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Anodic Oxidation Behavior of Al-Zn Alloy Lining Layer Produced by a Sacrificial-Core Method

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Abstract
We investigated the influence of Zn on anodic oxidation of planner Al-Zn lining layers produced by a sacrificial-core method. The Al-Zn lining layer was produced from aluminum powder and zinc plate. By comparison with experiments using sintered aluminum powder compacts, it was found that zinc hindered the formation of nanoporous alumina film. The nanoporous structure can be formed on the surface of the Al-Zn alloy lining layer by long time anodic oxidation of 7.2 ks.

Key words
Powder Metallurgy, Nanoporous Structure, Aluminum-Zinc Alloy, Anodic Oxidation, Infiltration

1. Introduction

There are many environmental and resource problems and they have become extremely serious. Catalysts are used in various fields for solving these problems. One of the important factors for improving a catalyst performance is the surface area of the reaction space in the reactor. A microreactor has a high specific surface area because of its microchannel structure with a characteristic length from several to several hundreds micrometer. A powder-metallurgical microchanneling process using a sacrificial-core method is one of the valid ways for producing microchannels in metal bodies [1-6]. In this process, a metal powder compact containing a different with lower melting point metal wire 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 was given by the configuration of the sacrificial-core metal. 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 of fabricating a nanoporous structure on a Ti-Al or Al-Zn lining layer by anodic oxidation [7-8]. Anodic oxidation is a method to produce a metal oxide film on the surface of metals. Especially, in the case of aluminum or titanium, a nanoporous oxide film was formed on the surface of the metal in a suitable condition [9-15].

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, on the other hand, nanopores formed but they were undeveloped [8]. 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.

In this study, we investigated the effect of zinc contained in the lining layer on the anodic oxidation behavior of the Al-Zn lining layer.

2. Experimental Procedure

2.1 Preparation of powder compact specimens

In order to eliminate the influence of the size and shape of reaction space, a planner lining layer was used. It was prepared by using a plate-like sacrificial core and then anodized under various conditions to explore the suitable condition for producing fully-developed nanoporous structure.

Figure 1 shows a schema of a compact specimen with a plate-like sacrificial core. Aluminum powder of about 2 g and a zinc plate were pressed to prepare a cylindrical compact specimen. The compact specimen was 20 mm in diameter. The compact specimen was sintered under argon gas atmosphere in 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. For comparison, a sintered aluminum powder compact with no zinc plate was also prepared under the same condition.

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 comparative specimen was also coated in the same manner. The specimen was anodized at 50, 100 or 150 V in 0.22 kmol/m^3 $(COOH)_2$ solution at room temperature. The specimen was used as the anodic electrode and a platinum plate was used as the cathodic electrode.

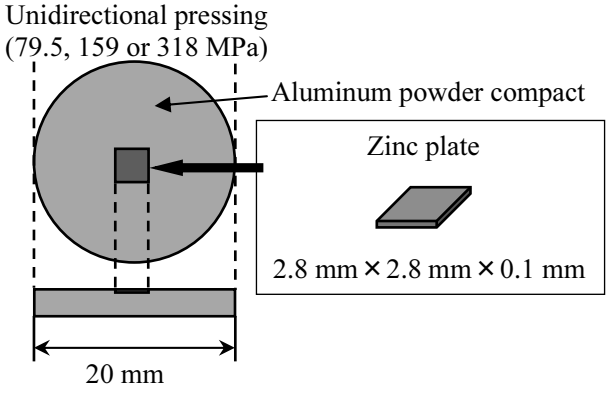

Fig. 1 Preparation of the compact specimen with a plate-like sacrificial core

Surface structure of the specimen was observed by FE-SEM. Surface composition of the specimen was analyzed by EPMA.

3. Results and Discussions

Figure 2 shows surface structures of the lining layers after anodic oxidation. Three kinds of compact specimens pressed under different compacting pressures are shown. The anodic oxidation condition was the same as that used for the microchannel lining layers in our previous study [8]: anodic oxidation at 50 V in 0.22 kmol/m^3 $(COOH)_2$ solution at room temperature for 1.8ks. In Fig. 2, nanoporous structure was not formed in every specimen. Figure 3 depicts the surface structures of the comparative specimens after anodic oxidation. The anodic oxidation conditions and compacting pressure were the same as those

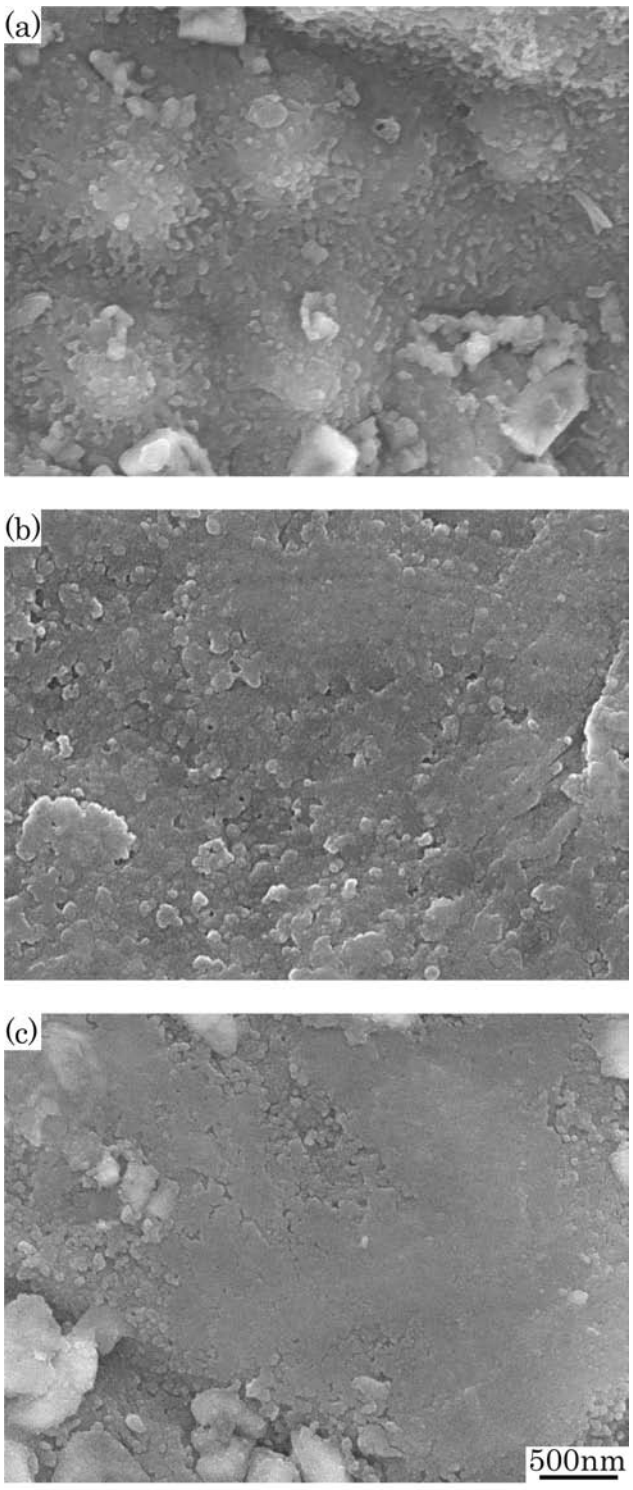

Fig. 2 Surface structures of the Al-Zn lining layers after anodic oxidation at 50 V for 1.8 ks. Compacting pressure: (a) 79.5 MPa, (b) 159 MPa, (c) 318 MPa

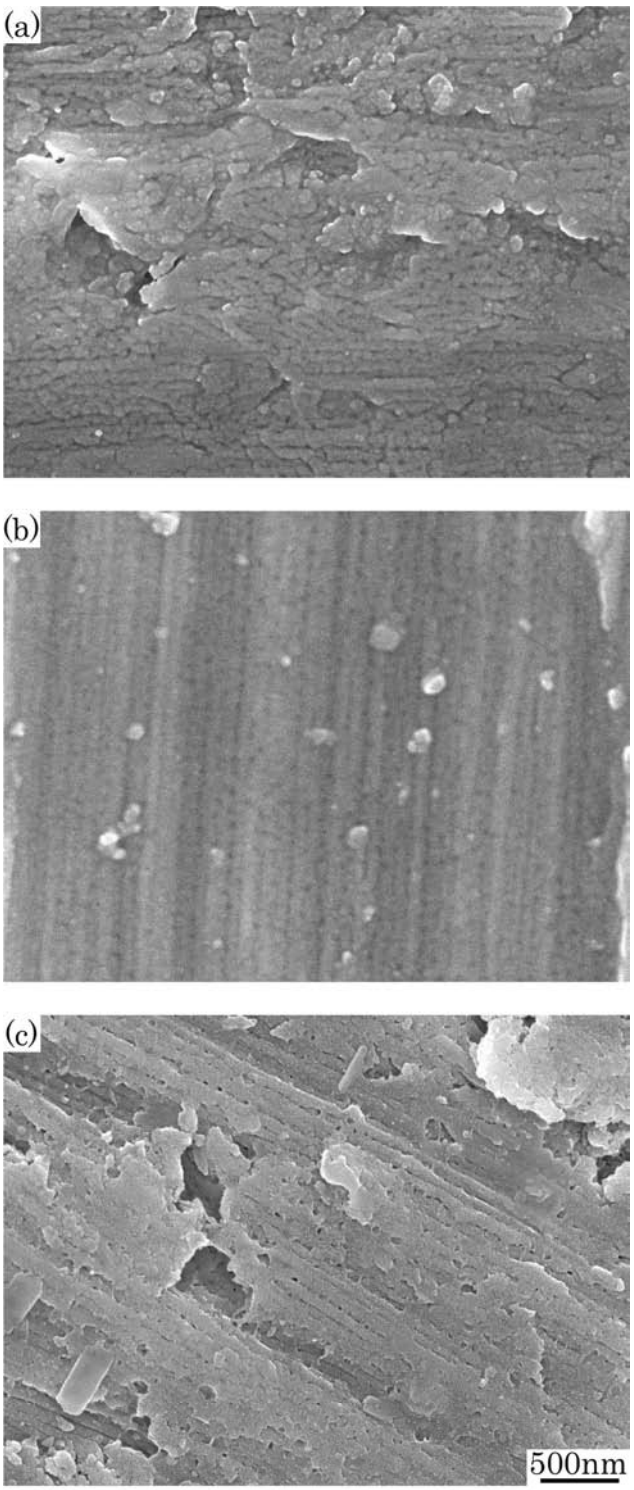

Fig. 3 Surface structures of the comparative specimens after anodic oxidation at 50 V for 1.8 ks. Compacting pressure: (a) 79.5 MPa, (b) 159 MPa, (c) 318 MPa

used for the specimens presented in Fig. 2. The nanoporous structures were formed on the surface of the comparative specimens although the nanopores were embryotic. Major difference was not seen in these specimens produced under different compacting pressures. In subsequent experiments, therefore, the compacting pressure was fixed at 79.5 MPa.

The above results indicated that zinc hindered the formation of nanoporous alumina film also in the case of the planner lining layer. We thus examined a longer process time or higher voltage for anodic oxidation.

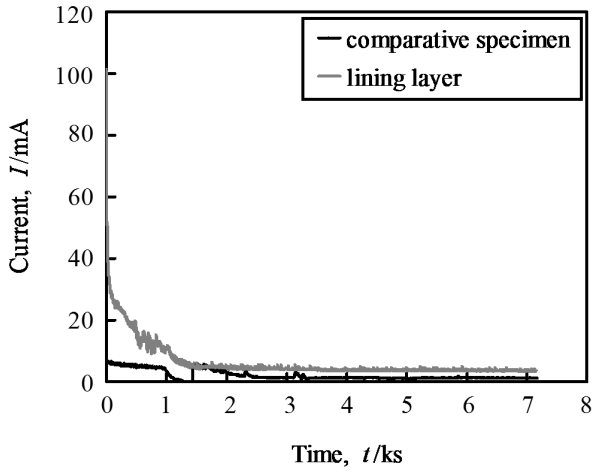

Fig. 4 Change in current with anodizing time at 50V

Figure 4 shows change in current with anodizing time in the 50V anodizing experiment. In the early period from 0 to about 1.5 ks, the current for the specimen with Al-Zn lining layer was higher than that for the comparative specimen. This result is probably caused by the preferential dissolution of zinc. Thus, the formation of the alumina film started to grow at about 1.5 ks. Therefore, the surface structure in Fig. 2 (a) corresponds to the stage of barrier layer formation.

Figure 5 shows the surface structures of the specimens after anodic oxidation at 50 V for 7.2 ks. As seen in Fig. 5 (a), a nanoporous structure formed on the surface of the Al-Zn lining layer. On the other hand, no major effect was

Table 1 surface compositions of the Al-Zn lining layer before and after anodic oxidation at 50 V.

Anodizing time (ks)	Concentration (mol%)			Nanoporous structure
	Al	Zn	O	
0	62	19	18	-
1.8	32	1.5	66	not formed
7.2	35	0.44	65	formed

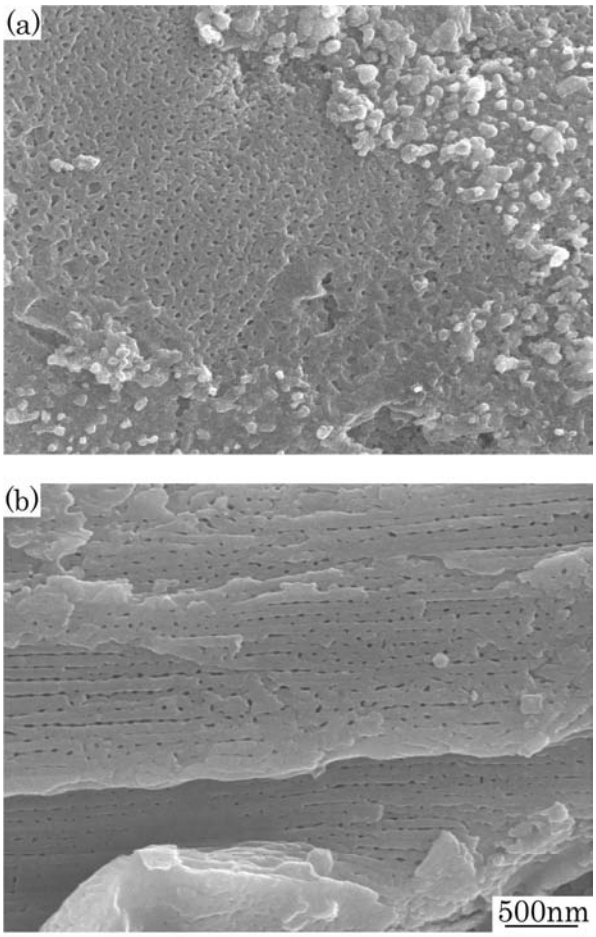

Fig. 5 Surface structures of the specimens after anodic oxidation at 50 V for 7.2 ks. (a) Al-Zn lining layer, (b) comparative specimen

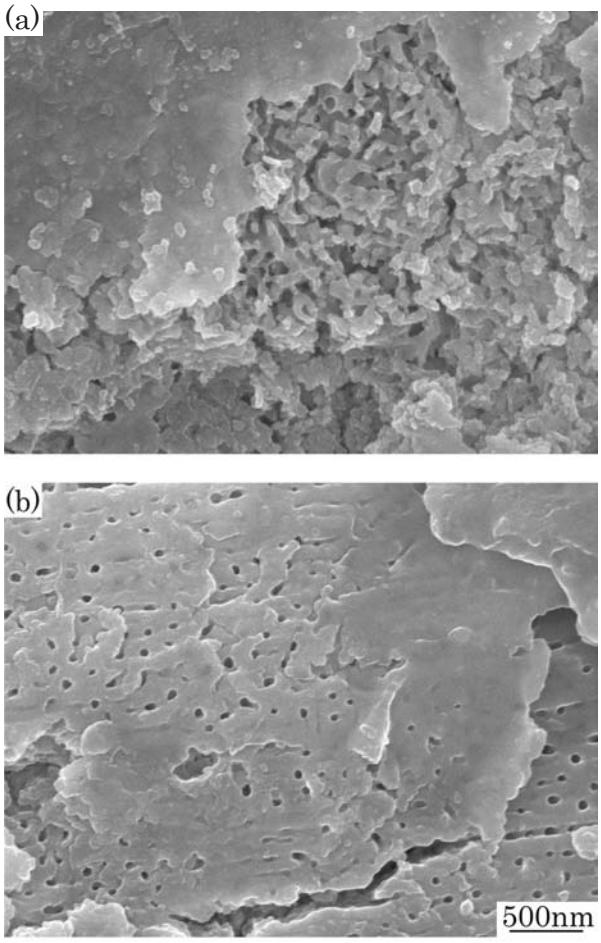

Fig. 6 Surface structures of the specimens after anodic oxidation at 100 V for 7.2 ks. (a) Al-Zn lining layer, (b) comparative specimen

confirmed on the comparative specimen with longer time anodic oxidation.

Table1 lists the surface compositions of the specimens before and after anodic oxidation. 1.5 mol% Zn was detected on the lining layer anodized for 1.8ks. This was probably because the alumina film was very thin and the EPMA data was influenced by the Al-Zn alloy substrate.

Figure 6 shows the surface structures of the specimens after anodic oxidation at 100 V for 7.2 ks. The pore size became larger than the case of 50 V. When the voltage was 150 V, both specimens were dissolved in the solution. Therefore, the suitable condition for fabricating the nanoporous structure within the conditions examined in this study was 100V anodization for 7.2 ks.

4. Conclusions

The effect of zinc contained in the lining layer on the anodic oxidation behavior was investigated and the suitable condition for producing fully-developed nanoporous structure was explored. The results obtained are summarized as follows.

(1) In the case of the anodic oxidation at 50 V for 1.8 ks, no nanopores were formed on the surface of the lining layer. In contrast, the nanoporous structures were formed on the surface of the comparative specimens although the nanopores were embryotic.

(2) A nanoporous structure formed on the surface of the Al-Zn lining layer with 7.2 ks anodic oxidation at 50 V.

(3) In the case of 100 V, the pore size became larger than the case of 50 V. However, both specimens were dissolved in the solution at 150 V.

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