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Kinetics and Mechanism of the Solid State Reaction $TlCl + KI \rightarrow TlI + KCl$

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The kinetics of the solid state displacement reaction $TlCl + KI \rightarrow TlI + KCl$ was investigated by the diffusion couple method (using single crystal disks and pellets) in the temperature range 215–300°C. Two distinct layers are present: the first, in contact with TlCl, formed by a solid solution of TlI in TlCl, grows with a linear rate; the second, in contact with KI, formed by two solid solutions of TlCl in TlI and in KCl, respectively, grows according to the parabolic law. From marker experiments and X-ray analyses on product layer surfaces parallel to the original interface, along with a comparison of the rate constants and the diffusion coefficients, it was possible to deduce that the overall process is governed by diffusion of Tl^+ and Cl^- in the iodide-rich solid solution Tl(I, Cl) and that the rate-determining step is the diffusion of Tl^+.

Introduction

Among the solid state reactions, that of type $AX + BY \rightarrow AY + BX$ often shows a very complex mechanism, and its kinetic study, to date, has been restricted to a few cases (*1*). To explain its course, Jost (*2*) and Wagner (*1*) proposed two mechanisms, the applicability of which is limited to systems whose components mainly have cation mobility and slight or negligible mutual solubilities in the solid state.

To obtain further information on reactions of this type, a research on univalent metal halide systems was undertaken. These systems are relatively simple and show manifold characteristics depending on the transport properties and mutual solubilities of the components. Moreover, very often, the structural and thermodynamic parameters of these halides are well known and carefully determined.

This work reports the results obtained in the study of the process $TlCl + KI \rightarrow TlI + KCl$ which represents the metathetical reaction of the reciprocal ternary system Tl, K/Cl, I (*3*), characterized by two ternary eutectics at 420 and 316°C; further, the two binary systems $TlCl + TlI$ (*4*) and $KCl + TlCl$ (*5*) show appreciable solubilities in the solid state.

The kinetic investigation was carried out by unidimensional diffusion measurements on the reacting systems TlCl|KI using single crystals or pellets, in the temperature range 215–300°C. The analysis of the product layers was performed by optical microscopy and above all by X-ray diffraction intensity measurements. Moreover, the latter technique on product layer surfaces parallel to the original interface, allowed the obtaining of the trend of the reflection intensities of the products as a function of the spatial coordinate.

On the basis of the results obtained, along with a comparison of the rate constants and the diffusion coefficients of the ions involved in

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the transport process, it was possible to deduce the reaction mechanism.

Experimental

Materials. The diffusion couples TlCl|KI were formed by single crystal (K. Korth) disks (diameter 8 mm, thickness 1–2 mm) cut along the (100) plane; in some cases TlCl (Fluka "puriss.") and KI (Merck "suprapur") pellets prepared by pressing the powders at 4×10^3 kg/cm^2 were used. The reacting systems TlCl|TlI and TlCl|KCl were also used; TlI (Fluka "puriss.") and KCl (Merck "suprapur") were in the form of pellets.

Kinetic measurements. The diffusion couples (single crystals or pellets in triplicate) were placed in a horizontal furnace (*6*) at the desired temperature for periods of 10 to 240 hr. Care was taken to ensure good contact between the flat surfaces of the reagents; e.g., the surfaces were accurately polished, and the two nickel rods, subjected to a suitable pressure, were properly assembled. The observed product layer thicknesses x (μm) were then microscopically determined.

X-Ray analysis. The Philips equipment used was composed of a generator PW 1011, a vertical goniometer, a proportional counter, and a recording system (CuK radiation, Ni-filtered). For measurements at $T > 25°C$ an MRC camera was employed in which the heating system, devised in this Institute in substitution for the original system, enabled us to maintain good temperature constancy (*7*).

First, the diffraction patterns of the pure components, in the temperature range 25–300°C, were taken. For TlI$_\alpha$ (stable form at $T > 169°C$ (*8*)) and TlCl, the thermal expansion was also measured. The dependence of the lattice constant a on the temperature (°C) can be expressed by the following linear relations.

For TlCl: $a = 3.836 + 2.5 \times 10^{-4}\,T$ $(20 < T < 300)$;

For TlI$_\alpha$: $a = 4.195 + 2.7 \times 10^{-4}\,T$ $(180 < T < 300)$.

Second, measurements of X-ray diffraction intensities were performed for the systems TlCl|KI, TlCl|TlI, and TlCl|KCl on the reaction product layers reached by progressively slicing off substance from both ends of the cylindrical specimens formed by a reagent, the products, and the second reagent. To obtain these layers, with surfaces parallel to the reaction interface, a microtome constructed in this Institute was employed, which allowed the advancement of a specimen holder to which the diffusion couple was firmly fixed. The minimum available increment was 5 μm while the cutoff thicknesses were $\geqslant 50$ μm.

Thermal and optical determinations. The compositions of the solid solutions for the systems TlCl + TlI were determined by means of thermal measurements (900 Differential Thermal Analyzer and DSC cell, Du Pont) and optical observations (Hot-Stage Microscope, Leitz). In the temperature range 200–300°C the observed solubility of TlCl in TlI is between 8 and 17 mole%, while that of TlI in TlCl is between 3 and 9 mole%.

Results and Discussion

For the kinetic study of the reaction, isotherms at 215, 230, 250, 275, and 300°C were carried out. The diffusion couples TlCl|KI, after annealing, showed two new layers of different colors. A typical result of an experiment carried out at 300°C for 144 hr is shown in Fig. 1; the original contact interface of the reagent pellets was marked with Pt powder.

The section, obtained by cutting the couple parallel to the diffusion direction, shows a red uniform layer (130 μm thick) in contact with TlCl and a second yellow layer (220 μm thick) with aggregate morphology adherent to the KI pellet. The Pt powder lies at the red–yellow layer interface.

Figure 2 shows the thicknesses x (mean value determined on three diffusion couples) of both the observed layers relevant to the 215 and 300°C isotherms. No significant

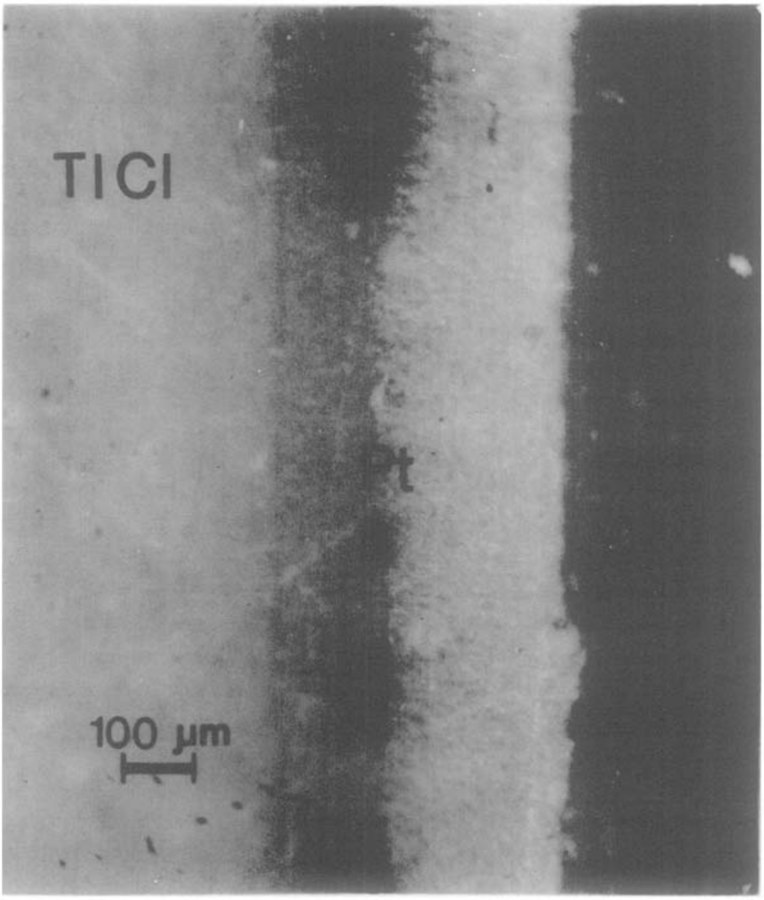

FIG. 1. Reaction between TlCl and KI: transverse section of a reacted specimen after annealing for 144 hr at 300°C.

differences between employing single crystals and employing pellets were observed. For each isotherm the x, t (time) values pertinent to the yellow layer follow the parabolic law $x^2 = 2kt$ with good agreement, while the corresponding values of the red layer show a linear trend. For the 300°C isotherm the ratio between the thicknesses of the two layers ($x_{\text{yellow}}/x_{\text{red}}$) as a function of time is reported in Fig. 3.

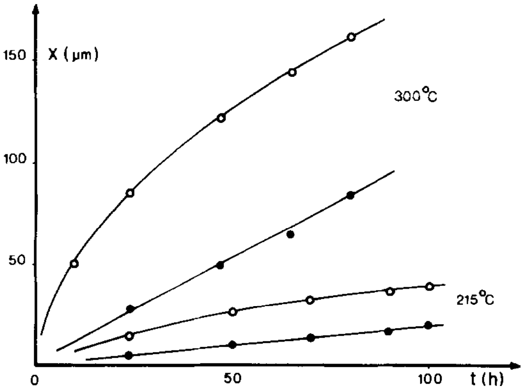

FIG. 2. Isotherms for the reaction between TlCl and KI. Open circles: yellow layer; filled circles: red layer.

Only for the yellow layer was the kinetic constant (k) determined: the logarithmic values show a linear dependence on $1/T$ according to the equation

$$\log k = -1.97 - \frac{19\,315}{4.576T},$$

where k is in square centimeters per second and T is in degrees Kelvin. To characterize the phase nature in the product layer, diffraction measurements on a diffusion couple after 140 hr at 300°C were performed.

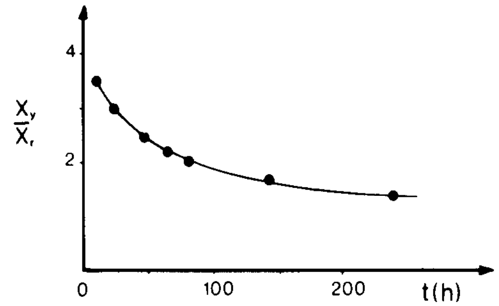

FIG. 3. Ratio between the yellow and red layer thicknesses as a function of time, for the 300°C isotherm.

An X-ray analysis of the red product surface at the marker level, carried out repeatedly and alternately at 25 and 300°C, revealed the characteristic reflections of TlCl and TlI at 25°C, and only the TlCl reflections at 300°C; this denotes the presence of a chloride-rich solid solution at the latter temperature. The same procedure used for the corresponding yellow layer surface showed the KCl (broad), TlI, and TlCl peaks at 25°C, but no thallium chloride peaks at 300°C.

By comparing these patterns with those obtained at the same temperatures on pure TlI and KCl, the presence of solid solutions of TlCl both in TlI and in KCl can be deduced. By diffraction angle displacement measurements on the TlI_α and TlCl reflections at 300°C it was possible to estimate the composition $\mathrm{Tl(Cl_{0.92}I_{0.08})}$ for the solid solution present at the red layer surface, and the composition $\mathrm{Tl(I_{0.90}Cl_{0.10})}$ for that present at the yellow layer surface.

To obtain more kinetic information on these solid solutions, the diffusion couples TlCl|TlI and TlCl|KCl were heated at 300°C for 50 hr. For the first couple two red layers at both sides of the original interface were observed; the thicknesses (850 μm total) of the layers were in a ratio of about 8/1 in favor of the thickness in contact with TlI. X-Ray diffraction measurements on surfaces parallel to the original interface performed at room temperature soon after the thermal treatment enabled us to evaluate the trend of the most intense reflection of TlCl (110), TlI_α (110), and TlI_β (111) as a function of the spatial coordinate (Fig. 4).

It is interesting to observe that at room temperature TlI preponderantly keeps the red α cubic form in the layers relevant to the solid solutions. In fact the abscissa value corresponding to the intersection of the (110) and (111) reflection intensities of TlI, α, and β, respectively, corresponds to the solid-solution layer thickness as optically measured. For the TlCl|KCl couple, it was observed from microscopic observations and X-ray analysis that the layer thickness of the solid solution of TlCl in KCl is about 100 μm.

Finally, an X-ray analysis of the system TlCl|KI annealed at 300°C for 240 hr was

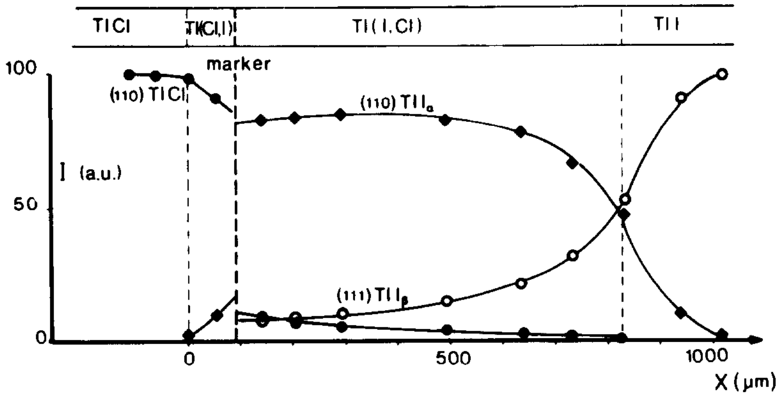

FIG. 4. TlCl|TlI diffusion couple after 50 hr at 300°C; trend of the intensities (at 25°C) of the (110) TlCl, (110) TlI_α, and (111) TlI_β reflections.

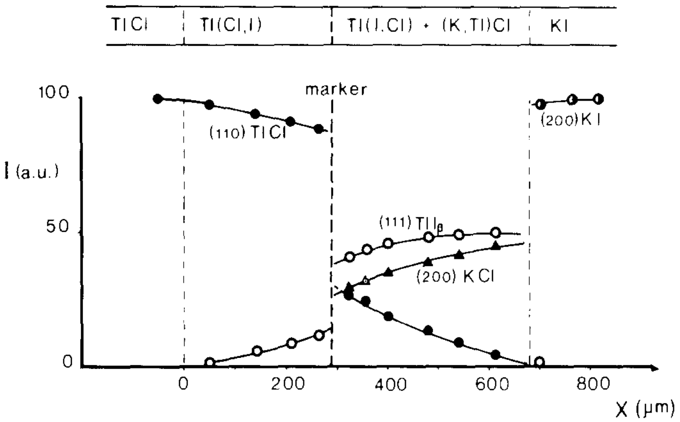

FIG. 5. TlCl|KI diffusion couple after 240 hr at 300°C; trend of the intensities (at 25°C) of the (110) TlCl, (111) TlI_β, (200) KCl, and (200) KI reflections.

performed. The results obtained at room temperature after complete transformation of TlI into stable form (β) are shown in Fig. 5. It can be seen that in the yellow layer the peak intensities of TlI_β and KCl progressively increase on going toward the products|KI interface, while the peak intensity of TlCl progressively decreases and disappears at the same interface. The intensity trends of these peaks are consistent with the presence of solid solutions (K, Tl)Cl and Tl(Cl, I).

Moreover, the reaction products KCl and TlI are not separately layered, as the Jost limiting mechanism (*2*) would require: the first product is present only in the layer between the markers and KI, while the second is also present in the layer between the markers and TlCl as solute in the Tl(Cl, I) solid solution. On the other hand the thickness increase of the red layer at the expense of that of the corresponding yellow layer (see Fig. 3) indicates that the diffusion process determining the solid solution formation is faster than that governing the TlI and KCl growth. Therefore it can be deduced that the overall process mechanism is governed by the diffusion of Tl^+ and Cl^- through the two observed layers toward KI and that the reaction takes place there. The contact of the reaction products with TlCl yields the observed solid solutions.

From Fig. 4 it can also be seen that for the TlCl–TlI solid solutions the diffusion coefficient of Cl^-, D_{Cl^-}, in the iodide-rich solid solution must be greater that D_{I^-} in the chloride-rich solid solution. A comparison of the diffusion coefficient for the ions involved in the transport process (Tl^+ and Cl^-) with the values of the kinetic constant determined by the contact method enables us to individuate the rate-determining ion. This was done at 250°C, the highest temperature at which the transport number of Tl^+ in TlI_α is known; from its value, together with that of the electrical conductivity (*9*), the diffusion coefficient $D_{\mathrm{Tl}^+} = 5.8 \times 10^{-10}$ cm^2/sec was determined.

Moreover at this temperature the diffusion coefficients of Tl^+ and Cl^- ions in KCl are $D_{\mathrm{Tl}^+} = 2.93 \times 10^{-13}$ cm^2/sec (*10*), and $D_{\mathrm{Cl}^-} < 10^{-20}$ cm^2/sec, which are very low in comparison with the kinetic constant k (1×10^{-10} cm^2/sec) determined by us. Therefore the Tl^+ and Cl^- transport in the KCl phase can be excluded.

By considering that in compounds of type TlI_α the anions are faster than the cations it may be concluded that the rate-determining step of the reaction is the diffusion of Tl^+ in the TlI_α phase.

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