

Formation of a Porous Nickel Electrode in Zinc Chloride-Alkali Chloride Melts

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When a nickel electrode was kept at a low potential and then at a high potential in a $\text{ZnCl}_2\text{-NaCl}$ (60-40 mol %) melt at 450°C , $\gamma\text{-NiZn}$ alloy was first formed which was then dealloyed to give a porous layer of $\alpha\text{-NiZn}$ alloy [1]. The present paper describes the mechanism of formation of the porous structure in the anodic dealloying as studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), and electron probe microanalysis (EPMA).

Cathodic and anodic treatments of a nickel electrode were performed in $\text{ZnCl}_2\text{-NaCl}$ (60-40 mol %) and $\text{ZnCl}_2\text{-KCl}$ (60-40 mol %) melts at $300\text{-}450^\circ\text{C}$ in a Pyrex cell. Nickel foils (0.1 mm thick) were used as the starting material. The reference electrode was zinc metal in $\text{ZnCl}_2\text{-NaCl}$ (saturated with NaCl) which was separated from the main compartment by a small piece of sodium β -alumina. Potential E or current i was controlled, and quantities of electricity in cathodic (Q_C) and anodic (Q_A) treatments were measured.

In order to identify the alloy phases in different stages of dealloying, X-ray diffraction measurements were performed on samples which were cathodically treated at $Q_C = 35 \text{ C/cm}^2$ and then anodically treated at $Q_A = 1\text{-}29 \text{ C/cm}^2$. γ -, β_1 -, and $\alpha\text{-NiZn}$ alloys were found depending upon Q_A . This suggests that the dealloying occurs stepwise from γ - to β_1 -, and from β_1 - to $\alpha\text{-NiZn}$ alloy. An SEM image of a sample containing β_1 - and $\alpha\text{-NiZn}$ alloys (prepared by $Q_C = 35 \text{ C/cm}^2$ and $Q_A = 20 \text{ C/cm}^2$ at 400°C) exhibited a porous structure which was relatively uniform. EPMA measurement (Fig. 1) also indicated that the Zn and Ni contents were almost constant in the porous layer. These observations suggest that the β_1 - and α -phases were uniformly dispersed. It seems that deep pores or crevices are formed in an early stage of dealloying, and therefore the anodic dissolution of zinc occurs easily even from the deepest point of the alloy layer.

Reference

[1] A. Katagiri, M. Nakata, *J. Electrochem. Soc.*, **150**, C585-C590 (2003).

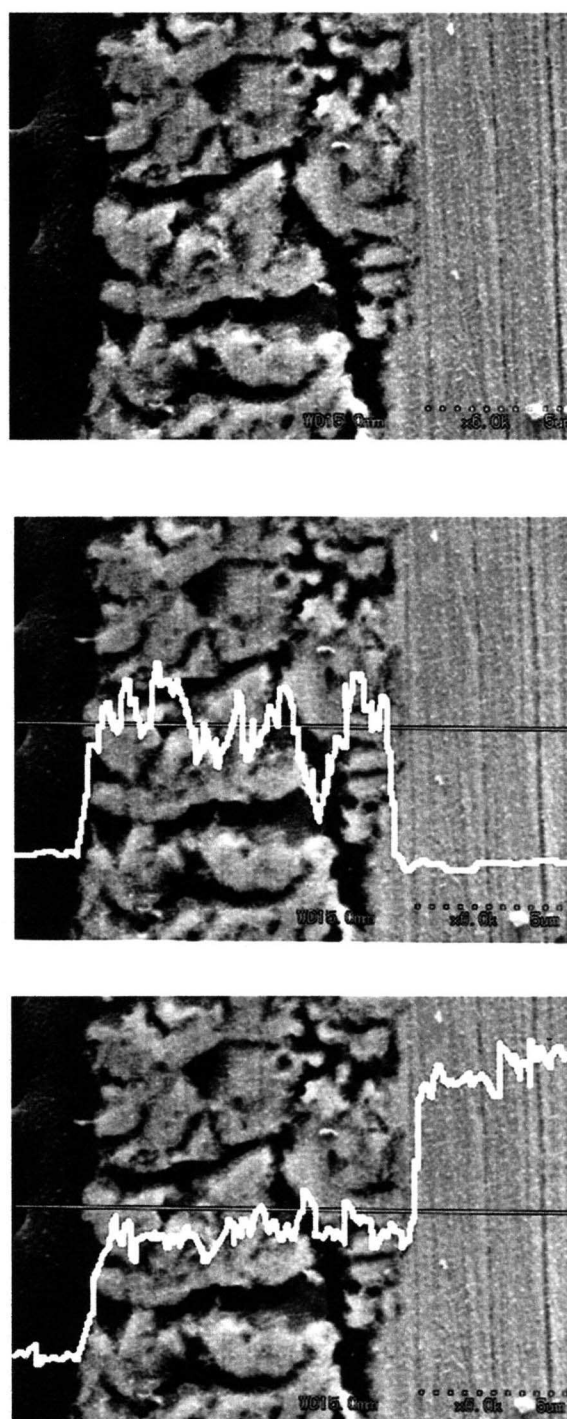


Fig. 1 SEM photograph (top) and composition profiles in EPMA line analysis (middle, Zn; bottom, Ni) of a cross section of a nickel electrode after cathodic treatment ($i_C = 20 \text{ mA/cm}^2$, $Q_C = 35 \text{ C/cm}^2$) and anodic treatment ($i_A = 20 \text{ mA/cm}^2$, $Q_A = 20 \text{ C/cm}^2$) at 400°C . The width of each photograph corresponds to $19.2\mu\text{m}$.