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Formation of Nanoporous Structures on Planner Al-Zn Alloy Lining Layers by Anodic Oxidation

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Abstract
We investigated the anodic oxidation of planner Al-Zn lining layer in a phosphoric acid solution to produce a nanoporous oxide film. The Al-Zn lining layer was produced by a sacrificial-core method using aluminum powder and zinc plate. No nanoporous structure was observed in the specimen after anodic oxidation at 50 V and 100 V for 7.2 ks. On the other hand, well-developed nanoporous structure was formed in the entire region in the case of 150 V for 7.2 ks or longer.

Key words
Powder Metallurgy, Microreactor, Anodic Oxidation, Aluminum-Zinc Alloy, Nanoporous Oxide Film

1. Introduction

Catalytic reactions play various important roles in formulation of sustainable society. On the other hand, resources of catalyst materials will run out sooner or later. The efficient use of them is getting more important. For chemical reactors, the surface area of the reaction space is one of the most important factors to improve the catalyst performance. A microreactor has a high specific surface area because of its microchannel structure with a characteristic dimension from several to several hundreds micrometers. A sacrificial-core method is one of the valid ways for producing microchannels in metal bodies [1-9]. In this process, a metal powder compact containing thin wire of the other metal with lower melting point is sintered at temperatures between the melting points of these metals. The former metal is called the body metal and the latter metal is called the sacrificial-core metal. During sintering, the sacrificial-core metal melts and migrates to the body metal region. Finally, the microchannel is formed at the site initially occupied by the sacrificial-core metal. The shape of the microchannel is given by the configuration of the sacrificial core. In addition, a lining layer, an alloy layer consisting of the body metal and the sacrificial-core metal is formed around the microchannel.

We recently investigated a method to form a nanoporous structure on a Ti-Al or Al-Zn lining layer by anodic oxidation [7-9]. The anodic oxidation is an electrochemical method to produce a metal oxide film on the surface of metals. Especially, in the case of aluminum or titanium, a nanoporous oxide film can be produced on the surface of the metal by partial dissolution and reformation of oxide in a suitable condition [10-16].

In the case of the Ti-Al microchannel lining layer, a well-developed nanoporous structure was produced by anodic oxidation in a H_2SO_4-HF mixed solution [7]. In the case of the Al-Zn microchannel lining layer in the oxalic acid solution, in contrast, nanopores were formed but they were undeveloped [8-9]. We discussed that this result could be attributed to the following two facts. First, the reaction field was in the microchannel. Second, zinc was contained in the lining layer as the alloying element. According to our study using a plate-like sacrificial core [9], zinc hinders the formation of the nanoporous alumina film, and thus the nanoporous structure was not well-developed even under the optimum condition. A higher voltage for anodic oxidation seemed to be favorable for nanoporous alumina formation. However, the specimen was dissolved at the higher voltage. A phosphoric acid solution is one of the solutions used for anodic oxidation of aluminum and it can be used at higher voltage than the oxalic acid solution. In this study, therefore, the phosphoric acid was examined for anodic oxidation solution in order to explore the conditions to produce a well-developed nanoporous structure.

2. Experimental Procedure

2.1 Preparation of powder compact specimens

In order to eliminate the influence of the size and shape of the reaction space, a planner lining layer was used as it was for the previous study [9]. The lining layer was prepared by using a plate-like sacrificial core and then anodized under various conditions.

Figure 1 shows a schema of a compact specimen with a plate-like sacrificial core. Aluminum powder of 2 g with a zinc plate was pressed to prepare a cylindrical compact specimen 20 mm in diameter. The compact specimen was sintered under argon gas atmosphere with the following heating pattern. It was heated at a constant rate of 0.2 K/s from room temperature to 873 K, kept at 873 K for 9.0 ks and then furnace-cooled at 0.4 K/s.

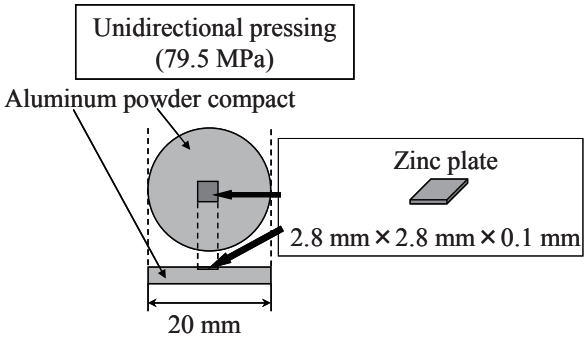


Fig. 1 Preparation of the compact specimen with a plate-like sacrificial core

2.2 Anodic oxidation of the lining layer

The sintered specimen was coated by silicone resin exclusive of the sites initially occupied by the sacrificial core. The specimen was anodized at 50, 100 or 150 V in 0.22 kmol/m^3 H_3PO_4 solution at room temperature. The specimen was used as the anodic electrode and a platinum plate was used as the cathodic electrode. Current during anodic oxidation was measured. Surface structure of the specimen was observed by FE-SEM.

3. Results and Discussion

Figures 2 and 3 depict the surface structures of the specimens after anodic oxidation at 50 V for 7.2 ks and 14.4 ks, respectively. No nanoporous structure was observed in the specimen shown in Fig. 2. On the other hand, a nanoporous structure was formed on a part of the specimen shown in Fig. 3. Figure 4 presents change in current with anodizing time at 50V. Current started to increase after about 7 ks. In the case of Fig. 2, the oxide film probably started to dissolve but the nanoporous structure was not yet formed.

Figures 5 and 6 show the surface structures of the specimens after anodic oxidation at 100 V for 7.2 ks and 14.4 ks, respectively. As with the case of 50 V anodic oxidation, no nanoporous structure was formed on the surface of the specimen after anodic oxidation for 7.2 ks, but it was formed on a part of the specimen when anodic oxidation time was increased to 14.4 ks. Figure 7 depicts change in current with anodizing time at 100V. Similar is the case of 50 V anodic oxidation, current started to increase after about 7 ks. From these results, longer anodic oxidation is needed to form the nanoporous structure on the surface of the specimen by 50 V or 100 V anodic oxidation.

Figures 8 and 9 present the surface structures of the specimens after anodic oxidation at 150 V for 7.2 ks and 14.4 ks, respectively. In both specimens, well-developed nanoporous structures were observed in the entire region. Figure 10 shows a cross-sectional structure near the surface of the lining layer after anodic oxidation at 150 V for 7.2 ks. Three kinds of phases were observed in this region. Phase (C) was composed of aluminum containing 5 mol% O. In this phase, zinc and phosphorus were trace. This result shows that Phase (C) corresponds to the body metal. Phase (B) was Al-Zn alloy containing 7 mol% O. Thus, Phase (B) constituted the lining layer. In contrast, Phase (A) observed at the surface of the lining layer was mainly composed of aluminum and oxygen. The molar ratio of these elements in Phase (A), M_O / M_{Al}, was 1.7, which was comparable with the ratio of alumina (1.5). This result indicates that the Phase (A) was formed by anodic oxidation. The composition of the lining layer before anodic oxidation was Al-11mol%Zn-11mol%O. Its zinc concentration was higher than that of Phase (B). This result suggests that the actual alumina formation started after selective dissolution of a certain amount of zinc. Figure 11 shows change in current with anodizing time at 150V. Intensive fluctuation of current was observed. This is caused by frequent generation and detachment of bubbles. They were probably produced by a side reaction such as electrolyzation of water. For the inner wall of the microchannel, a new devisal is needed to prevent the bubbles from stagnation in the microchannel. Circulation of the solution through the microchannel will be one of the resolution methods. Verification of the potency of this method is our topic for future investigation.

4. Conclusions

A phosphoric acid was examined for anodic oxidation solution in order to explore conditions to produce a well-developed nanoporous structure on the surface of the Al-Zn lining layer. The results obtained are summarized as follows.

(1) No nanoporous structure was observed in the specimen after anodic oxidation at 50 V or 100 V for 7.2 ks.

(2) In the case of longer anodic oxidation time, 14.4 ks, the nanoporous structure was found on a part of the specimen after anodic oxidized at 50 V and 100 V.

(3) The nanoporous structure was formed in the entire region of the lining-layer surface by anodic oxidation at 150 V for 7.2 ks or longer.

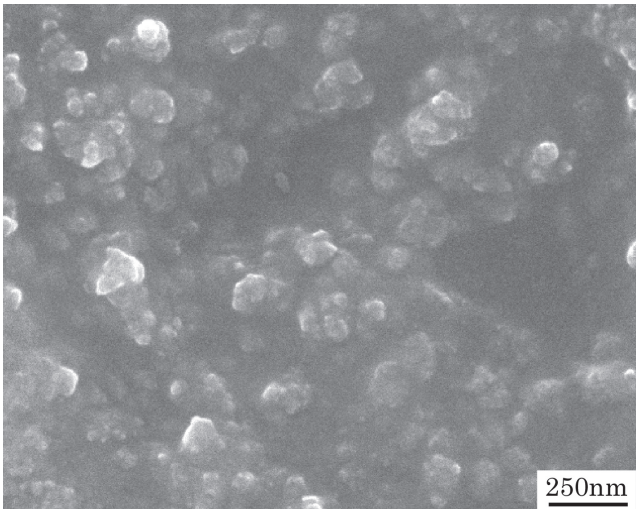


Fig.2 Surface structure after anodic oxidation at 50 V for 7.2 ks

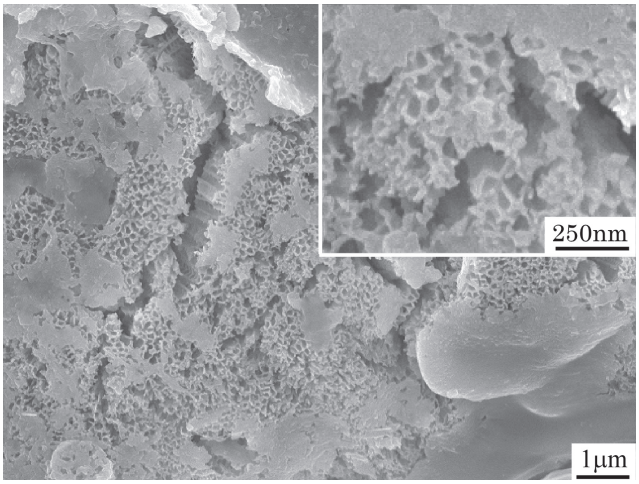


Fig. 3 Surface structure after anodic oxidation at 50 V for 14.4 ks

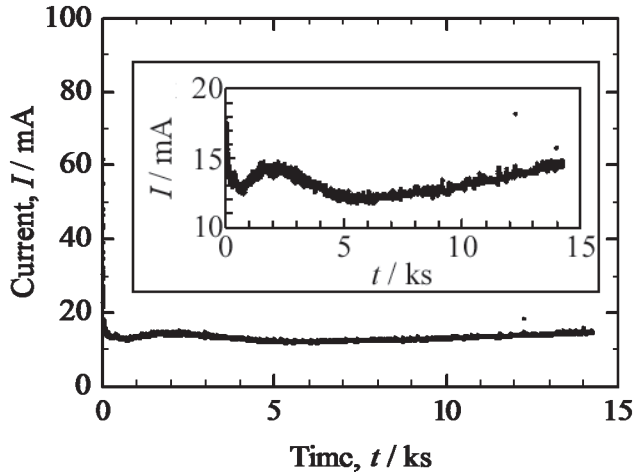


Fig. 4 Change in current with anodizing time at 50 V

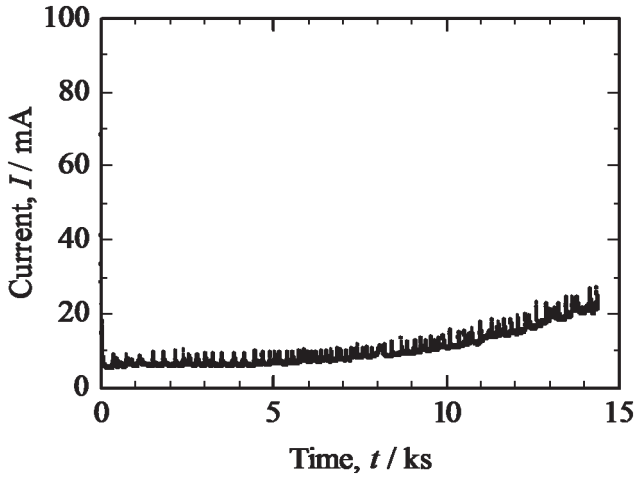


Fig. 7 Change in current with anodizing time at100 V

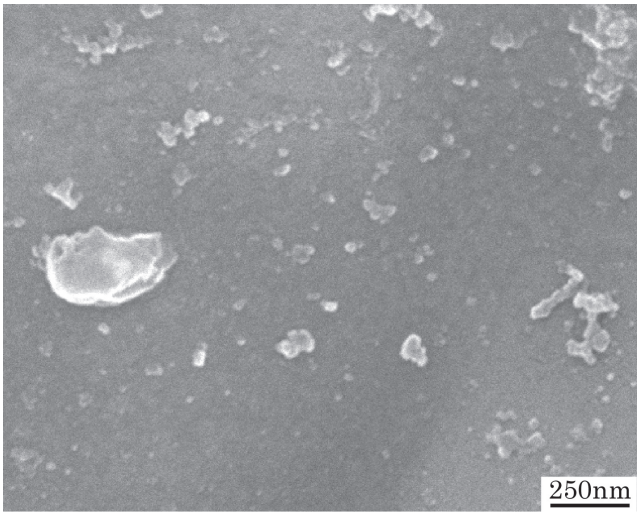


Fig. 5 Surface structure after anodic oxidation at 100 V for 7.2ks

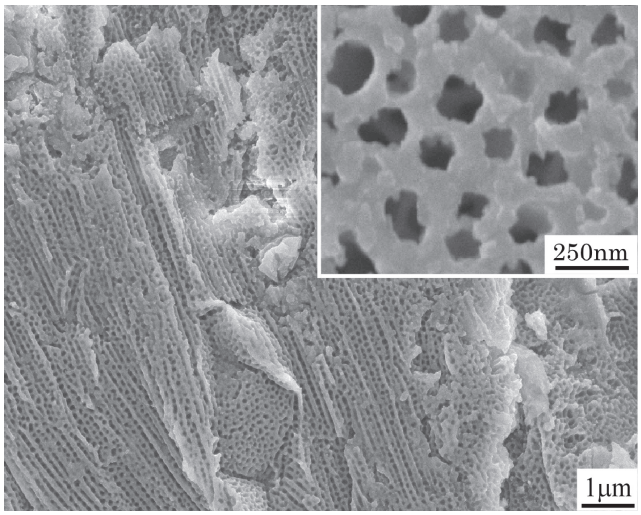


Fig. 8 Surface structure after anodic oxidation at 150 V for 7.2 ks

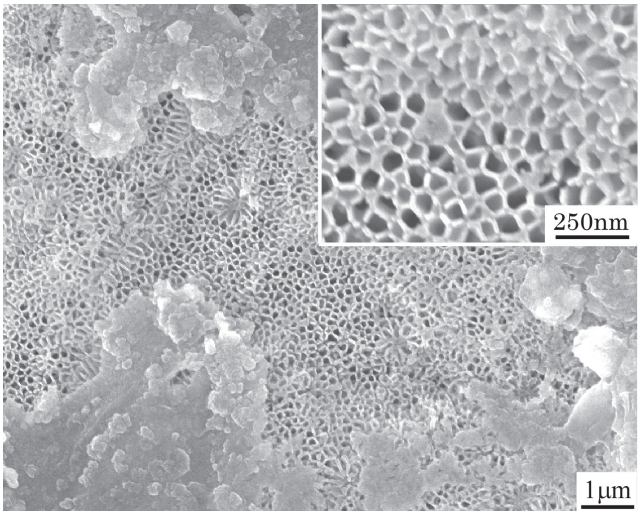


Fig. 6 Surface structure after anodic oxidation at 100 V for 14.4ks

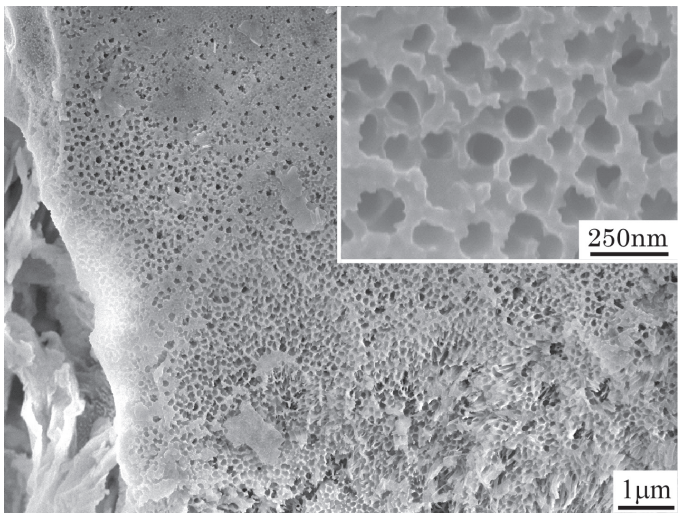
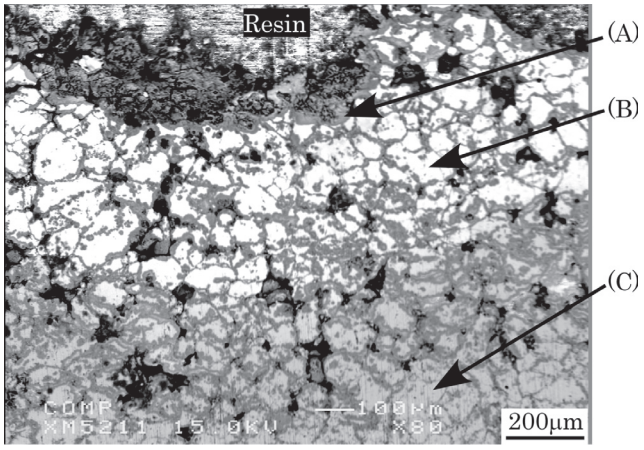


Fig. 9 Surface structure after anodic oxidation at 150 V for 14.4 ks



Phase	Concentration (mol%)			
	Al	Zn	O	P
(A)	35	1	61	3
(B)	86	6	7	Trace
(C)	95	Trace	5	Trace

Fig. 10 Cross-sectional structure near the surface of the lining layer after anodic oxidation at 150 V for 7.2 ks and compositions of the phase (A), (B) and (C)

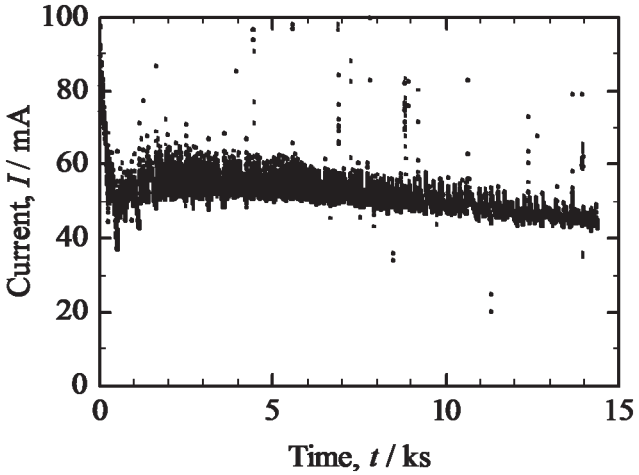


Fig. 11 Change in current with anodizing time at 150 V

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