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Structure Control of Cu-Zn Microchannel Lining Layers with Electrochemical Dissolution

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Abstract

The effect of potentiostatic dissolution on the structure of a Cu-Zn alloy microchannel lining layer was investigated. The microchannel lining layer was fabricated by a powder-metallurgical process using copper powder and zinc wire. The lining layer became more porous after potentiostatic dissolution at a constant potential of -0.5 V vs. Ag/AgCl. The lining layer was remarkably dezincified and it contained many open pores under the dissolution condition at $+0.5$ V. These results indicate the possibility of precise structure control of the microchannel lining layer.

Key words

Powder Metallurgy, Potentiostatic Dissolution, Copper-Zinc Alloy, Catalyst, Microreactor, Microchannel

1. Introduction

A catalyst is one of the most important materials in terms of removal of pollution substances and synthesis of useful materials. The representative examples of catalytic reactions are Haber-Bosch process using a porous iron catalyst and the methanation reaction using a nickel catalyst [1]. These catalytic reactions are often performed in hazardous conditions with harmful substances at high temperatures. Therefore, devices for stabilizing reactions are demanded. Recently microreactors have drawn attentions as an efficient channel device for catalytic reactions. This device contains flow channels with a characteristic dimension from several to several hundreds of micrometers. This narrow channel makes it possible to control catalytic reactions exactly because it provides a small reaction space and has a large specific surface area.

As a part of study for producing a microreactor with catalyzed lining layer, we investigated the effect of dealloying on a Cu-Zn alloy microchannel lining layer with a powder metallurgical process. Figure 1 shows the sequence of the processes for producing a microchannel and a catalyzed lining layer [2].

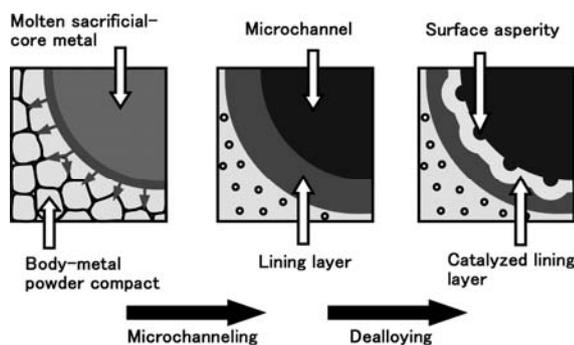


Fig. 1 Sequence of the processes from microchanneling to dealloying

In the microchanneling process, two kinds of metals are used: a body metal and a sacrificial-core metal. The former metal composes the device body. The latter has lower melting point than the body metal and melts during the process to give the shape of the microchannel. A body-metal powder compact is sintered at temperatures between the melting points of these metals. During sintering, molten sacrificial-core metal migrates into the body-metal region by infiltration or diffusion. As a result, a microchannel is formed at the initial site of the sacrificial-core metal. Furthermore, an alloy lining layer often formed around the microchannel [3]. In the case of a combination of copper as the body metal and zinc as the sacrificial-core metal, a porous Cu-Zn alloy lining layer is produced. It was reported that a Cu-Zn alloy and its complex oxides had catalytic activity for a methanol synthesis reaction from carbon oxides and its reverse reaction, steam reforming of methanol [4, 5]. Therefore, the microreactor containing the Cu-Zn microchannel lining layer can be a useful device for catalytic reactions if it is possible to control the composition and structure of the lining layer. In our previous study, we tried dealloying of the Cu-Zn microchannel lining layers by immersion corrosion of zinc in a HCl solution. As a result, the lining layer was gradually dezincified during dealloying. This showed the possibility to control the composition of the lining layer by the dealloying treatment. However, there was a limitation for controlling the surface structure of the lining layer.

Potentiostatic dissolution is an effective method to control the dissolution behavior. This method can control the dissolved phases by setting the potential. In the present study, we investigated the effect of applied potential on the structure of the Cu-Zn alloy microchannel lining layer, in order to exceed the limit of the dealloying treatment by immersion corrosion.

2. Experimental

2.1 Sample preparation

Cylindrical green compacts of copper powder containing two straight zinc wires were prepared by unidirectional pressing at room temperature. The mass of the copper powder was 14 g. The purity and average diameter of the copper powder were 99.9 mass% and 45 μm , respectively. The zinc wires, which were used for the sacrificial cores, were 500 μm in diameter and 15 mm in length. The purity of the zinc wires was 99.99 mass%. The compacting pressure was 156 MPa and the resultant green compact specimen had a diameter of 20 mm and a height of about 8 mm. The specimens were heated at a constant rate of 0.2 K/s from room temperature to 1123 K, and then furnace-cooled at about 0.1 K/s.

Figure 2 shows the procedure for preparation of the sample for potentiostatic dissolution. The sintered specimen was sliced perpendicular to the microchannel to make a platy sample 5 mm in thickness. Then, the cut surface was polished. The specimen surface to be dipped in the solution besides the lining layer was coated with silicone resin.

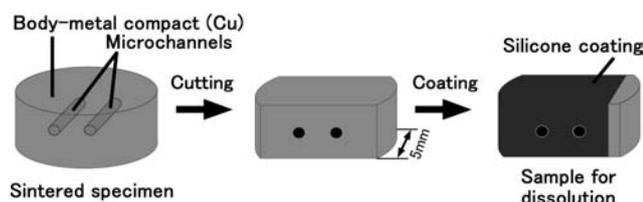


Fig. 2 Preparation procedure of the sample for potentiostatic dissolution

2.2 Potentiostatic dissolution of the lining layer

Potentiostatic dissolution was carried out at constant potentials of -0.5 V or $+0.5$ V for 86.4 ks in a 0.1 kmol/m³ sodium chloride solution at room temperature [6]. Platinum was used for a counter electrode and silver-silver chloride for a reference electrode. Before and after dissolution, cross-sectional structures of the lining layer 1.5 mm inside from the exposed surface were examined by scanning electron microscopy (SEM) and electron probe microanalysis (EPMA). For comparison, only immersed specimen in the same solution for 86.4 ks was also analyzed. To investigate dissolution behavior of the Cu-Zn lining layer, potentiodynamic polarization of zinc and copper sheets were measured. The sweep rate was 4 mV/s.

3. Results

3.1 Structure of the Cu-Zn microchannel lining layer before the dissolution treatment

Figure 3 shows a back-scattered electron image of a cross-sectional structure of the Cu-Zn alloy microchannel lining layer before the dissolution treatment. The lining layer illustrated in Fig. 3 (a) contained many pores near the microchannel. Figure 3 (b) depicts a magnified view image of the structure near the inner wall. Two kinds of phases with different brightness were observed in the lining layer. According to EPMA, these were copper solid solution and zinc oxide. This result was different from that of our previous report [2] which described lining layers consisted of only copper solid solution. This was caused by the difference in the copper powder size. In this study, the copper powder size was 3 times larger than that in the previous study. Because of the large copper powder particles with large voids, diffusion of zinc was not completed and the residual zinc was oxidized in the atmosphere containing a trace of oxygen. The composition of the copper solid solution near the microchannel was about Cu-36mol%Zn (mol% is abbreviated to % in what follows).

3.2 Cu-Zn lining layer after immersion into the solution

Figure 4 presents the structure of the Cu-Zn alloy microchannel lining layer after immersion into the sodium

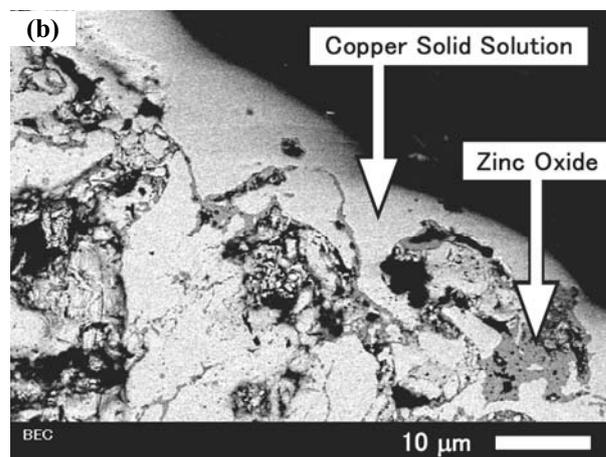
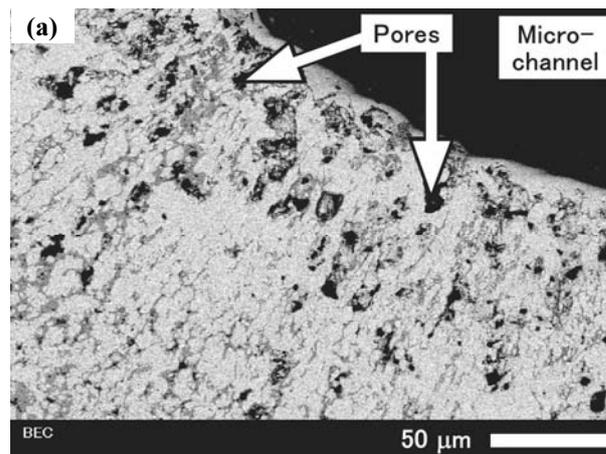


Fig. 3 Back-scattered electron image showing the structure of the Cu-Zn microchannel lining layer before dissolution treatment (a) and a magnified view image near the inner wall (b)

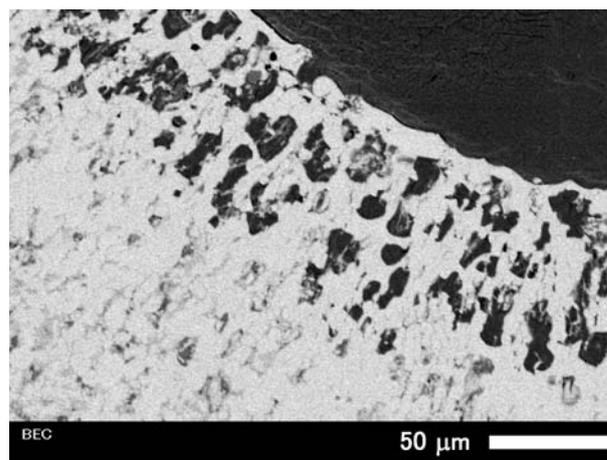


Fig. 4 Structure of the lining layer after immersion into the sodium chloride solution for 86.4 ks

chloride solution. An immersion potential of the specimen was about -0.12 V. Compared to the structure before the treatment, the volume of the pores in the lining layer near

the inner wall increased with dissolution of zinc oxide. The composition of the copper solid solution was Cu-33%Zn-6%O. The ratio of copper to zinc was hardly changed. These results indicate that immersion of the Cu-Zn lining layer into the sodium chloride solution increased the porosity through dissolution of zinc oxide, but it did not affect the composition of the copper solid solution.

3.3 Effect of potentiostatic dissolution

Figure 5 shows the structure of the lining layer after potentiostatic dissolution at a constant potential of -0.5 V for 86.4 ks. The structure was similar to that of the comparison specimen illustrated in Fig. 4 in terms of the depth of dissolution and the volume of enlarged pores. Furthermore, the composition of copper solid solution was about Cu-35%Zn, which was almost the same as that of the comparison specimen only immersed into the solution. These results mean that the dissolution behavior of the lining layer during potentiostatic dissolution at -0.5 V resembles that in the immersion potential.

Figure 6 depicts polarization curves of copper and zinc. Both potentials, -0.5 V (applied potential of potentiostatic dissolution) and -0.12 V (immersion potential during immersion), were in the range of the potential which didn't cause the copper dissolution.

Figure 7 and 8 illustrate the structures of the lining layers after potentiostatic dissolution at a constant potential of $+0.5\text{ V}$ for 86.4 ks. The lining layer consisted of two kinds of sublayers: Sublayer (i) and Sublayer (ii) in Fig. 7. The thickness of Sublayer (i) was about $50\text{ }\mu\text{m}$. This layer contained extremely minute open pores. The composition was changed from Cu-36%Zn to Cu-0.5%Zn-23%O-9%Cl. This means that Sublayer (i) was almost completely dezincified by potentiostatic dissolution. Sublayer (ii) was observed inside Sublayer (i). Compared to the structure before the treatment, many pores formed in Sublayer (ii). This structure resembled that near the inner wall of the specimen after -0.5 V potentiostatic dissolution. However, the composition of Sublayer (ii) was changed to Cu-7%Zn-22%O-9%Cl. Dissolution of Sublayer (ii) was probably in progress.

Figure 9 shows changes in current with time during potentiostatic dissolution at -0.5 and $+0.5\text{ V}$. Both curves were on the downside. As for the result of -0.5 V , negative current was measured through the experiment probably because cathode current flowed on the surface of copper solid solution. The cathode current gradually increased as the surface area increased by dissolution of zinc oxide. The result of $+0.5\text{ V}$ dissolution shows that anode current gradually decreased as dissolution of zinc proceeded. This means that the composition of the Cu-Zn lining layer can be controlled by change of dissolution time.

The above results show that potentiostatic dissolution changes the structure of the Cu-Zn lining layer by applied potential. Compared to the results of immersion corrosion of Cu-Zn microchannel lining layers in our previous study, more remarkable structure change was observed in the lining layer after potentiostatic dissolution. This indicates the possibility of structure control of the lining layer by the methods in this study.

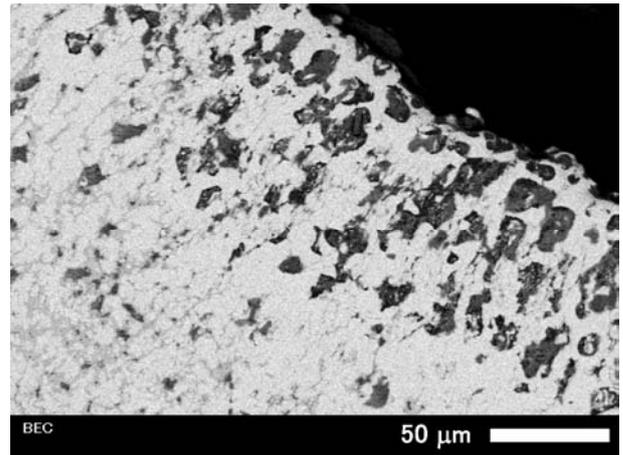


Fig. 5 Structure of the lining layer after potentiostatic dissolution at a constant potential of -0.5 V for 86.4 ks

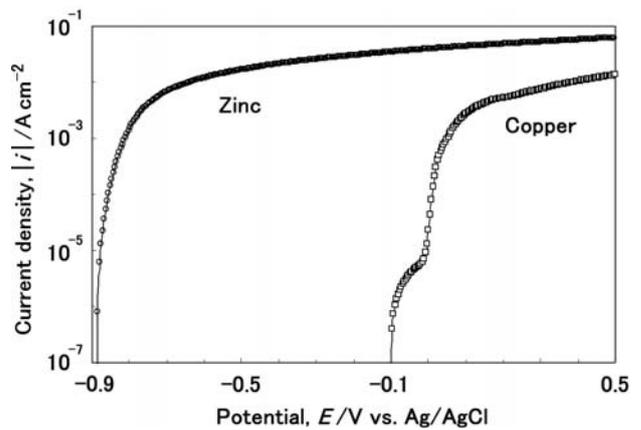


Fig. 6 Polarization curves of copper and zinc in a 0.1 kmol/m^3 sodium chloride solution at room temperature

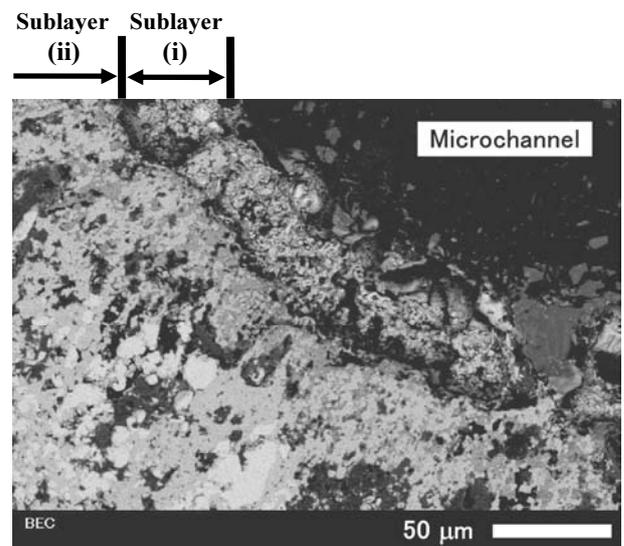


Fig. 7 Structure of the lining layer after potentiostatic dissolution at a constant potential of $+0.5\text{ V}$ for 86.4 ks

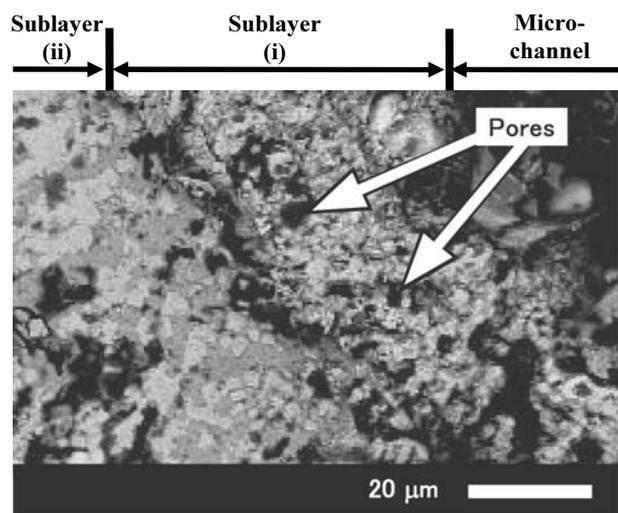


Fig. 8 Magnified view image of the lining layer after potentiostatic dissolution at a constant potential of +0.5 V for 86.4 ks

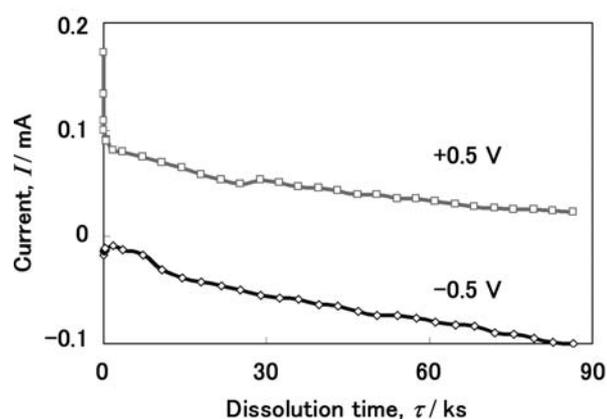


Fig. 9 Changes in current with time during potentiostatic dissolution

4. Conclusion

Potentiostatic dissolution of the Cu-Zn alloy microchannel lining layer was carried out for structure control of the lining layer. Changes in the structure and composition inside the specimen were investigated. The results obtained are summarized as follows.

(1) The structure of the Cu-Zn lining layer before the treatment was composed of copper solid solution and zinc oxide when the copper powder size was 45 μm .

(2) The Cu-Zn lining layer became more porous after potentiostatic dissolution at a constant potential of -0.5 V due to the dissolution of zinc oxide. The copper solid solution was not affected.

(3) The structure of the lining layer after potentiostatic dissolution at a constant potential of $+0.5$ V consisted of two kinds of sublayers. Sublayer (i), the outer layer, was almost completely dezincified and it contained many interconnected pores. Sublayer (ii), the inner layer, was in progress of dissolution.

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