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## Dealloying of Cu-Zn Alloy Microchannel Lining Layers for Producing Microporous Catalyst

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### Abstract

A Cu-Zn alloy microchannel lining layer was fabricated by a powder-metallurgical process using Cu powder and Zn wire. The effects of the dealloying treatment on the composition and structure of the lining layer were investigated. The lining layer became more porous and dezinced as the dealloying time increased. In the case of long-time dealloying, Zn-based corrosion products precipitated. These results indicated the possibility of the control of the structure and composition of the inner wall of the microchannel.

### Key words

Powder Metallurgy, Dealloying, Copper-Zinc Alloy, Catalyst, Microreactor

### 1. Introduction

Progress of the catalytic technologies is one of the most valid means for solving the environmental problems including global warming, air pollution and ozone depletion. The assignments of the catalytic technologies are searching for new remarkable catalytic materials and developing the method of catalyst supporting. For the latter assignment, the microreactor technology draws attentions as a new approach for producing an efficient reactor for catalytic reactions. The microreactor contains flow channels with a characteristic dimension from several to several hundreds of micrometers. This microchannel structure with high specific surface area is suitable for catalytic reactions. Some of the authors have studied powder-metallurgical microchanneling process to produce metallic microreactors [1]. The concept of the process is shown in Fig. 1.

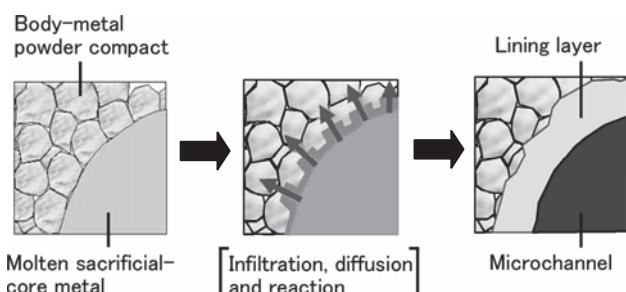


Fig. 1 Concept of the powder-metallurgical microchanneling process [1]

In this process, two kinds of metals with different melting points are used: the body metal and the sacrificial-core metal. The body metal has a higher melting point and composes the device body. The sacrificial-core metal flows out to the body-metal powder region and gives

the shape of the microchannel. Initially, body-metal powder with a sacrificial core is unidirectionally pressed into a cylindrical compact. Then, the powder compact is sintered at temperatures between the melting points of the metals. During sintering, molten sacrificial-core metal migrates into the body-metal region by infiltration and/or diffusion. Eventually, a microchannel is formed at the initial position of the sacrificial-core metal. Moreover, an alloy lining layer is often formed around the microchannel.

This process is simple and easy to produce the microreactor containing three-dimensional microchannel networks with arbitrary shapes, which is difficult to fabricate for conventional processes. In addition, the composition and structure of the lining layer are changed depending on the combination of the body metal and the sacrificial-core metal [1]. For instance, the combination of Cu for the body metal and Zn for the sacrificial-core metal produces a porous Cu-Zn lining layer. It was reported that a Cu-Zn alloy and its complex oxides have catalytic activity for methanol synthesis reaction from carbon oxides and its reverse reaction, steam reforming of methanol [2,3]. Therefore, the microreactor containing the Cu-Zn microchannel lining layer can be a useful device for these catalytic reactions if it is possible to control the composition and porous structure of the lining layer.

Based on these backgrounds, we focus on dealloying of the Cu-Zn alloy microchannel lining layers. It is well known that Cu-Zn alloys are dealloyed by various solutions [4]. The structure and composition at the surface of a Cu-Zn alloy may be controlled by dealloying. In this study, we researched the influence of dealloying on the structure and composition of the Cu-Zn alloy microchannel lining layer.

### 2. Experimental

#### 2.1 Sample preparation for dealloying

A cylindrical copper powder compact containing two zinc wires was prepared by unidirectional pressing at room temperature. The compacting pressure was 156 MPa. The mass of the copper powder was 14 g. The purity and average diameter of the Cu powder were 99.9 mass% and 15  $\mu\text{m}$ , respectively. Two straight zinc wires 500  $\mu\text{m}$  in diameter and 15 mm in length were used for the sacrificial cores. The purity of the zinc wires was 99.99 mass%. The obtained powder compact specimen had a diameter of 20 mm and a height of about 8 mm.

The compact 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. The porosities of the specimens before and after sintering were calculated from the following equation, and the results were about 38% and 26%, respectively.

$$X_C = \left\{ 1 - \frac{(M_C - M_S)}{\rho_{Cu} (V_C - V_S)} \right\} \times 100$$

where  $X_C$  is the porosity of the specimen.  $M_C$  and  $V_C$  are the mass and volume of the specimen, respectively.  $M_S$  and  $V_S$  are those of the sacrificial core.  $\rho_{Cu}$  is the density of copper.

Figure 2 shows the preparation procedure of the sample for dealloying. The sintered specimen was sliced perpendicular to the microchannel to make a platy sample 5 mm in thickness. Then, the cut surface was buffed, and the remaining area was coated by silicone resin.

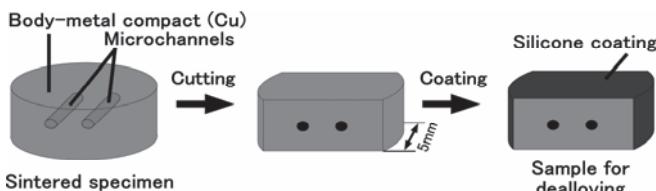


Fig. 2 Preparation procedure of the sample for dealloying

## 2.2 Dealloying of the microchannel lining layer

The sample was immersed in a 0.5 kmol m<sup>-3</sup> HCl solution at room temperature for dealloying. Dealloying time,  $t$ , was 7.2, 21.6 or 86.4 ks. The surface structure and the cross-sectional structure 1.5 mm inside from the surface of the sample after dealloying were observed by using SEM. Element analysis was performed using EPMA. XRD analysis was also performed on the Cu-Zn lining layer.

## 3. Results

### 3.1 Structure and composition of the Cu-Zn lining layer before dealloying

Figure 3 shows the cross-sectional structure of the Cu-Zn alloy microchannel lining layer and the copper-and-zinc concentration profiles measured along the line AB. In XRD analysis on the lining layer, only Cu peaks were detected. This result demonstrated that the Cu-Zn lining layer was mainly composed of copper solid solution. Figure 4 depicts a magnified SEM image of the lining layer near the microchannel. Many pores were distributed in the lining layer.

### 3.2 Dealloyed structure of the lining layer at the surface of the sample

Figure 5 shows the dealloyed structures of the lining layers at the surface of the samples prepared with different dealloying times. Table 1 lists the results of composition analyses at each position shown in Fig. 5.

In the structure dealloyed for 7.2 ks (see Fig. 5(a)), microasperities and a trench structure were formed on the lining layer region. From the composition analyses at the position a1 (see Table 1), the structure with microasperities was mainly composed of Cu. It clearly demonstrates the dezincification of the Cu-Zn alloy. As for the trench structure, it formed at about  $x = 200$   $\mu$ m. The location is

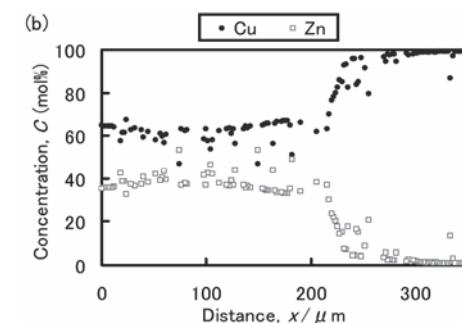
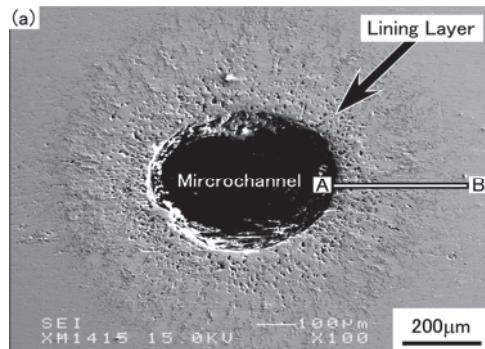


Fig. 3 SEM image of the lining layer near the microchannel (a) and the copper-and-zinc concentration profiles measured along the line AB (b). The compact specimen was pressed under 156 MPa

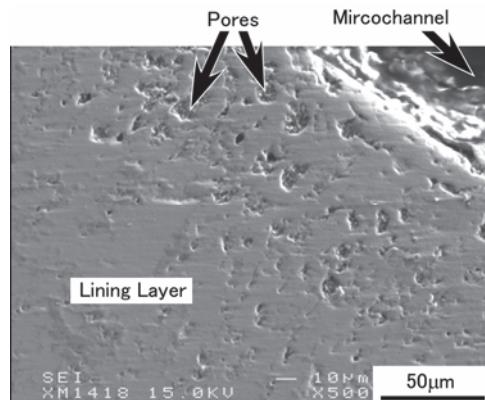


Fig. 4 Magnified SEM image showing the lining layer with many pores. The compact specimen was pressed under 156 MPa

corresponding to the boundary between the concentration plateau and the graded concentration region in Fig. 3(b). The difference in zinc concentration might affect the formation of the trench structure. It is also noteworthy that the zinc concentration at the position a1 was richer than that at a2. This result came out the opposite of the concentration profile in Fig. 3(b). The lining layer at the surface of the specimen after dealloying for 21.6 ks was depicted in Fig. 5(b). Crack-like structures and two kinds of phases (b1 and b2) were observed. According to Table 1, the composition of the phase at the position b1 was similar to that before dealloying, and the other (b2) consisted of CuCl. The phase at b1 derived from the dezincined lining

layer. The CuCl phase was probably a corrosion product precipitated from the solution containing dissolved Cu. Most of the valleys of the microasperities were filled with the CuCl precipitates. The remained parts looked like cracks. In the case of 86.4 ks-dealloying (Fig. 5(c)), the valley-like structure observed in Fig. 5(a) was completely filled with the CuCl precipitates.

The above results indicate that the Cu-Zn lining layer can be dealloyed in an appropriate condition. However, excessive treatment produces copper chloride precipitates on the surface.

Table 1 Composition at each measured position in the dealloyed lining layer shown in Fig. 5. *t*: dealloying time

Position	<i>t</i> (ks)	Concentration, <i>C</i> (mol%)			
		Cu	Zn	Cl	O
a1	7.2	99.3	0.264	0.470	Nd
a2	7.2	89.2	6.73	2.92	1.12
b1	21.6	94.9	Nd	5.12	Nd
b2	21.6	50.0	Nd	50.0	Nd
c1	86.4	62.2	Nd	37.8	Nd
c2	86.4	50.8	Nd	49.2	Nd

### 3.3 Dealloyed structure of the lining layer 1.5 mm inside from the surface of the sample

Figure 6 shows the influence of the dealloying time on the inner structures of the lining layers. Table 2 lists the compositions measured at the positions shown in Fig. 6.

Figure 6(a) depicts the lining layer of the specimen after dealloying for 7.2 ks. Compared to the structure before dealloying, the size of the pores in the lining layer became larger. According to the EPMA results for the measured positions a1' and a2', two kinds of phases could be detected. The phase at the position a1' had the composition comparable to the lining layer before dealloying. The other position (a2') was mainly composed of copper, zinc and oxygen. The latter phase is a kind of corrosion product formed by HCl solution soaking into the lining layer.

Figure 6(b) presents the cross-sectional structure of the lining layer after dealloying for 21.6 ks. The pores in the lining layer became larger and many precipitates were observed in the lining layer. The metallic phase at the position b1' near the inner wall of the microchannel was more dezincified than the position a1'. At the position b2', the pore was filled with a corrosion product. It consisted of three elements except for copper. It was richer in zinc and poorer in copper than the position a2'.

Figure 6(c) shows the lining layer of the sample dealloyed for 86.4 ks. Unlike the cases of 7.2 or 21.6 ks, precipitates were widely distributed in the lining layer. The composition measurement at the position c1' showed that the metallic region in the lining layer mainly consisted of copper. This indicates remarkable dezincification of the lining layer. On the other hand, the composition of the precipitates at the position c2' was similar to that at b2'. These results indicate the formation of a complex structure composed of copper and the zinc-based corrosion products.

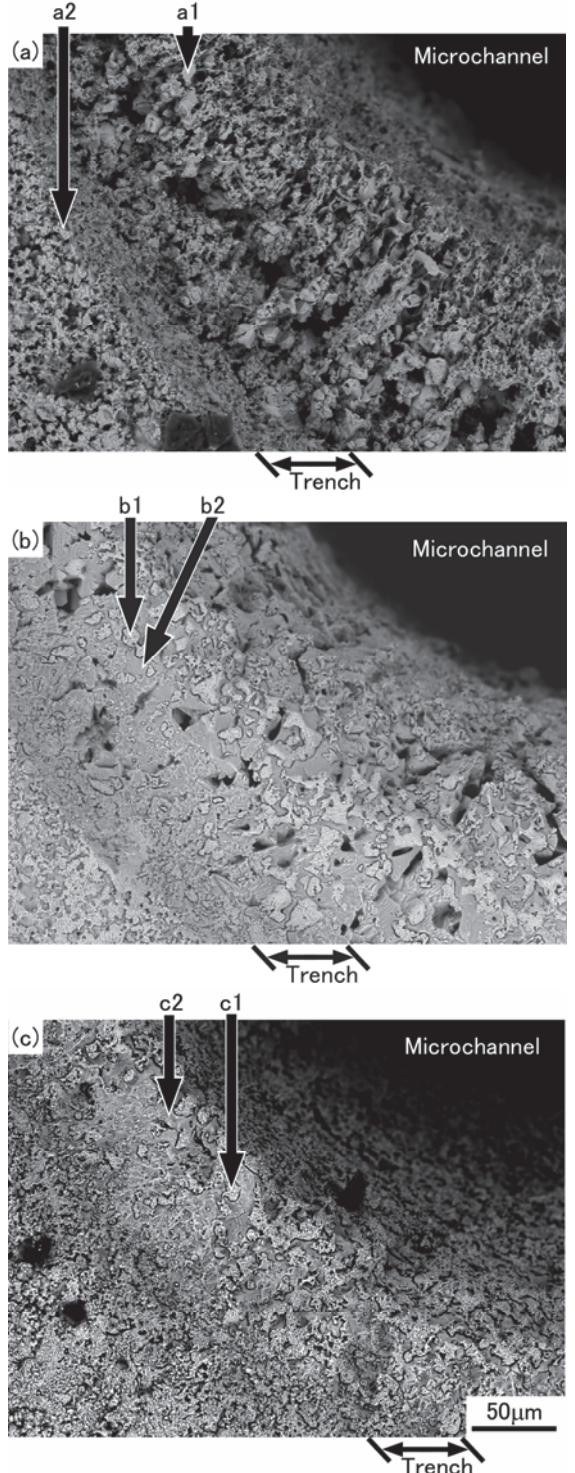


Fig. 5 SEM images showing the structures at the surface of the samples dealloyed in the hydrochloric acid solution at room temperature. Dealloyed time:

(a) 7.2 ks, (b) 21.6 ks and (c) 86.4 ks

The above results show that the dealloying treatment changes the composition of the lining layer and increases the size of the pores. Joo *et al.* reported that a mixture of CuO and ZnO had high catalytic performance for CO<sub>2</sub> hydrogenation when the molar ratio of Cu and Zn was 3 to 1 [5]. According to Table 2, the Cu/Zn ratio was 1.9 at the

position a1' and 4.3 at the position b1'. Therefore, we can produce the CuO/ZnO catalyst by oxidation of the lining layer after dealloying for a certain time between 7.2 and 2.16 ks. At the position c1' in the specimen dealloyed for 86.4 ks, Cu concentration was near 100%. This result suggests that a Raney copper catalyst can be produced by long-time dealloying. As for the corrosion products composed of Zn, Cl and O, it may be dechlorinated by roasting. This is an issue in the future.

Table 2 Composition at each measured position in the dealloyed lining layer shown in Fig. 6.  $t$ : dealloying time

Position	$t$ (ks)	Concentration, $C$ (mol%)			
		Cu	Zn	Cl	O
a1'	7.2	59.6	32.1	0.0763	7.44
a2'	7.2	19.9	36.8	0.0712	43.2
b1'	21.6	78.2	18.1	0.834	2.98
b2'	21.6	2.71	38.0	9.81	49.5
c1'	86.4	97.9	1.94	0.109	Nd
c2'	86.4	4.07	37.9	10.6	47.4

#### 4. Conclusion

Dealloying of the Cu-Zn alloy microchannel lining layer was performed for the purpose of giving catalytic activity to the lining layer. The influence of dealloying on the lining layers at the surface and 1.5 mm inside of the samples was investigated. The results obtained are summarized as follows.

- (1) The structure of the Cu-Zn lining layer before dealloying was composed of copper solid solution ( $\alpha$ ).
- (2) The Cu-Zn lining layer at the surface of the specimen dealloyed in a 0.5 kmol m<sup>-3</sup> HCl for 7.2 ks was composed of 99 mol%Cu. In the case of 21.6 or 86.4 ks dealloying, the precipitates of copper chlorides formed.
- (3) The composition of the lining layer 1.5 mm inside from the surface of the specimen can be controlled by dealloying. The micropores in the lining layer had grown in the samples dealloyed for 7.2 and 21.6 ks. In the case of 86.4 ks dealloying, the complex structure consisting of copper and the zinc-based corrosion product formed.

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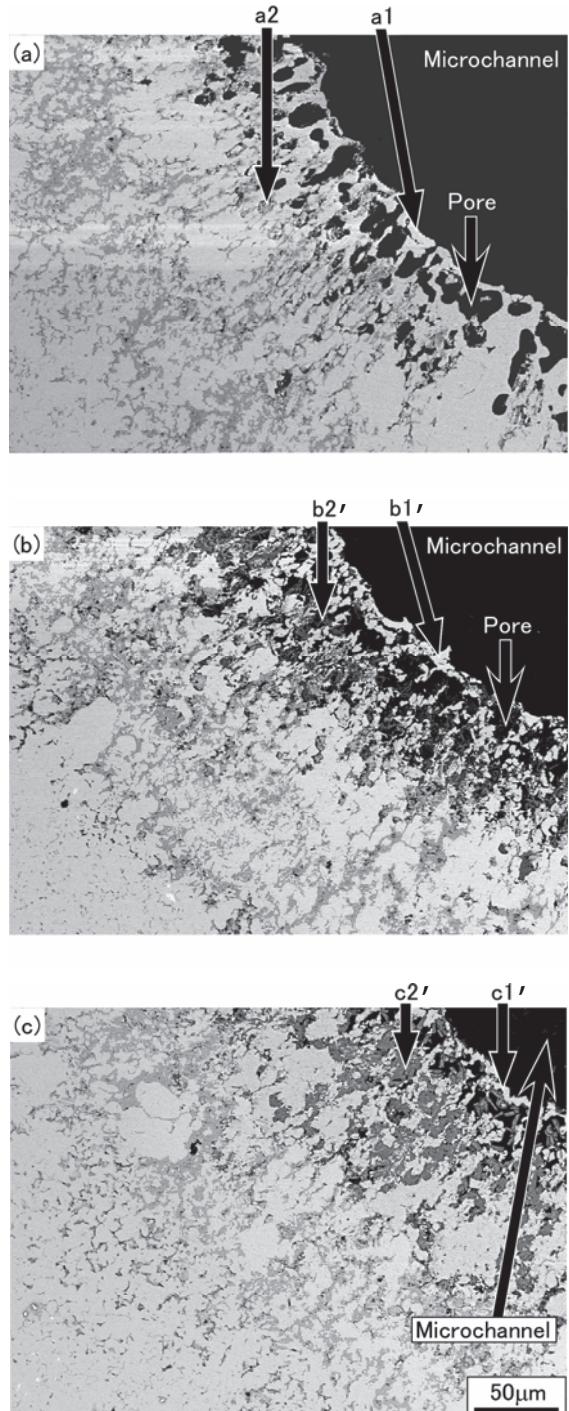


Fig. 6 SEM images showing the influence of dealloying treatment on the cross-sectional structures of the lining layers 1.5 mm inside from the surface of the samples. Dealloying time: (a) 7.2 ks, (b) 21.6 ks and (c) 86.4 ks

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