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Application of Anodically Oxidized Aluminium Wire to an Electrically Temperature-controlled Catalyst

Nobuyuki OHJI, Nobuhito ENOMOTO, Takanori MIZUSHIMA, Noriyoshi KAKUTA, Tetsuya NANBA, +Yoshio MORIOKA, +and Akifumi UENO+
Toyohashi University of Technology, Tempaku, Toyohashi 440
+Shizuoka University, Johoku, Hamamatsu 432

Nickel metal particles incorporated into pores formed in the anodic alumina films on an aluminium wire was applied to electrically heated catalyst for hydrogenation of 1-butene.

Mechanism of the formation of macro-pores on the anodic alumina films have been of much intersts in the field of corrosion chemistry,[1,2] since Keller et al. have proposed hexagonal pillar cells as a model of the pores formed during anodic oxidation of an aluminium plate.[3] The application of the porous alumina films to novel functional materials has been another interests in the fields of magnetic data storage[4] and catalysis,[5] since these pores have been expected to be nanotemplates for small size metal or metal oxide particles to be incorporated.[6] Problems are in the techniques how these particles could be incorporated inside the pores of alumina formed on aluminium plates. In the present work, anodic alumina films were immersed with the sols, composed of ethylsilicate and nickel nitrate dissolved in ethylene glycol. In this sol solution, most of nickel ions were trapped in -Si-O-Si- net frame of silica sols, forming -Si-O-Ni-O-Si- structure,[7] which might be reproduced on the pore walls of anodic alumina films. After the calcination and reduction of the immersed films, finely-divided nickel metals, dispersed in silica, were expected to be inside the pores. This is the first purpose of this work and the other is to apply this device to an electrically heated catalyst (EHC) by charging it a small voltage.

Experiments were carried out in the following three parts; preparation, characterization and the measurements of catalytic activity. An aluminium plate or wire was employed for the preparation of porous alumina films, by anodizing it at 50 V for 10 min in an oxalic acid (0.16 M) electrolyte. The current passing through the plate or the wire was rapidly depressed in the first 10 s of the anodizing, and then gradually increased to a constant within 100 s. The depression means the formation of anodic alumina films over the surface of the aluminium specimen, and the successive increase in the current suggests the dissolution of alumina into the electrolyte. The constant current was observed, as a steady-state between the formation and the dissolution of alumina films was established. In Table 1 are given the dimensions and the current at the steady-state anodizing observed for the aluminium plate and the wire. The current density in Table 1 was obtained by dividing the current at the steady-state by apparent surface areas of the fresh specimen. The anodic films were dried and calcined at 623 K.

Table 1. Dimensions, steady-state currents, and current density of the aluminium plate and wire at steady-state anodizing

specimen	dimension (mm)	steady-state current (mA)	current density (mA cm^{-2})
plate	40x30x0.23	165	6.78
wire	1000x0.25Ø	51	6.70

Characterizations of the calcined alumina films were carried out by SEM (Hitachi S-900) using the alumina films on aluminium plate, since the films on wire was hard to be focused for SEM observation. SEM photographs of the plane and sectional view of the calcined films are given in Fig. 1-a and b, respectively. From these photographs the pore size was estimated about 350 A, and the film thickness was measured about 2 um. It should be noted that the pore size was controlled only by the voltage charged and that the film thickness was a function of the current density at steady-state anodizing, as well as the voltage loaded. As is seen in Table 1, the current density at the steady-state anodizing of the aluminium wire was almost the same as that of the aluminium plate, in addition to the same charge (50 V), which likely suggests that the pores formed on the anodic alumina films over the aluminium wire have the same dimensions as those observed on the aluminium plate.

The calcined alumina films were immersed with the sols consisting of ethylsilicate (30 mL) and nickel nitrate (8.9 g), dissolved in ethylene glycol (150 mL) with a small amount of nitric acid (2 mL). In this sols, most of the nickel ions were trapped in an atomic scale in the -Si-O-Si- net frame of silica sols, forming -Si-O-Ni-O-Si- structure.[7] During the immersion, it is expected that this structure is reproduced on the pore walls of the alumina films. The immersed films were dried, calcined and then reduced in flowing hydrogen at 673 K for 1 h.

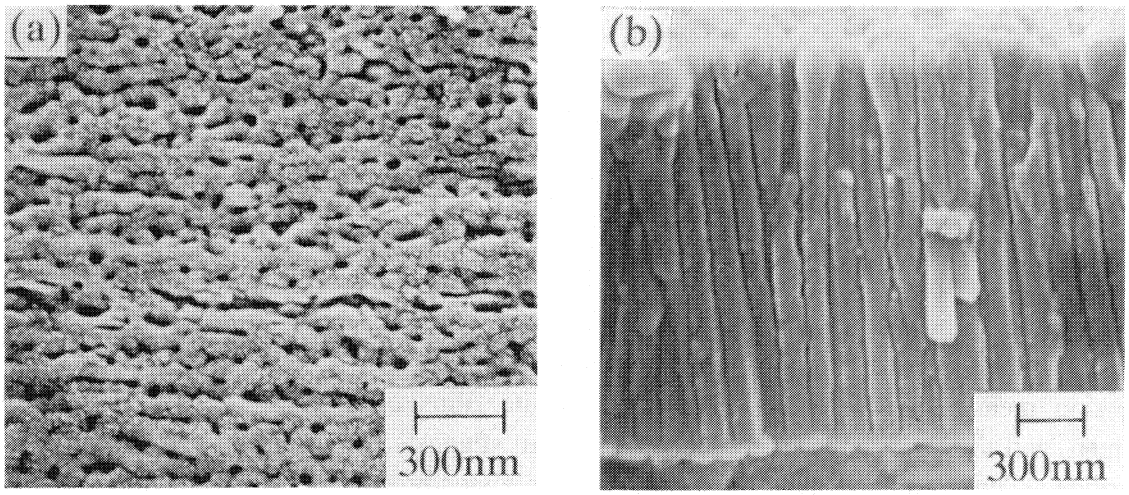

Fig. 1. SEM photographs of the calcined alumina films formed on the aluminium plate: (a) plane view, and (b) sectional view.

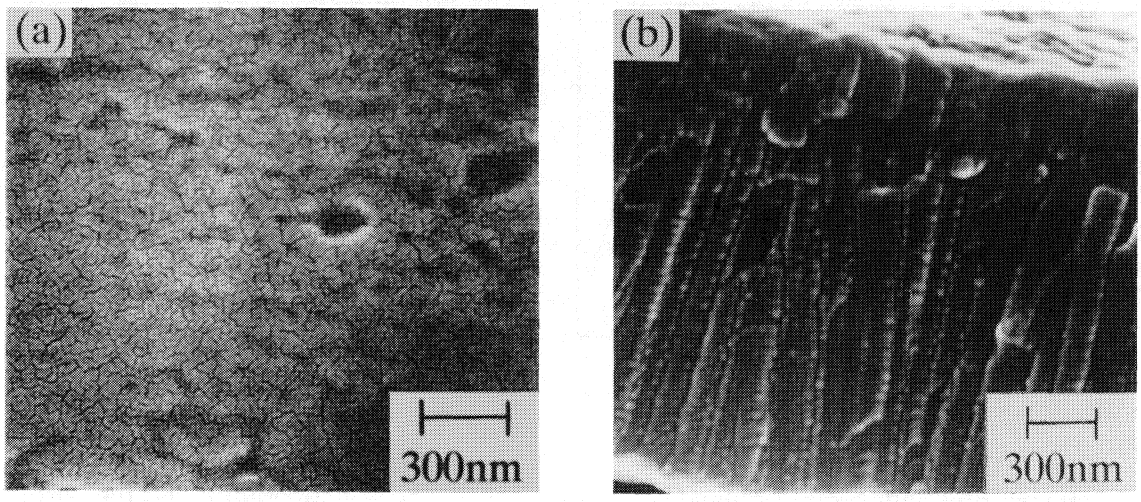

Fig. 2. SEM photographs of the incorporated Ni/SiO2 in aluminium films formed on aluminium plate: (a) plane view, and (b) sectional view.

In Fig. 2-a and b are given SEM photographs of the plane and sectional view of the reduced aluminium films, where silica particles, probably including small-sized nickel crystallites, were observed inside the pores, although most of Ni/SiO_2 catalyst deposited over the external surface of the alumina films. Formation of nickel metal crystallites on the reduced films was measured by X-ray thin film diffraction, which revealed, however, the presence of the considerable amounts of nickel oxides even after the reduction by hydrogen. This is because of the lower temperatures (673 K) for the reduction of nickel oxide to metal. The melting point of aluminium is around 973 K, which might not allow the heat treatment at temper-atures higher than 673 K. Nickel loading in the plate catalyst was 1.9 wt% of the aluminium films, which was measured by immersing the catalyst with an aqueous solution of mercurry(II) chloride, where alumina films were separated from the aluminium metal plate because of the formation of Hg-Al amalgam during the immersion.[8)]

Because of a low electrical resistance through both sides of the plate, the plate catalyst was heated up to, at most, 323 K even with a high charge of 10 V. While the wire catalyst was readily heated up to 573 K in a minute only by charging a small voltage, as shown in Fig. 3. The relationship between the current passing through the wire catalyst and the temperature is given in Fig. 4, where the temperatures was measured by fixing a thermocouple on the wire surface with a heat resistant resin. Since the rate of temperature rise of the wire catalyst was significantly high, as shown in Fig. 3, it might be possible to be employed as a catalyst for the abatement of pollutants in the cold-start-exhausts of automobiles when finely-divided three-way catalysts, in place of the nickel particles, were incorporated into the pores of alumina films. Conventional honeycomb catalysts could not work well for the cold-start-exhausts.

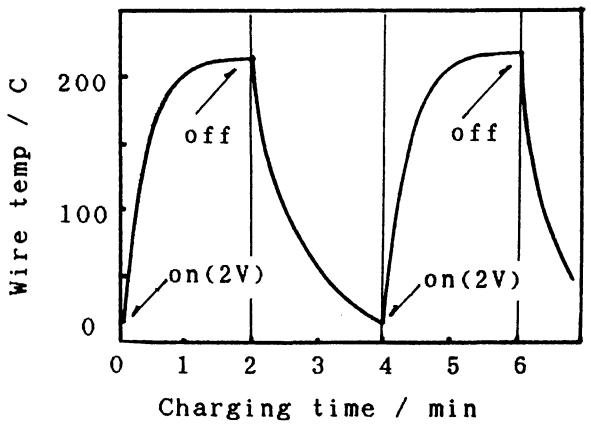

Fig. 3. Dynamic change of the wire temperature with turning on and off.

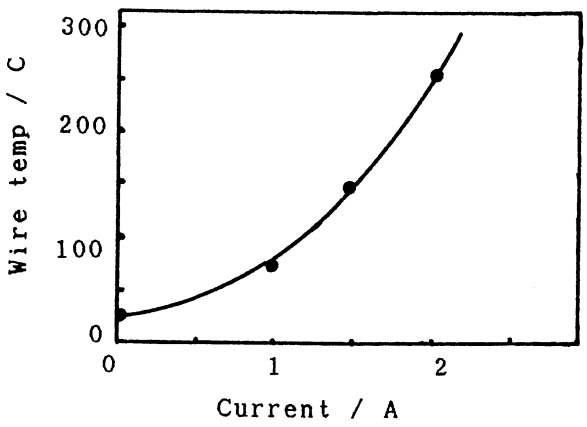

Fig. 4. Relationship between the wire temperature and the current.

The wire catalyst was placed in a glass reactor of a closed circulating system in order to apply it to a catalyst for hydrogenation of 1-butene at 419 K, corresponding to 1.5 A passing through the wire. The reaction was carried out for 24 h with gases consisting of 1-butene (53 kPa) and hydrogen (53 kPa), and the results are given in Table 2. For comparison, the results obtained for a wire catalyst without nickel metal (only silica loaded) are also given, suggesting that the reaction actually took place on nickel, but not on silica . The activation energy for the hydrogenation was estimated to be 2.3 kcal mol^{-1}, by measuring the rate at 419, 388 and 358 K, respectively. This value is almost the same as the values reported on the supported nickel catalysts (2.1 - 2.5 kcal mol^{-1}), indicating no effects of the local electric fields around the wire upon the catalysis of the metal supported on it.

Table 2. Catalytic activity of the wire catalyst at 419 K

	wire catalyst	wire without nickel
conversion of 1-butene / %	27.9	0.07
selectivity to n-butane / %	37.9	-
selectivity to t-2-butene / %	40.0	-
selectivity to c-2-butene / %	22.1	-

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