

M_D mass of dispenser and powder measured by the load cell
 Q_g volumetric gas flow rate
 W_s solids mass flow rate
 ω screw rotation speed

REFERENCES

1. G. A. Irons: *Transactions of the Iron and Steel Society*, 1984, vol. 5, pp. 33-45.
2. L. R. Farias and G. A. Irons: *Metall. Trans. B*, 1986, vol. 17B, p. 77.

Phase Diagram Studies of the Systems KCl-K₃MoCl₆ and LiCl-K₃MoCl₆

GEORGES J. KIPOUROS and DONALD R. SADOWAY

As part of an investigation of fused salt electroplating of molybdenum coatings,¹ the phase diagrams of the two binary systems, LiCl-K₃MoCl₆ and KCl-K₃MoCl₆, have been determined. These compounds are the principal constituents of the electrolyte employed in the plating studies which had as one of their goals to minimize thermal damage to the substrate through the use of a "low temperature" electrolyte.

Phase diagrams were determined by cryoscopy. Each sample weighed approximately 30 g and was contained in an evacuated heart-shaped fused quartz ampoule. The ampoule had a glass well which allowed a thermocouple to be placed at the center of the salt sample. For immersion into a vertical tube resistance furnace the ampoule was surrounded by a grounded metal sheath which served to prevent induction of spurious voltages in the thermocouple by the ac field of the furnace windings. The temperature of the furnace was controlled by means of a programmable temperature controller connected in series with a thyristor. Each sample was cooled several times at different rates ranging from 0.5 K min⁻¹ to 2.5 K min⁻¹ to obtain data that were free from the effects of undercooling. As further precautions against undercooling the ampoules were seeded with broken quartz glass, and during the experiments the furnace was rocked in order to agitate the samples. A 22 gauge chromel-P vs alumel, ASTM type K, thermocouple was used. Prior to use the thermocouple was calibrated in this laboratory against a platinum -13 pct rhodium vs platinum standard thermocouple. For optimal response to temperature fluctuations, the bottom inch of the thermocouple wire was not insulated.

Partially compensated by a dc offset device, the thermocouple output was recorded continuously on a one millivolt full-scale strip chart recorder. Periodically, the temperature was measured by a potentiometer. Phase changes were ob-

served in the measured temperature vs time curves. On the basis of the determination of the melting point of potassium chloride the total absolute error in estimating the liquidus temperature with this apparatus is about 2 K.

Potassium hexachloromolybdate, K₃MoCl₆, was supplied by Climax Molybdenum Company as 99.74 wt pct pure, the remainder being excess potassium chloride. Prior to use K₃MoCl₆ was treated by heating under vacuum for several hours at 120 °C. The alkali chlorides were of analytical grade and were dehydrated by prolonged heating under vacuum according to the procedure recommended in the literature.²

Figure 1 shows the phase diagram of the KCl-K₃MoCl₆ system, which forms a simple eutectic at 18.4 mole pct K₃MoCl₆ and 697 °C. The compound, potassium hexachloromolybdate, melts congruently at 882 °C.

Actually, the system KCl-K₃MoCl₆ may be considered a pseudobinary within the system KCl-MoCl₃. The latter has been studied by Drobot and Sapranova³ by differential thermal analysis of sealed samples containing intimate mixtures of the principal components. Thermal features were identified by heating the specimens, which weighed as little as 1.5 g, at rates of 4 to 8 K min⁻¹. Based on the results of only four samples over the composition range from KCl to K₃MoCl₆, those authors reported a melting point of 865 °C for the compound, K₃MoCl₆, which is lower than the value of 882 °C determined in this work. This is probably due to the presence of impurities in their samples since they prepared MoCl₃ by reducing MoCl₅ with anhydrous tin (II) chloride. Temperature gradients caused by the relatively high heating rates and weighing errors may also account for the discrepancy with the values found in this work.

Drobot and Sapranova³ found the KCl-K₃MoCl₆ eutectic to be at 12 mole pct MoCl₃ (which is equivalent to 18.8 mole pct K₃MoCl₆ in the KCl-K₃MoCl₆ subsystem) and 698 °C. These are in excellent agreement with the values 18.4 ± 0.4 mole pct K₃MoCl₆ and 697 ± 2 °C determined in the present study. In contrast to the findings of the other authors there was no evidence in this investigation that K₃MoCl₆ undergoes polymorphic transformation at 460 °C.

As shown in Figure 1 the K₃MoCl₆ peak in the phase diagram is somewhat flattened; this could be an indication of dissociation. Grjotheim,⁴ in an analogous situation in the

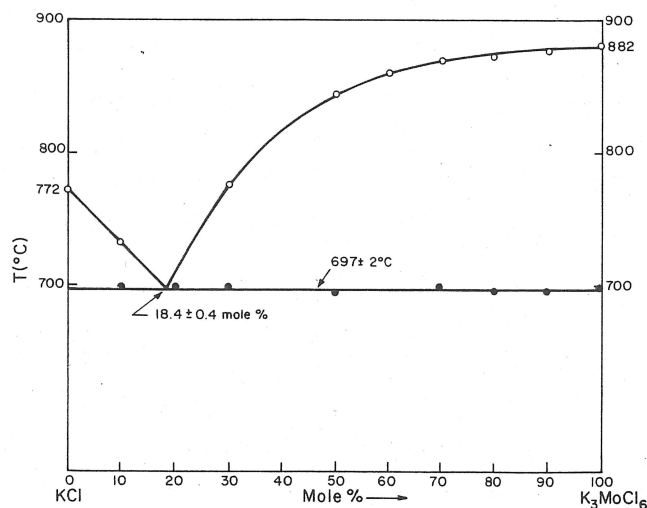


Fig. 1 — Phase diagram of the KCl-K₃MoCl₆ system.

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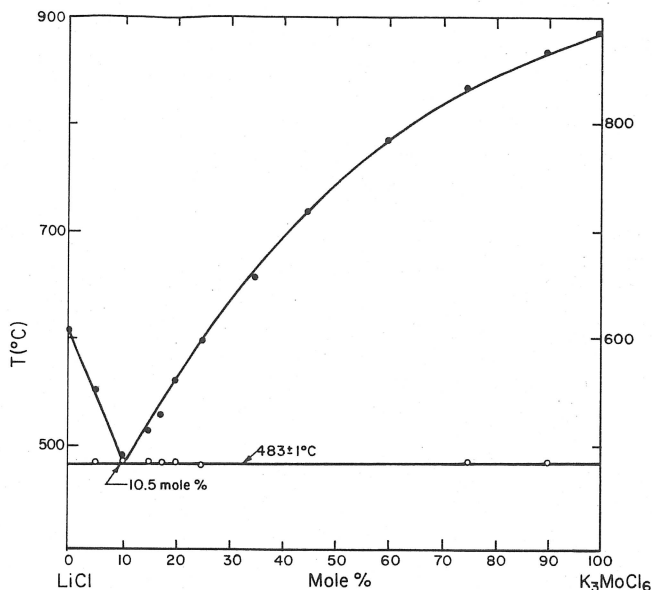
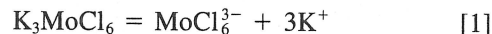


Fig. 2—Phase diagram of the LiCl-K₃MoCl₆ system.

NaF-Na₃AlF₆ system, used the known heat of fusion of Na₃AlF₆ in order to postulate a mechanism of dissociation of cryolite that most closely agrees with the experimentally determined liquidus line. Unfortunately, the heat of fusion of K₃MoCl₆ has not been reported, and the liquidus line of the binary system K₃MoCl₆-MoCl₃ is not accurately known. It has been assumed,⁵ with reasonable justification, that potassium hexachloromolybdate dissociates upon melting according to the reaction



creating the molybdenum-bearing complex ion, MoCl₆³⁻, which is electroreduced to molybdenum metal.

Figure 2 shows the phase diagram of the LiCl-K₃MoCl₆ system which forms a simple eutectic at 10.5 mole pct K₃MoCl₆ and 483 °C. There are no other reports in the literature for this system.

As shown in Figure 2, on the composition interval from 25 to 75 mole pct K₃MoCl₆ it was not possible to detect a thermal arrest at the eutectic temperature. Furthermore, at temperatures below the eutectic, the cooling curves showed evidence of other phase transformations. However, these results were inconclusive and cannot be interpreted. Similar problems were encountered by Drobot and Saprano³ in the KCl-MoCl₃ system.

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REFERENCES

1. G. J. Kipouros and D. R. Sadoway: "Molybdenum coatings by Molten Salt Electrolysis," in *Energy Reduction Techniques in Metal Electrochemical Processes*, R. G. Bautista and R. J. Wesely, eds., TMS/AIME, Warrendale, PA, 1985, pp. 471-78.
2. G. J. Janz: in *Proceedings of the Third International Symposium on Molten Salts*, G. Mamantov, M. Blander, and G. P. Smith, eds., The Electrochemical Society, Inc., Pennington, NJ, 1981, pp. 52-67.
3. D. V. Drobot and E. A. Saprano: *Russ. J. Inorg. Chem.*, 1973, vol. 18, pp. 1067-68.

4. K. Grjotheim: *Kgl. Norske Videnskab. Selskabs Skrifter*, 1956, no. 5, pp. 1-90.
5. S. Senderoff and G. W. Mellors: *J. Electrochem. Soc.*, 1967, vol. 114, pp. 556-60.

On the Separation of TiCl₄ from AlCl₃

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The anhydrous chloride reduction route to aluminum requires a chloride feed of high purity.¹ In a project at the Albany Research Center of the Bureau of Mines, United States Department of the Interior, investigating the preparation of a suitable aluminum chloride feed from domestic kaolin, the separation of byproduct chlorides from aluminum chloride has been studied. An earlier publication resulting from this work indicated that ferric chloride, a coproduct of kaolin carbochlorination and a detrimental contaminant, could be separated from aluminum chloride by pressure distillation.² Research reported here shows that silicon chloride does not pose a serious separation problem, but that separation of titanium chloride from aluminum chloride by vaporization or condensation is more difficult than indicated by a cursory examination of their respective vapor pressures.

Preliminary screening tests were run to determine if condensing aluminum chloride promoted the condensation of the more volatile silicon and titanium tetrachlorides. These tests were conducted with metal chloride vapor made by heating aluminum alloyed with silicon and/or titanium in a flowing dried mixture of 50 pct chlorine in nitrogen. The resulting gas-vapor stream passed through a controlled-temperature condenser where essentially all of the aluminum chloride condensed. After 1 hour, condensate from approximately 2 grams of chlorinated alloy was rinsed out of the condenser with 2-pct hydrochloric acid and analyzed for the metals of concern.

Conditions and results of the tests are displayed in Table I. The tetrachlorides of silicon and titanium condensed with the aluminum chloride in the order expected, the less volatile titanium tetrachloride content being two orders of magnitude higher. There was, however, no statistically significant effect caused by temperature. This concentration of titanium tetrachloride would be a serious problem in aluminum chloride feed for direct reduction to the metal, and, therefore, the AlCl₃-TiCl₄ system was chosen for further study.

A two-compartment glass apparatus was used to study the equilibrium composition of condensed aluminum chloride-titanium chloride at several temperatures and under various titanium chloride pressures. Originally, the apparatus was connected to a chloride inlet system in which fresh chlorides were prepared from an aluminum-titanium (75-25) alloy. The chlorides were condensed in the cooled apparatus while excess chlorine and the inert carrier gas exited through a

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