JOURNAL OF SOLID STATE CHEMISTRY **28**, 133–136 (1979)

Mechanism of the Solid State Reaction NaCl + KF → NaF + KCl

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Received May 19, 1978

The mechanism of the solid state displacement reaction NaCl + KF → NaF + KCl was investigated, employing diffusion couples (single crystals), in air at 550°C.

The product layer obtained was formed with NaF and (Na, K)Cl solid solution.

From cation concentration profiles, photometrically determined, for the NaCl|KF and NaCl|KCl systems after annealing at 550°C, and from X-ray diffraction analysis on product layer surfaces for the NaCl|KF system, it was possible to state that the overall process is governed by a cation–counterdiffusion mechanism.

A comparison between the diffusion coefficient evaluated through the rate constant and that calculated by means of the Boltzmann–Matano analysis for the system NaCl–KCl, allows one to deduce that the cations Na^+ and K^+ are transported in the (Na, K)Cl solid solution.

Introduction

The present paper, dealing with the kinetic study of the solid state displacement reaction NaCl + KF → NaF + KCl, is a part of a research undertaken on reactions of the same type between univalent metal halides (*1, 2*).

The overall process represents the metathetical reaction of the reciprocal ternary system Na, K/Cl, F (*3*), where the temperature minimum at which the liquid phase exists is 582°C and corresponds to a ternary eutectic, the only invariant point of the system. Moreover the reaction product KCl forms solid solutions with NaCl over the whole concentration range.

The kinetics were investigated at 550°C on the reacting system NaCl|KF using single crystal disks (K. Korth; diameter 8 mm, thickness 2 mm) cut parallel to the (100) plane. In every diffusion couple the reaction interface was marked with Pt powder.

The determination of the cations concentration profiles in the product layer (as a function of spatial coordinate) was carried out by means of a flame photometer (Corning EEL-100), while the trend of the X-ray diffracted intensity, pertinent to the principal reflection of the four components, was also determined as a function of the same coordinate.

Finally, for the system NaCl|KCl at 550°C, the chemical diffusion coefficient $\tilde{D}$ according to the Boltzmann–Matano analysis was estimated on the basis of the cation concentration profiles.

The techniques employed were already described (*2*).

Results and Discussion

Figure 1 reports, for the system NaCl|KF (after 168 hr at 550°C), the concentration m (m = cation mass per mass unity of analyzed

0022-4596/79/040133-04$02.00/0

Printed in Great Britain

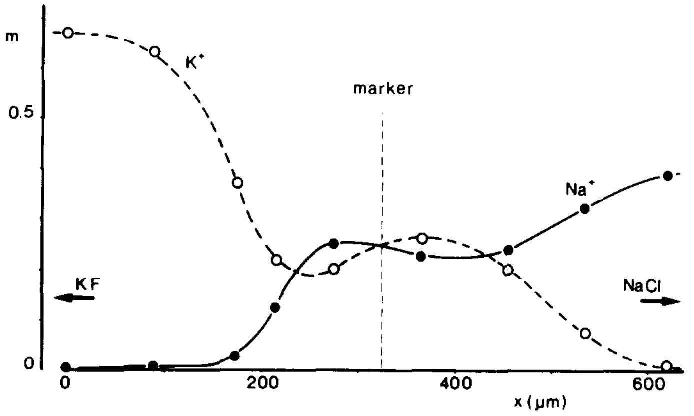

FIG. 1. Cation concentration profiles of the NaCl|KF reacting system. ($T = 550°C$; $t = 168$ hr.)

sample) of Na^+ and K^+ as detected in the product layer; the m values were determined photometrically on sections obtained by progressively slicing off substance from the annealed couple.

From the concentration trend one may assume that the reaction products NaF and KCl preferentially grew in two layers at both sides of the original interface (as individuated by marker position), the former consisting mainly of NaF, the latter of KCl, in contact with KF and NaCl respectively.

In order to single out the phases present in the product layer, X-ray diffraction measurements at room temperature on a couple NaCl|KF immediately after the thermal treatment (168 hr at 550°C) were also carried out.

Figure 2a reports the (200) peak intensities (arbitrary units) of KF, KCl, NaF and

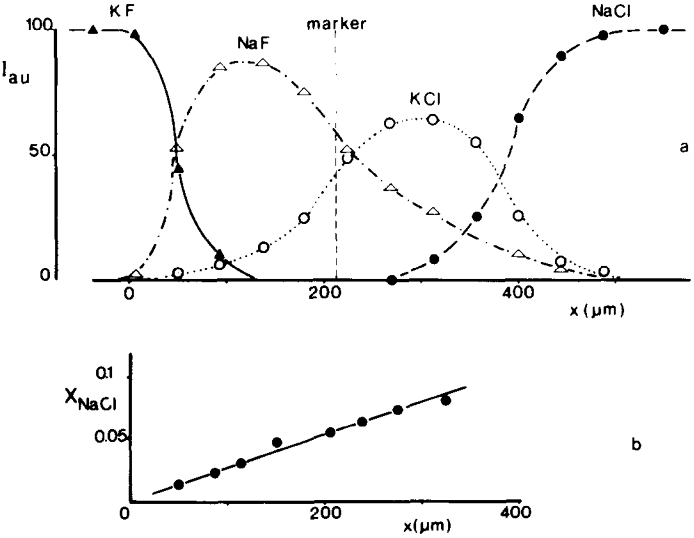

FIG. 2. (a) NaCl|KF diffusion couple after 168 hr at 550°C; trend of the intensities (at 25°C) of the (200) KF, KCl, NaF and NaCl reflections. (b) NaCl concentration in the residual (Na, K)Cl solid solution for $0 < x < 325$ μm.

NaCl as a function of the spatial coordinate.

From an accurate analysis of the angular positions of the KCl reflections on several sections it was possible to individuate a residual solid solution (K, Na)Cl, the relevant composition of which (in molar fraction of NaCl, X_{NaCl}) was evaluated by means of the Vegard additivity rule (*4*) for $0 < x < 325$ μm (Fig. 2b).

From Fig. 2a it is apparent that the reaction products are present in the whole observed thickness, even if they show intensity maxima in two distinct regions of the product layer, in agreement with the photometrical results.

Therefore it can be assumed that the overall process develops through a cation counter-diffusion.

From Figs. 2a and 2b it can also be deduced that the reagent NaCl too is present through the whole layer: for $0 < x < 275$ μm only as a component of the solid solution with KCl and for $x > 275$ μm also as demixing product of the solution itself.

In order to obtain more information on the reacting system, photometric determinations on the couples NaCl|KCl after annealing at 550°C for 42 to 168 hr were performed; the resulting molar fractions of the components are related to the coordinate $\lambda = x\sqrt{t}$ (cm $\mathrm{sec}^{-1/2}$) as shown in Fig. 3.

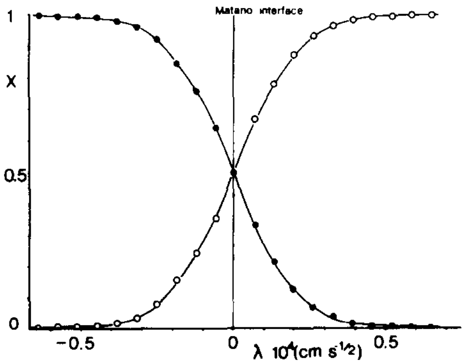

FIG. 3. Diffusion profiles of NaCl|KCl system. The molar fractions are plotted against $\lambda = x/\sqrt{t}$ ($T =$ 550°C). Open circles: KCl data; filled circles: NaCl data.

The composition dependent chemical diffusion coefficient $\tilde{D}$ can be now calculated by means of the Boltzmann–Matano equation (*5*)

$$\tilde{D}(c) = -\frac{1}{2}\left(\frac{\mathrm{d}\lambda}{\mathrm{d}c}\right) \int_{c_0}^{c} \lambda \, \mathrm{d}c$$

with the following initial conditions:

$$c = c_0 \qquad \text{for } \lambda = -\infty$$

$$c = 0 \qquad \text{for } \lambda = +\infty$$

and the additional condition:

$$\int_{c_0}^{0} \lambda \, dc = 0.$$

The calculated $\tilde{D}$ values, the trend of which is reported in Fig. 4, range between $1.5 \cdot 10^{-10}$ and $1.9 \cdot 10^{-10}\ \mathrm{cm^2\,sec^{-1}}$ with a maximum at $X_{\mathrm{KCl}} \cong 0.35$. A similar behavior was observed for the system KCl–RbCl by Schmalzried and coworkers (*6*, *7*) who correlated the maximum in the $\tilde{D}$ values with a corresponding maximum in the curve of cation vacancy concentration, ($c_{\mathrm{v(c^+)}}$) vs KCl molar fraction, the cation mobility being constant.

By considering that Barret and Wallace (*8*) obtained a maximum value for $c_{\mathrm{v(c^+)}}$, at

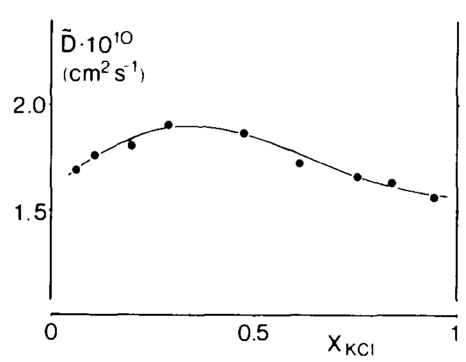

FIG. 4. Trend of the diffusion coefficients as a function of (Na, K)Cl solid solution composition ($T =$ 550°C).

$X_{KCl} \cong 0.3$ (for Schottky defect concentration at 630°C), the same correlation may be assumed also for the system NaCl–KCl.

The kinetic constant of the reaction $NaCl + KF \rightarrow NaF + KCl$ was determined at 550°C employing the couples NaCl|KF for $30 < t < 168$ hr; the thickness of the product layer was evaluated both through microscopical observations and by X-ray diffraction measurements. The parabolic law $x^2 = 2kt$ was satisfied, with $k = 1.5 \cdot 10^{-9}$ cm^2 sec^{-1}.

Using the value of 6418 cal mol^{-1} (*9*) for the molar standard free energy of the considered reaction, it is possible to obtain (*10, 11*) the following average value of the diffusion coefficient for the rate determining ion: $D = 3.8 \cdot 10^{-10}$ cm^2 sec^{-1}, which is of the same order of magnitude as those determined at the same temperature in the solid solution (Na, K)Cl by the Boltzmann–Matano method.

It can be therefore deduced that the NaF and KCl formation is governed by a mechanism which involves the Na^+ and K^+ diffusion in the (Na, K)Cl phase. This conclusion is supported also by a comparison between the cation migration enthalpy values (*12*) in NaF, NaCl, and KCl phases.

Acknowledgment

The authors wish to thank Dr. Maria Rosa Invernizzi Massarotti for having carried out the photometric measurements.

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