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LiCl-KCl Induced Corrosion of Copper at Low Temperature

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1. Introduction

PRIDE system which is one of reprocessing methods of spent fuel uses the molten salts of LiCl-KCl at low temperature, so corrosion of structural materials is one of the main problems. Structural materials for PRIDE system are stainless steel and copper mainly. And these are known for maintaining integrity when there is no oxygen and water. But physicochemical behavior of structural materials of PRIDE system when there is some of oxygen and water is lack of research. And when local corrosion is occurred, it can cause crack, so that it will be a big problem of safety and economic efficiency. So evaluation of thermodynamical and mechanical stabilities of structural materials for PRIDE system is necessary to predict lifetime of materials and time to replace the part of the equipment.

There is no research of evaluation of long-term structural stability of structural materials for PRIDE system now. The present work investigates how LiCl-KCl molten salts influence the low temperature corrosion of copper. It can be used for standardization of structural materials for equipment of molten salt and establishment of life of equipment.

2. Methods and Results

2.1 Experimental setup

The material investigated is the copper. Samples has circular shape and the geometrical area of the samples was 4.906cm^2, (25 ∅ x 2 mm). Before exposure, the samples were ground to 1000-grit SiC and polished with colloidal silica until a mirror-like surface appeared. After polishing, the samples were cleaned in acetone and ethanol using an ultrasonic bath. LiCl-KCl salt was applied on all surface by using micro pipette with a saturated solution of LiCl-KCl in distilled water. Sample mass was recorded prior to and after exposure using a six decimal Sartorius balance.

The exposures were performed in silica tube furnaces with ex-situ recording of the weight. The temperature was kept at 30, 40, 60 and 80℃. The experiments were carried out in saturated vapor pressure to keep saturated solution of LiCl-KCl from evaporating. The experiments lasted 24, 48, 72 or 96 hour.

The oxidized samples were analyzed by SEM and AES in order to characterize corrosion product. After that, the mass of samples was measured to know corrosion rate.

2.2 Surface analysis

After corrosion test, we confirmed that corrosion products were formed on the surface generally. Its amounts were bigger as the temperature goes up.(Fig. 1.)

	30°C	40°C	60°C	80°C
Copper				

Fig. 1. Surface of samples after 72 hours corrosion test

The SEM images in Fig. 2. show samples exposed for 24 and 72 hr at 30 and 60^{o}C. After 24h the oxide is occurred. But after 72hr, the oxide has increased both in number and size comparing to 24hr. And it is more noticeable when the temperature is 60^{o}C.

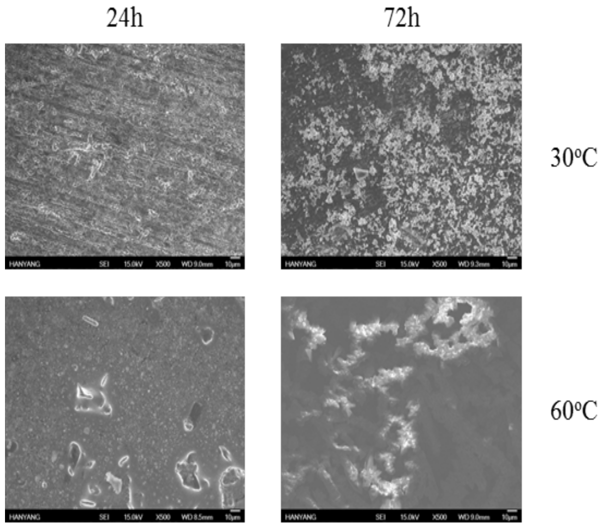

Fig. 2. SEM images with a magnification of 500x.

After 24hr, the oxide thickness was about 150nm, the outer part consisting mainly of copper oxide. And chlorine was only detected at the metal interface. But 72hr, the oxide had a thickness of about 750nm. Also chlorine was only detected at the scale surface.

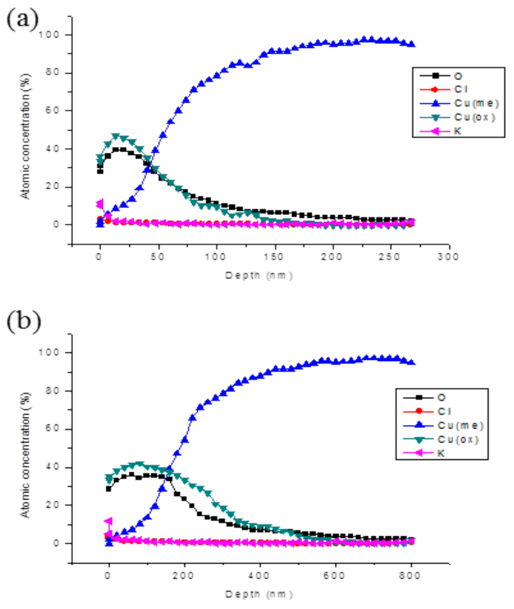

Fig. 3. AES depth profiling for samples exposed at 60°C for (a) 24h and (b) 72h

2.3 Corrosion rate

The corrosion rate in millimeters penetration per year can be calculated from equation 1.

$$mm/yr = \frac{87.6W}{DAT} \qquad (1)$$

W is weight loss in milligrams, D is density in grams per cubic centimeter, A is area in square centimeters.

To measure the value of weight loss, we have to get rid of corrosion product. So we used a chemical method of Korean standard(KS D ISO 8407).

The weight loss and corrosion rate were increased as the time is longer and the temperature is higher.

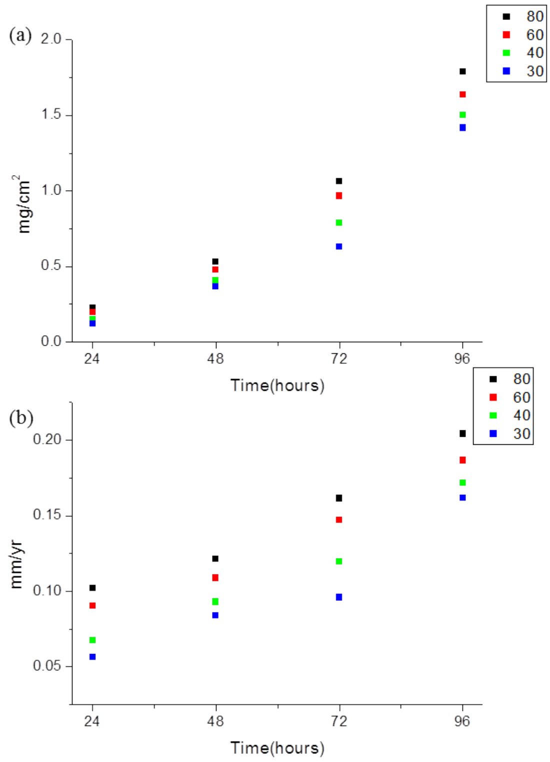

Fig. 4. Weight loss and corrosion rate depending on time and temperature : (a) weight loss, (b) corrosion rate

3. Conclusions

From the corrosion test, we can confirm that LiCl-KCl salt accelerates the corrosion of copper at low temperature. It was observed by surface analysis and gravimetry. The corrosion pattern is general corrosion and corrosion rate is increased as the temperature and time go up.

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