Selective Leaching of Brass – Electrochemical Aspects

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1. Introduction

Brass, an alloy of copper and zinc, has been used in various industries due to its higher malleability than bronze and zinc as well as its good flow characteristics for casting. In Korean nuclear power plants(NPPs), brass has been mainly used for tubes in some older model heat exchangers and some valve bodies in the fire protection systems. Notably, however, the use of brass may lead to selective leaching, one of corrosion phenomena.

Selective leaching is the preferential removal of specific alloying elements from a solid alloy via corrosion processes, leaving behind a weakened spongy or porous residual structure[1]. Materials that are known to be susceptible to selective leaching include gray cast iron and copper alloys that contain greater than 15 percent zinc[2].

Selective leaching proceeds slowly during a long period of time and causes a decrease in strength without changing the overall dimensions of original material, and consequently is difficult to identify. For this reason, as part of the One-Time Inspection Program according to the requirements of the guidelines for continued operation of pressured water reactors (PWRs) in Korea[3] and license renewals in the United States, entitled the 'Generic Aging Lessons Learned (GALL) report[2],' visual inspection and hardness measurement should be carried out to confirm that selective leaching exerts no effects on the structural integrity of the related components for continued operation of NPPs. In the newly released GALL report[2], the quantitative acceptance criteria for hardness are given: no more than a 20 percent decrease in hardness for gray cast iron and brass containing more than 15 percent zinc.

In the present work, the selective leaching of brass is investigated in terms of electrochemical aspects as part of an ongoing research project to study the changes in metal properties by selective leaching.

2. Methods and Results

2.1 Methods

The test material used in this study was ASTM B-135 C26000(70% Cu, 30% Zn) brass. Pure copper and zinc were also used for comparison, as brass is composed of these metals. The surfaces of these specimens were successively ground with silicon carbide papers to 1200 grit. The electrolyte used in this study was a 1% $CuCl_2$ aqueous solution.

A three-electrode electrochemical cell was employed for a potentiodynamic polarization experiment. The experiment was performed with a scan rate of 0.5mV/s to investigate the electrochemical behavior of the materials. A platinum gauze and a saturated calomel electrode (SCE) served as the counter and reference electrodes, respectively.

To confirm whether selective leaching of brass can be achieved chemically, the specimens were immersed in a 1% $CuCl_2$ solution at 75°C. Cross-sections of the specimens were then observed using an optical microscope.

2.2 Results

Fig. 1 shows the potentiodynamic polarization curve for ASTM B-135 C26000 brass in a 1% $CuCl_2$ solution. It is noted that active dissolution behavior is exhibited. In addition, an increase in current density caused by the breakdown of the oxide film is not observed in the anodic branch even in the presence of chloride ions. This indicates that the protectiveness of the oxide film against corrosion is relatively low and uniform corrosion dominantly proceeds on C26000 brass.

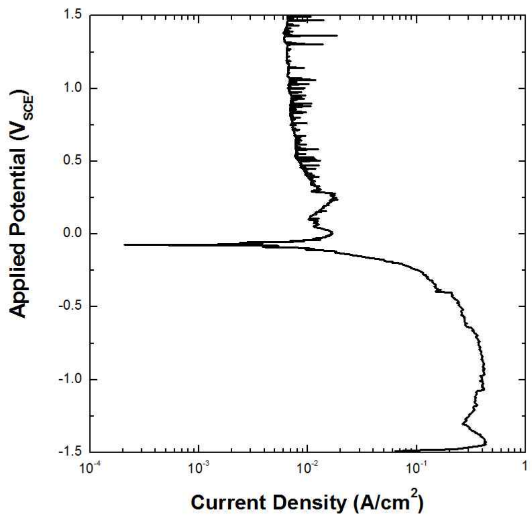

Fig. 1. Potentiodynamic polarization curve obtained for C26000 brass in a 1% $CuCl_2$ aqueous solution with a scan rate of 0.5mV/s.

Among alloying elements of brass, it can easily be predicted from the Galvanic series table that zinc will readily dissolve from brass, because zinc is electrochemically more active than copper. This also can be confirmed from the potentiodynamic polarization curves of pure copper and zinc in a 1% $CuCl_2$ solution given in Fig. 2; the corrosion potential of copper (-0.018V_{SCE}) is higher than that of zinc (-0.337V_{SCE}).

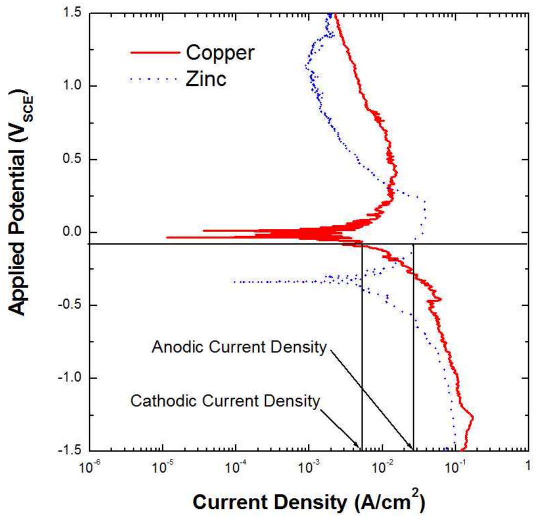

Fig. 2. Potentiodynamic polarization curves obtained for pure copper and zinc in a 1% $CuCl_2$ aqueous solution with a scan rate of 0.5mV/s.

Furthermore, it is worth noting that the corrosion potential of C26000 brass(-0.075V_{SCE}) is located between the corrosion potentials of pure copper and zinc. This reveals that selective leaching of brass proceeds electrochemically according to the mixed potential theory, which states that the corrosion potential of an alloy is determined by coupling all relevant anodic and cathodic reactions on the respective alloying elements. Thus, the total anodic current (corrosion current) is equivalent to the total cathodic current[4]. This can be thought of as a kind of natural conservation law in electrochemistry.

If we immerse C26000 brass in a 1% $CuCl_2$ aqueous solution, alloying elements (pure copper and zinc) in brass are inevitably exposed to -0.075V_{SCE}, since this potential is the corrosion potential of the brass in this solution. At this potential, the anodic current density of zinc is about five-fold higher than the cathodic current density of copper. From this result, we can draw the following two conclusions related to the mixed potential theory: one is that the area ratio of zinc to copper, exposed to the environment, can be estimated as 0.2(area ratio(Cu : Zn = 80: 20)) under the assumption of the mixed potential theory. This is comparable to the chemical composition of brass (70% Cu, 30% Zn). The other is that the selective leaching of brass can be controlled by electrochemical methods. In other words, selective leaching of brass can be electrochemically accelerated by the application of an external potential between -0.075V_{SCE} and -0.018V_{SCE}.

Fig. 3 shows a cross-sectional view of an optical micrograph of C26000 brass, taken after the specimen was immersed in a 1% $CuCl_2$ solution for 50 hours at 75°C. It is found that selective leaching can occur chemically on C26000 brass. Furthermore, as we noted previously, selective leaching of brass will be enhanced if an external anodic potential is applied. As the next step of this work, we plan to prepare selective leached brass specimens with various leached thicknesses for hardness measurement. These results will be useful to establish a correlation between the selective leached thickness and hardness value and finally to reduce conservatism in the acceptance criteria of hardness measurement given in the GALL report.

Fig. 3. Cross-sectional view of optical micrograph for C26000 brass, selectively leached for 50 hours in a 1% CuCl2 aqueous solution at 75 C.

3. Conclusions

Selective leaching of brass (ASTM B-135 C26000) was investigated in terms of electrochemical aspects. It was found that the selective leaching process proceeds according to the mixed potential theory. Accordingly, the selective leaching of brass can be controlled by electrochemical methods. The next step in this project will be to prepare selectively leached brass specimens with various leached thicknesses for use in a subsequent mechanical evaluation. This work will be useful to establish a correlation between selective leached thickness and the hardness value in order to reduce conservatism in the acceptance criteria of hardness measurement given in the Generic Aging Lessons Learned (GALL) report.

REFERENCES

[1] A.J. Bard, M. Stratmann, G.S. Frankel, Encyclopedia of Electrochemistry, Vol. 4 : Corrosion and Oxide Film, pp.156-186, 2001.

[2] USNRC, Generic Aging Lessons Learned (GALL) Report, Rev.2, 2010.

[3] KINS. Guidelines for Continued Operation of PWRs, 2008.

[4] C. Wagner, W. Traud, Z. Elektrochem. Ang. Phys. Chem., Vol.44, p.391, 1938.