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Note

REACTIONS OF CUPROUS CHLORIDE WITH CONTAINER MATERIALS AT ELEVATED TEMPERATURE

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This note is submitted to correct and reinterpret the differential scanning calorimeter results presented in this journal by Wynne and Wendlandt [1] in an article entitled Reactions of copper(I, II) salts in a potassium chloride matrix.

During the course of our investigation of the KCl—CuCl eutectic mixture as a potential intermediate temperature heat transfer fluid, our study included the differential thermal analysis examination of CuCl prepared by the same method [2] as Wynne and Wendlandt. In contrast to Wynne and Wendlandt, however, we found aluminum containers to be unacceptable because of gross reactions with CuCl. In accordance with the electromotive series, aluminum would be predicted to reduce CuCl. More noble container materials, such as copper, silver, platinum, or gold were found to be better choices as container materials for molten CuCl.

Thermograms are presented of CuCl heated to 575°C in sealed aluminum (Fig. 1) and gold (Fig. 2) pans. In an aluminum container, Fig. 1, the endothermic peak at 410°C is the crystal change from cubic to hexagonal as described by the earlier work of Lorenz and Prener [3], while the 425°C transformation is the melting point. As the temperature is increased to 480°C, a large exothermic peak is evident. This peak is believed to be the result of the reaction $3\ CuCl + Al \rightarrow AlCl_3 + 3\ Cu$. This explains the copper observed by Wynne and Wendlandt. With further heating, a large endothermic peak is noted at 548°C. This peak is assigned to the reaction of metallic copper with aluminum to form a eutectic, as shown in the aluminum-rich portion of the Al—Cu binary phase diagram [4].

In order to confirm these chemical reactions, several analyses were performed. A sample of CuCl was heated in a sealed aluminum pan at 6°C min^{-1}, to 490°C, and immediately free-cooled. Subsequent examination exhibited a metallic copper coating covering a large percentage of the container, while some CuCl still remained because the above reaction was not allowed to go to completion. The formation of $AlCl_3$ caused enough pressure increase to rupture the sealed pan, allowing this volatile material to escape, explaining the weight loss observed by the previous authors.

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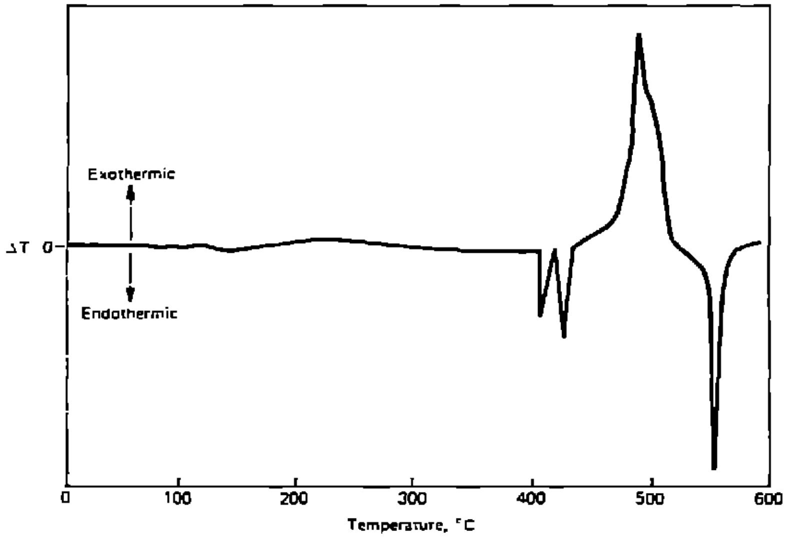


Fig. 1. DTA thermogram of CuCl sealed in an aluminum pan.

The coating proved to be copper when the following standard analytical color test [5] was performed.

(a) The remaining CuCl, as well as the aluminum pan, was dissolved in 50% HCl leaving a copper-appearing residue.

(b) The residue was dissolved in concentrated HNO_3, then NH_4OH was added, developing a blue color, thus demonstrating the presence of copper.

A post mortem of a similar sample, heated to 575°C under the above conditions, showed severe attack of the aluminum pan and the disappearance of the copper color. Scanning electron microscope examination of this pan clearly defines a eutectic formation as shown in Fig. 3. Additional evidence is exhibited in Figs. 4 and 5, which are energy dispersement X-ray analysis of the light and dark phases of the eutectic structure. The light phase shows

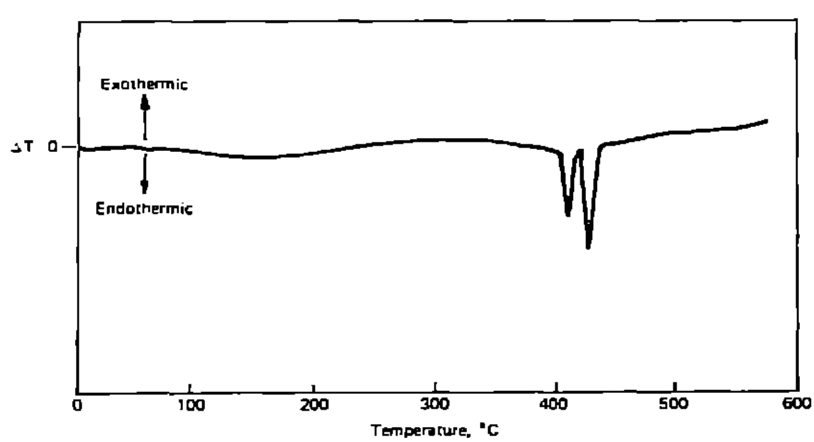


Fig. 2. DTA thermogram of CuCl sealed in a gold pan.

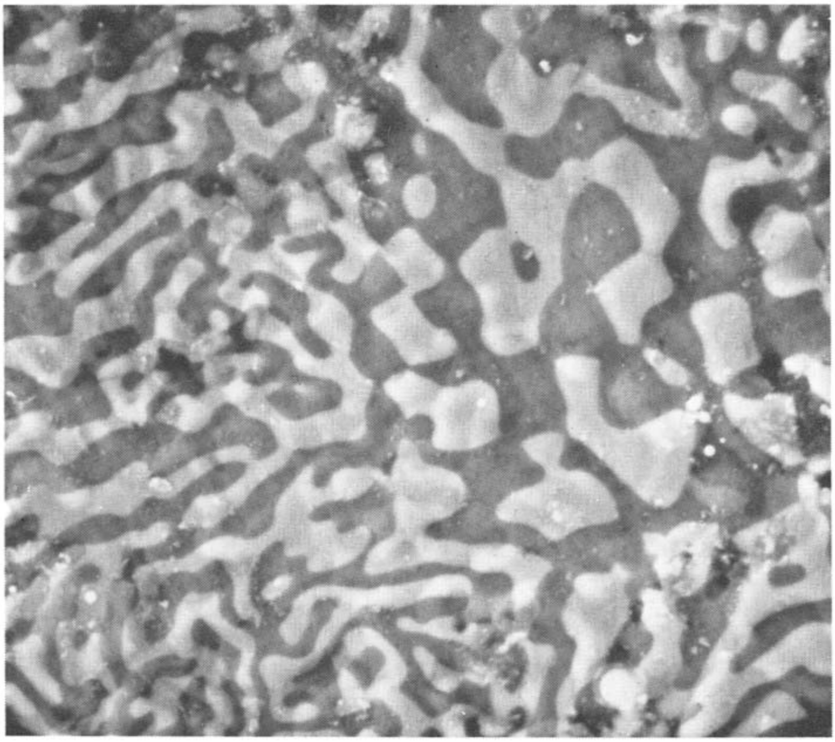
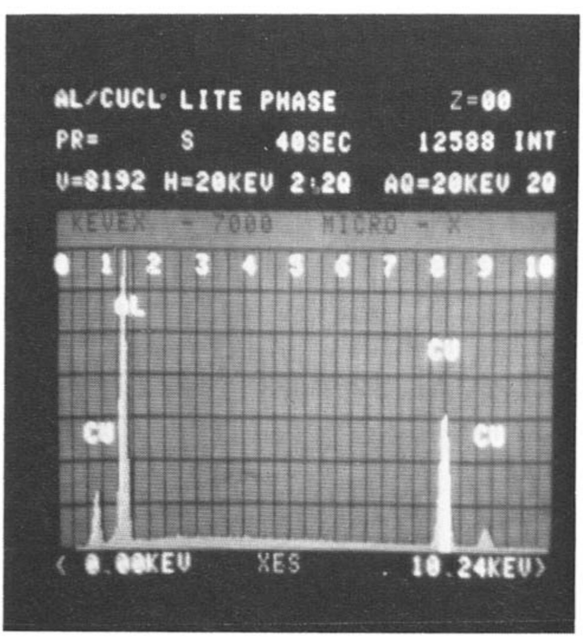


Fig. 3. Eutectic structure evident after heating CuCl in an aluminum pan to 575°C. × 2000.



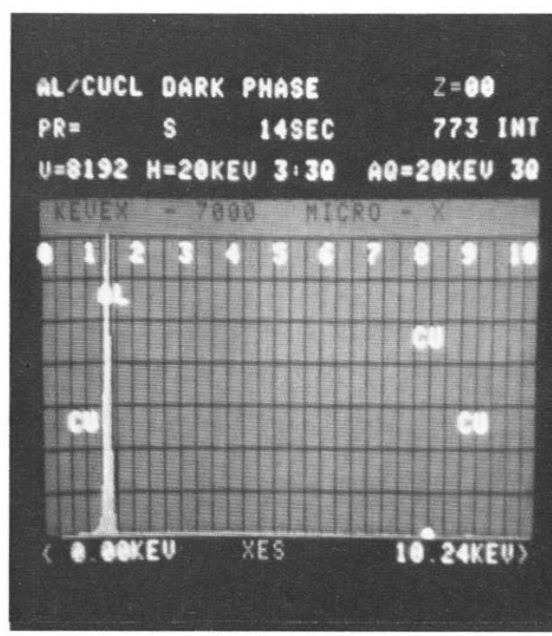


Fig. 4. Energy dispersement X-ray analysis of the light phase in Fig. 3.

Fig. 5. Energy dispersement X-ray analysis of the dark phase in Fig. 3.

considerable amounts of both aluminum and copper, while the dark phase is extremely aluminum-rich. These examinations strongly support the formation of the Al_2Cu—Al binary eutectic previously mentioned. The unknown 550°C endothermic peak seen by Wynne and Wendlandt most likely indicated the eutectic melting temperature.

In the thermogram of CuCl heated at 6°C min^{-1} to 575°C in a sealed gold pan, Fig. 2, the exothermic peak at 490°C is absent, along with the 550°C endothermic transition. The contrast between Figs. 1 and 2 and the metallurgical examinations strongly suggest gross reactions between aluminum pans and cuprous chloride. In addition, we have found that CuCl is very stable in the molten state and does not readily decompose as previously suggested by Wynne and Wendlandt.

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