitions in oxide and salt binary systems. It is actually information for optimization of single crystals growth technology and glass synthesis, which is important for science and engineering.

Acknowledgements

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