Phase diagram of the ternary system KBF_4—NaCl—KCl

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Dedicated to Professor RNDr PhMr S. Škramovský, DrSc, on his 75th birthday

The system KBF_4—NaCl—KCl has been studied by means of the thermal analysis and the phase equilibria have been determined in the binary systems KBF_4—NaCl and KBF_4—KCl, and in the ternary system KBF_4—NaCl—KCl in the composition range which is interesting with respect to the electrolytic boriding. The investigated ternary system was found to be a simple eutectic system, the coordinates of the ternary eutectic point being: 66.5 mole % KBF_4, 28.5 mole % NaCl, 5 mole % KCl and 427°C.

The experimental results were compared with the data determined by thermodynamic calculations. The data based on the theory of conformal ionic solutions are in good agreement with the experimental values.

Методом термического анализа была изучена система KBF_4—NaCl—KCl. Были определены двойные системы KBF_4—NaCl и KBF_4—KCl. Тройная система изучалась в концентрационной области интересной с точки зрения электролитического покрытия бором. Исследованная система имеет простой эвтектический характер. Координаты эвтектической точки: 66,5 мол.% KBF_4, 28,5 мол.% NaCl, 5 мол.% KCl и 427°C.

Результаты экспериментов были сопоставлены с данными термодинамических расчетов. Данные, полученные из теории конформных ионных растворов, находятся в хорошем согласии с экспериментальными значениями.

The study of the phase equilibria in the ternary system KBF_4—NaCl—KCl appears to be interesting mainly with regard to a possible application of the respective melts as electrolytes in the electrolytic boriding of steel bases. From the view-point of the technology of the thermal treatment of these materials as low temperature of electrolysis as possible is required in order to prevent the negative influence of high temperature on the mechanical properties of the base metal. For this purpose the electrolytes with a relatively low temperature of primary crystallization, *e.g.*, the molten KBF_4—NaCl—KCl mixtures, seem to be the best suited.

The investigated system is a subsystem of the quaternary reciprocal system $Na^+, K^+ \| Cl^-, BF_4^-$ and it is bordered by the binary systems KBF_4—NaCl,

KBF_4—KCl, and NaCl—KCl. The binary system KBF_4—NaCl is a diagonal section of the above reciprocal system and its phase diagram has not been published so far. The value of the Gibbs energy of the exchange (metathetic) reaction

$$KBF_4(l) + NaCl(l) = NaBF_4(l) + KCl(l)\,, \qquad (A)$$

$\Delta G^0_{800\,K} \doteq 18$ kJ, appraised on the basis of thermodynamic data in [1, 2] and an analogy between KBF_4 and $NaBF_4$, indicates the stability of this diagonal.

The system KBF_4—KCl has been investigated by *Samsonov et al.* [3] who found it to be divided due to the formation of a congruently melting compound, $11KBF_4$ KCl, with a melting point 590°C into two simple eutectic systems: KBF_4—$11KBF_4$ KCl with an eutectic point at 4 mole % KCl, 96 mole % KBF_4 and 508°C, and $11KBF_4$ KCl—KCl with an eutectic point at 20.5 mole % KCl, 79.5 mole % KBF_4 and 470°C. However, from an analysis of the presented data as well as from our own experience it follows that the cited authors, instead of pure KBF_4, used most probably a mixture of KBF_4 and KBF_3OH which is formed according to [4] when the method of preparation described in [3] is used. The presence of impurities in the used KBF_4 is also indicated by the low melting temperature (530°C as compared to the tabelated value 570°C [1]). The analytic determination of boron content, which was used in the cited work in order to prove the purity of KBF_4, is unreliable with regard to the similar boron contents in both KBF_4 and KBF_3OH, which are 8.6 and 8.7 wt. %, respectively. Consequently, the phase diagram presented in [3] corresponds probably to a linear section in the ternary system KBF_4—KBF_3OH—KCl.

The phase equilibria in the system NaCl—KCl have been investigated quite recently by *Peschl* [5]. The system is characterized by unlimited miscibility in both liquid and solid phases and it has a minimum with coordinates: 50 mole % NaCl, 50 mole % KCl and 665°C.

The phase diagram of the ternary system KBF_4—NaCl—KCl has not been published so far.

Experimental

The phase equilibria in the ternary system KBF_4—NaCl—KCl were investigated by means of the thermal analysis. The samples (30 g) in a platinum crucible were lodged in the Degussit shaft of a resistance furnace. Temperature was measured by means of a PtRh10—Pt thermocouple which was calibrated on the melting temperatures of NaCl, KCl, and KNO_3. The cooling curves were recorded on an EZ-2 recorder at a cooling rate max. 2°C min^{-1}. The accuracy of the temperature readings was better than ±3°C.

Reagent grade KBF_4, NaCl, and KCl (Lachema, Brno) were used for the preparation of samples. Before being used, the chemicals were dried at 300°C for 2 hrs and kept in a desiccator.

The phase diagram of the ternary system is based on the experimentally determined phase diagrams of the bordering binary systems KBF_4—NaCl and KBF_4—KCl, and of the two linear sections led from the KCl corner of the composition triangle and intersecting the opposite side in points with 60 and 70

mole % KBF_4 contents, respectively. As to the system NaCl—KCl, the phase diagram presented by *Peschl* [5] was accepted. Considering the technical aspect, *i.e.* the possibility of application of the molten KBF_4—NaCl—KCl mixtures in the electrolytic boriding, the attention was focused on the KBF_4-rich region of the system limited by the isotherm at 550°C.

Results and discussion

The phase diagram of the bordering pseudobinary system KBF_4—NaCl is shown in Fig. 1. It is a simple eutectic system, the coordinates of the eutectic point being: 70 mole % KBF_4, 30 mole % NaCl and 430°C. The mildly S-shaped NaCl liquidus curve is characteristic of the stable diagonal sections of reciprocal systems. The experimental results are consistent with the results of the cryoscopic measurements [6] confirmed by a thermodynamic analysis which showed that the exchange reaction $KBF_4 + NaCl \rightleftarrows KBCl_4 + NaF$ proceeds in the investigated system only in the range of very low concentrations of potassium tetrafluoroborate while at concentrations over 1.5 mole % KBF_4 the equilibrium of the exchange reaction is shifted completely to the left.

The experimentally determined liquidus curves were compared with the "ideal" curves calculated using the LeChatelier—Schröder equation

$$\ln a_i = \frac{\Delta H_i^t}{R}\left(\frac{1}{T_i^t} - \frac{1}{T}\right), \qquad (1)$$

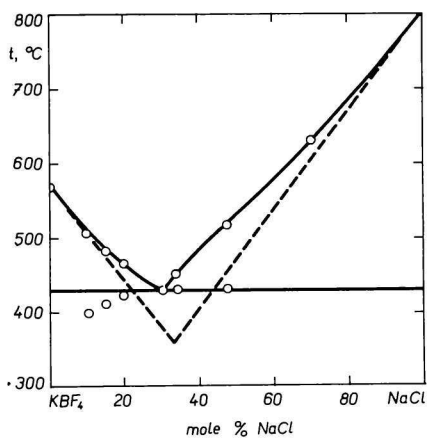

Fig. 1. Phase diagram of the quasi-binary system KBF_4—NaCl.
—— experimental; – – – – calculated according to eqn (*1*).

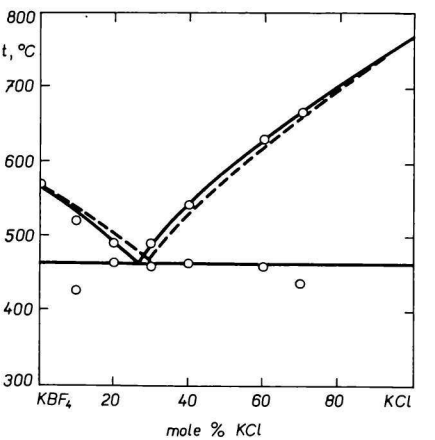

Fig. 2. Phase diagram of the binary system KBF_4—KCl.
—— experimental; – – – – calculated according to eqn (*1*).

where $a_i = x_i^2$ is the activity of the component i in the solution with the composition x_i; $\Delta H_i^f = \text{const}$ is the enthalpy of fusion of the component i with the melting temperature T_i^f; T is the temperature of primary crystallization of the respective mixture. The values of the enthalpy of fusion were taken from the tables [1]. As it is obvious from Fig. 1, the experimental liquidus curves exhibit a positive deviation from the course defined by eqn (*1*).

The phase diagram of the bordering system KBF_4—KCl is shown in Fig. 2. It is a simple eutectic system, the coordinates of the eutectic point being: 75 mole % KBF_4, 25 mole % KCl and 464°C. From a comparison of the experimental and calculated liquidus curves it follows that the system KBF_4—KCl differs only slightly from ideality.

Fig. 3 shows the phase diagram of the linear section with a constant molar ratio $KBF_4 : NaCl = 7 : 3$. It is obvious that this section represents a connection between the binary eutecticum and the opposite corner of the composition triangle, and that it passes through the ternary eutectic point.

Fig. 4 shows the phase diagram of the linear section with a constant molar ratio $KBF_4 : NaCl = 6 : 4$. No break which could be ascribed to the secondary crystallization was observed on the cooling curve of the sample containing 20 mole % KCl, most probably due to the small difference between the enthalpies of fusion of NaCl and KCl.

Fig. 5 shows the experimentally determined phase diagram of the ternary system KBF_4—NaCl—KCl. It is a system of a eutectic type with a large area of solid solutions of NaCl and KCl reaching probably up to *ca.* 55 mole % KBF_4. The

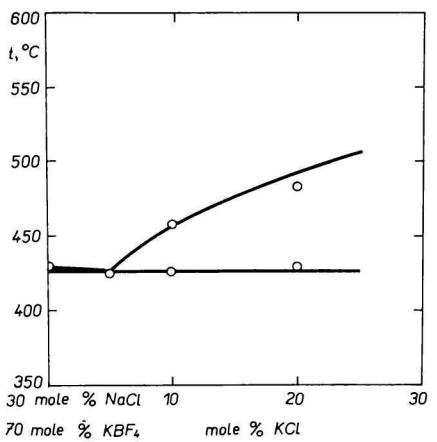

Fig. 3. Phase diagram of the linear section with a constant molar ratio $KBF_4 : NaCl = 7 : 3$.

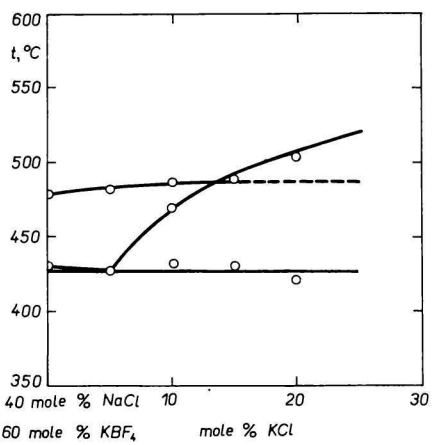

Fig. 4. Phase diagram of the linear section with a constant molar ratio $KBF_4 : NaCl = 6 : 4$.

coordinates of the eutectic point are: 66.5 mole % KBF_4, 28.5 mole % NaCl, 5 mole % KCl and 427°C.

So far, the phase equilibria in ternary systems were investigated mostly experimentally. Recently, a strong tendency may be observed to prognosticate the

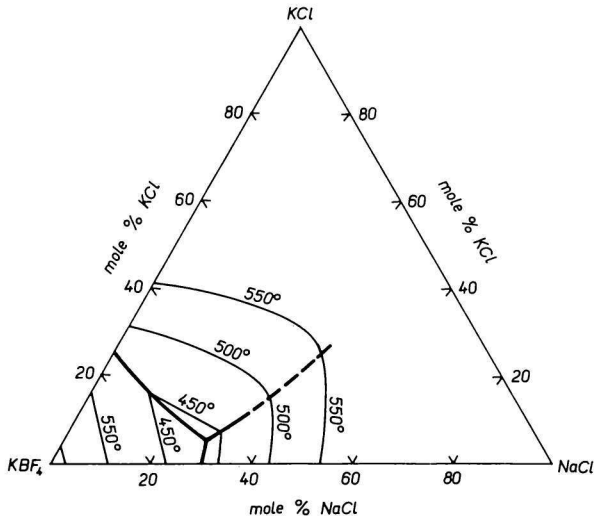

Fig. 5. Experimental phase diagram of the ternary system KBF_4—NaCl—KCl.

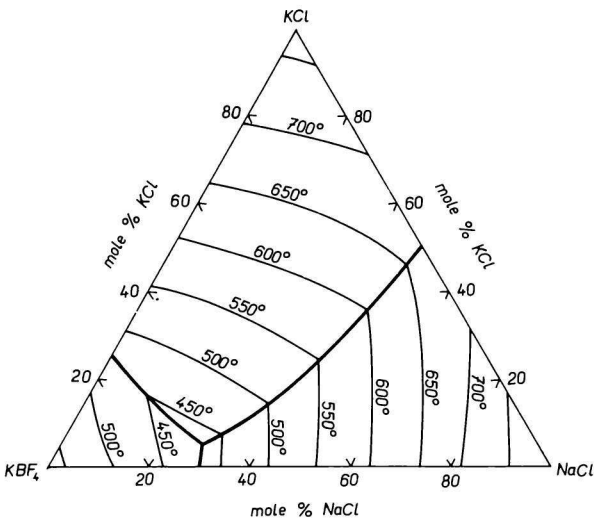

Fig. 6. Calculated phase diagram of the ternary system KBF_4—NaCl—KCl.

character and the form of the ternary liquidus on the basis of the available data for the corresponding binary systems. From among the different theories especially the theory of conformal ionic solutions has been successfully applied to the calculation of the phase equilibria [7]. The application of this theory to the molten salts mixtures resulted in a good agreement between the experimental and the calculated ternary liquidus in systems of various types [8—12]. This theory has been also applied to the calculation of the phase diagram of the system KBF_4—NaCl—KCl.

The ternary phase diagram calculated on the basis of the known data of the phase diagrams of the bordering binary systems is shown in Fig. 6. The standard ideal mixture as defined by *Haase* [13] has been chosen as a reference system for the calculation of the excess thermodynamic functions. The Gibbs free energy for the ternary system was obtained as a sum of the Gibbs free energies of the bordering binary systems. The calculation proceeding and the applied equations are described in [12]. The calculated coordinates of the eutectic point are: 67 mole % KBF_4, 28 mole % NaCl, 5 mole % KCl and 425°C.

In spite of the fact that the application of the theory of the conformal ionic solutions to systems containing a complex ion is more or less formal, there is a very good agreement between the calculated and experimental values of the coordinates of the ternary eutectic point as well as of the temperatures of primary crystallization of the ternary mixtures.

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