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Effects of Alkali Leaching on Composition and Surface Structure of Cu-Al Alloy Layer Produced by Powder-Metallurgical Method

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Abstract

In order to produce a Raney copper catalyst on the inner wall of microchannels, alkali leaching of Cu-Al alloy microchannel lining layers was investigated. Aluminum concentration of the lining layer decreased with leaching time when the lining-layer surface was exposed to a leaching solution. Furthermore, a fine copper structure was formed where aluminum was leached. This result indicates a possibility of fabrication of Raney copper catalyst.

Key words

Microchannel, Microreactor, Powder Metallurgy, Alkali Leaching, Raney Copper Catalyst

1. Introduction

Many efforts have been made on application of microreactor technologies to catalytic reactions [1, 2]. Typical microreactors consist of narrow flow paths (microchannels) in which reactant gases or liquids flow. The microchannel structure provides a large specific surface area. Therefore, it is suitable for catalytic reactions. Furthermore, the microchannel structure enables to avoid significant problems often appeared in conventional packed-bed reactors, such as high pressure drop and partial plugging of flow paths due to non-uniformity of the catalyst beds. In particular, metallic microreactors have attracted attentions with their high thermal conductivity [2-4]. This characteristic enables strict temperature control for highly exothermic or endothermic reactions.

In the previous reports, some of the authors investigated a powder-metallurgical method for producing the microchannels in metal bodies [5-8]. A body-metal powder compact containing fine wires of a sacrificial-core metal with a lower melting point than the body metal's was sintered at temperatures between the melting points of these metals. The molten sacrificial-core metal migrated to the body-metal powder region, and as a result a cavity formed

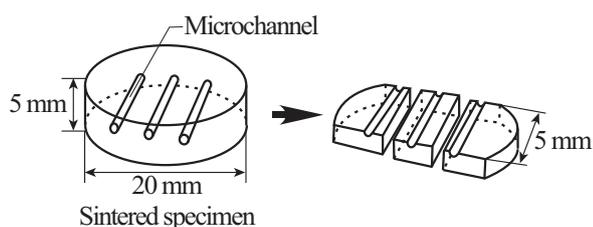


Fig. 1 Preparation of specimens for alkali leaching

at the site where the sacrificial core initially existed. An advantage of this method is ease of fabricating a three-dimensional network of microchannels. Furthermore, an alloy lining layer composed of the body metal and the sacrificial-core metal formed around the microchannel in many cases. Some of the authors have been examined some chemical treatments for the alloy lining layers to control their composition and surface structure for the purpose of catalyst fabrication on the inner wall of the microchannels.

Kobayashi *et al.* [7] attempted dealloying of Cu-Zn alloy microchannel lining layers with HCl solution to produce Cu or Cu-Zn catalysts. The zinc concentration of the lining layer was decreased by the dealloying treatment, and at the same time, the surface structure of the lining layer was changed to be porous. Saitoh *et al.* [8] carried out an alkali leaching treatment for Ni-Al alloy microchannel lining layers to produce a Raney nickel catalyst.

In this study, we have focused on Cu and Al for the constitute elements of the lining layer. The Cu-Al alloys such as Cu-50mol%Al and Cu-60mol%Al are well known as precursor alloys for Raney copper catalysts with nanoporous structures [9, 10]. The Raney copper catalysts have catalytic activities for hydrogenation reactions of various organic compounds. Furthermore, it has been industrially used for the acrylamide production. As a part of the study to develop a simplified process for manufacturing the microreactors with Raney copper catalyst, we have investigated the effects of alkali leaching on the composition and surface structure of the Cu-Al lining layer produced by the sacrificial-core method.

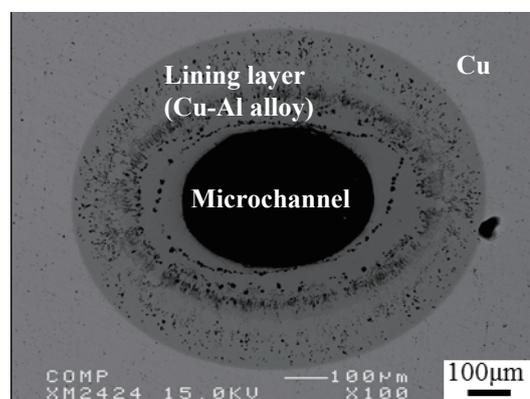


Fig. 2 Cross-sectional structure near the microchannel before alkali leaching

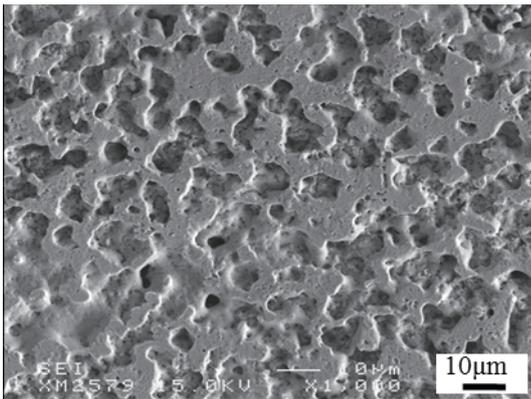


Fig. 3 SEM image of the lining-layer surface before alkali leaching

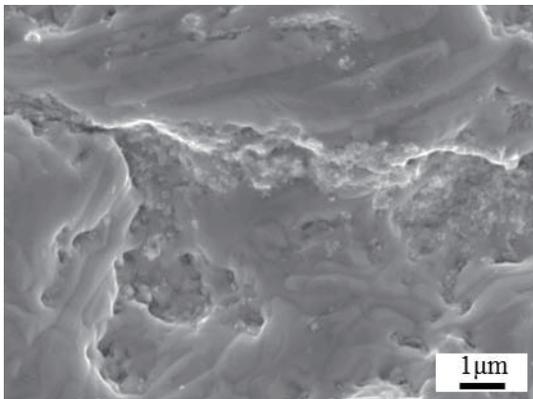


Fig. 4 FE-SEM image of the convex part in Fig. 3

2. Experimental Procedure

2.1 Sample preparation for alkali leaching

Copper powder with an average diameter of 45 µm was used for the body-metal powder. The body-metal powder containing three sacrificial cores were compacted into a cylindrical compact at a unidirectional pressure of 530 MPa. The sacrificial cores were thin aluminum wires of 500 µm in diameter and 15 mm in length. The specimens were heated at a constant rate of 0.2 K/s from room temperature to 1123 K in an argon gas atmosphere, and then, furnace-cooled at about 0.4 K/s.

2.2 Alkali leaching treatment

The sintered specimens were sliced into 5 mm in thickness. After that, the microchannels were cut in half lengthwise so that the lining-layer surfaces could be certainly exposed to a leaching solution during the alkali-leaching treatments (see Fig. 1). The specimens were dipped in a 7 kmol/m³ NaOH aqueous solution at 323 K. The leaching time, τ, was varied from 10.8 ks to 86.4 ks.

The surface structures of the lining layers were observed by SEM and FE-SEM. The compositions of the lining-layer surfaces were measured by EPMA.

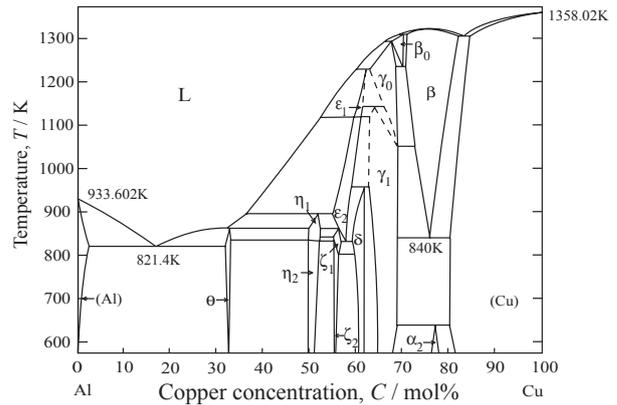


Fig. 5 Cu-Al binary alloy phase diagram based on the report by Massalski *et al.* [11]

3. Results and Discussion

3.1 Structure and composition of the lining-layer surface before alkali leaching

Figure 2 shows a cross-sectional SEM image of a microchannel and a lining layer before alkali leaching. The microchannel was successfully produced in the specimen. The microchannel was cut in half lengthwise to observe its lining-layer surface structure. Figure 3 shows a SEM image of the lining-layer surface. A concavo-convex structure with flat convexity was observed on the lining-layer surface. The depth of the concavity area was lower than about 10 µm. Considering the average diameter of the body-metal powder (45 µm), the concavo-convex structure was produced by the phenomena accompanying the powder-metallurgical process, such as infiltration of the liquid phase, diffusion of the alloying elements and sintering of the solid phases. The flat convexity area was probably originated in the contact interface between the body metal and the sacrificial core.

Figure 4 depicts a FE-SEM image of the convex part of the lining-layer surface shown in Fig. 3. A lamellar microstructure specific to a eutectoid structure was observed. According to the EPMA result, the average composition of the lining-layer surface was Cu-24.5mol%Al. Near the peak temperature, 1123 K, during sintering, the surface of the lining layer was composed of β phase according to the Cu-Al binary alloy phase diagram illustrated in Fig. 5. Probably, the β phase separated into Cu solid solution and γ₁ phase by the eutectoid reaction in the course of furnace cooling. The composition and structure of the lining-layer surface differed from those of the precursor materials that have been conventionally used [9, 10]. In addition, the lining-layer composition and structure changes depending on the interaction between the molten sacrificial-core metal and the body-metal powder during sintering. There is room for further investigation to optimize the sintering condition.

3.2 Change of lining-layer surface structure by alkali leaching

Figures 6(a) to (c) show SEM images of lining-layer surfaces after alkali leaching for 10.8, 21.6 and 86.4 ks, respectively. The flat convexity parts in Fig. 2 changed to

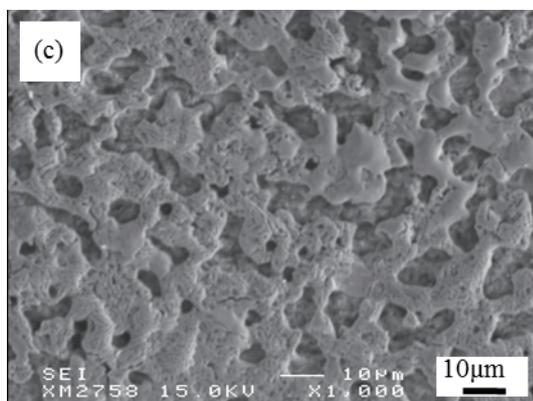
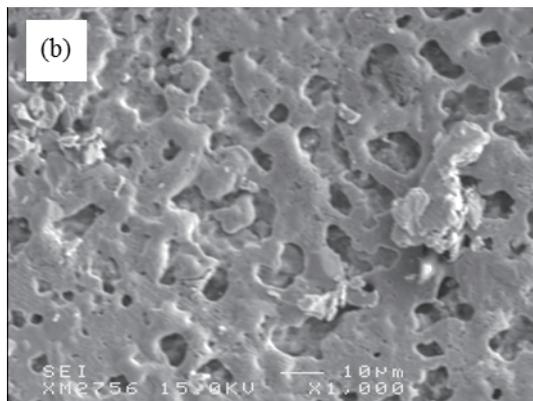
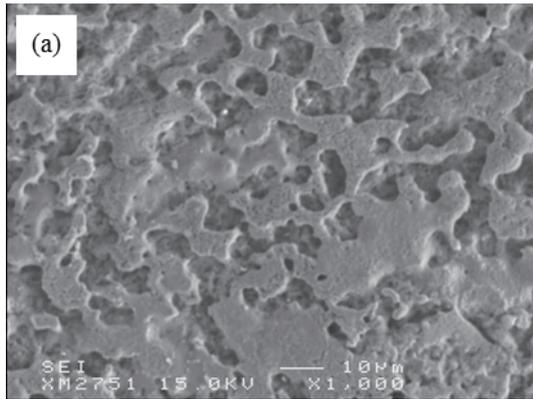


Fig. 6 SEM images of the lining-layer surfaces after alkali leaching for 10.8 ks (a), 21.6 ks (b) and 86.4 ks (c)

be more roundish as the leaching time increased. Figures 7(a) and (b) show the cross sectional shapes of the lining-layer surfaces before alkali leaching and after 86.4 ks alkali leaching, respectively. The concavo-convex shape in the case of 86.4 ks alkali leaching was roundish compared with that of the specimen before alkali leaching. Figure 8(a) shows a FE-SEM image of the lining-layer surface leached for 21.6 ks. The lamellar structure is clearly observed. This is because aluminum was leached mainly from the γ_1 phase.

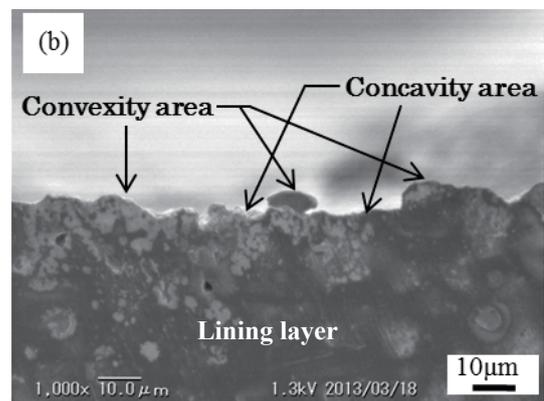
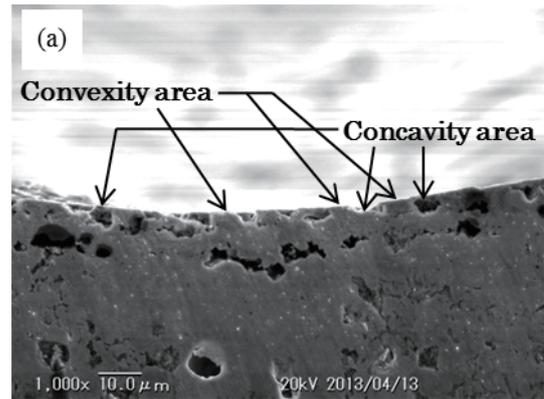


Fig. 7 Cross-sectional shapes of the lining-layer surfaces before alkali leaching (a) and after alkali leaching for 86.4 ks (b)

Figure 8(b) and (c) show close-up images of the structures framed by the white-line squares in Fig. 8(a). Fine structures were formed at the positions of the former γ_1 phases. This result indicates the possibility of fabrication of multi-scale porous devices that have microchannels of several hundred micrometers in diameter, a concavo-convex structure of several decade micrometers in size (see Fig. 6(b)) and a fine structure of several hundred nanometers in size (see Figs. 8(b) and (c)). The fine structure in Figs. 8(b) and (c) did not have facet surfaces, but had ligaments characteristic of the Raney copper catalysts. We will carry out a further investigation to identify the phase of the fine structure. Figure 9 shows a FE-SEM image of the lining-layer surface after 86.4 ks alkali leaching. The fine structures which are observed on the lining layer after 21.6 ks alkali leaching (see Figs. 8(b) and (c)) was not observed. Similar phenomenon in which excessive leaching decreases the specific surface area of Raney copper catalysts has been reported by Sato *et al.* [12].

Two types of mechanisms have been discussed for a Raney-catalyst formation by alkali leaching treatment [13].

(1) Both a noble and a less noble element dissolve simultaneously, and after that, the noble element redeposits on the metal surface of the noble element. (2) Solely the less noble element is selectively leached and the atoms of

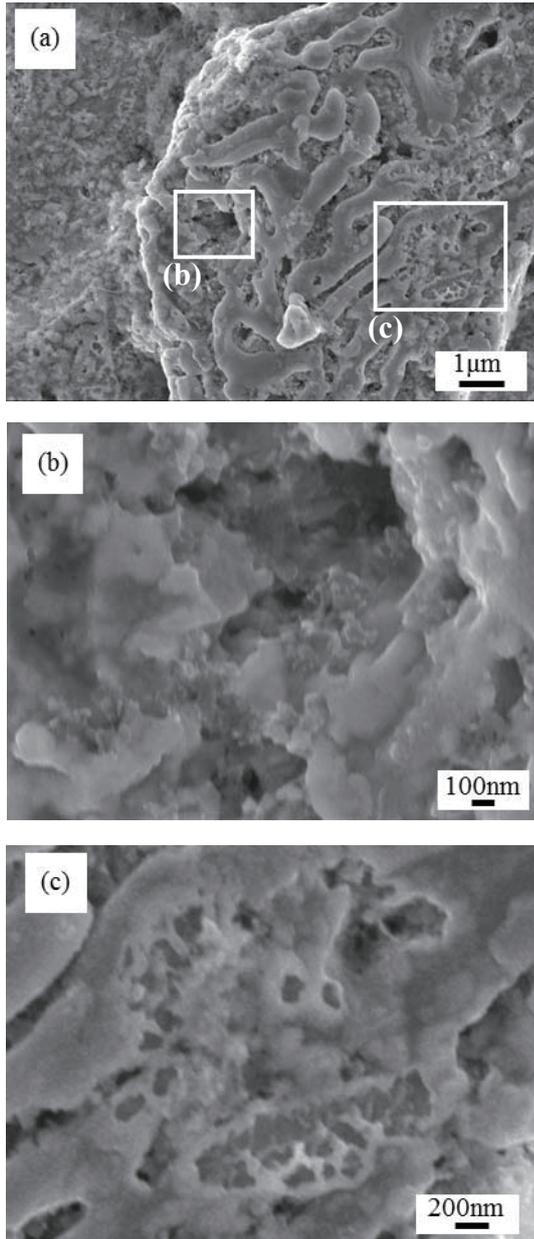


Fig. 8 FE-SEM image of the lining-layer surface after 21.6 ks alkali leaching (a) and close-up image of the structure framed by the white-line square (b) and (c)

the noble element migrate by the surface diffusion or the volume diffusion to form a nanoscale structure. Considering these mechanisms, we have speculated a process of the structure formation as follows. The γ_1 phase was etched preferentially in the first step, and thus the lamellar structure of the Cu solid solution was embossed. The fine structure was also produced by selective leaching of Al. However, the Cu atoms migrated by surface diffusion or volume diffusion to decrease the surface energy during leaching treatment. Thus the fine structure disappeared during the excessive leaching treatment.

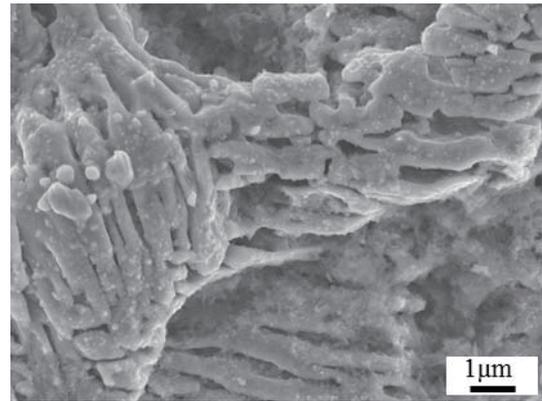


Fig. 9 FE-SEM image of the lining-layer surface after 86.4 ks alkali leaching

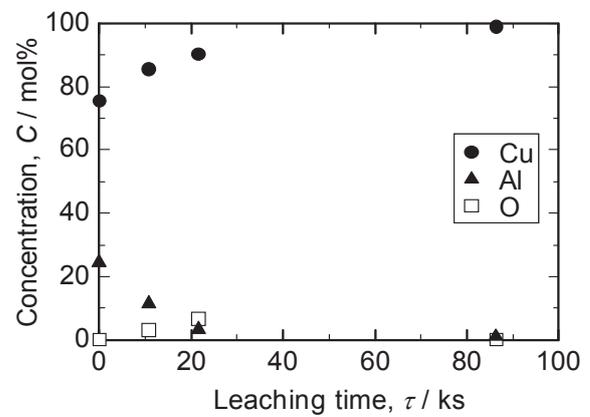


Fig. 10 Changes in Cu, O and Al concentrations of the lining layers with leaching time

3.3 Effect of leaching time on the lining-layer composition

Figure 10 shows the changes in Cu, O and Al concentrations of the lining-layer surface with leaching time, τ . The concentration of aluminum decreased with τ . In contrast, that of copper increased with τ . Finally at $\tau = 86.4$ ks, the lining-layer surface became almost pure copper. A low amount of oxygen was detected in the cases of $\tau = 10.8$ ks and 21.6 ks, but not detected in $\tau = 0$ ks and 86.4 ks. In consideration of the fact that copper with a fine structure is easily oxidized due to the large specific surface area, the change in the oxygen concentration corresponded to the formation and dissipation behaviors of the fine structure.

3.4 Alkali leaching for whole microchannels

The Cu-Al alloy lining layer was successfully leached when the longitudinally-halved microchannel was exposed to the leaching solution. Although, cutting the microchannels for alkali leaching is not a practical method. Therefore, we also examined specimens containing whole microchannels (see Fig. 11). After the 86.4 ks leaching treatment, the composition of the lining layer was measured by EPMA. In spite of the plenty leaching time, the composition of the lining layer was Cu-24.8mol%Al which is almost same as

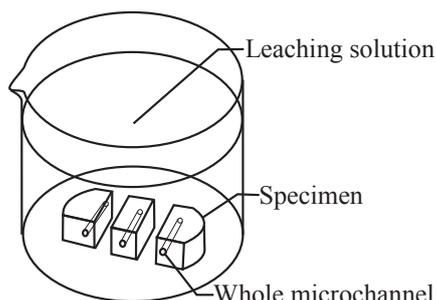


Fig. 11 Schematic of experimental apparatus for alkali leaching of whole microchannels

that of the unleached lining layer. We speculated that H_2 gas bubbles formed with aluminum dissolution, and they remained in the microchannels and prevented the leaching solution from contacting with the lining-layer surface. An additional device is required to remove the bubbles and feed the leaching solution into the microchannels. That is a subject of our future investigation.

4. Conclusions

Alkali leaching of the Cu-Al alloy microchannel lining layer was performed to fabricate the Raney copper catalyst on the inner wall of the microchannels. The effects of alkali leaching treatment on the lining-layer surface structure and the composition were investigated. The results obtained are summarized as follows.

(1) Aluminum was successfully leached from lining-layer surface when it was exposed to a leaching solution.

(2) A fine structure was formed where the γ_1 phase was leached. That indicates the possibility of the catalyst formation on the inner wall of the microchannels.

(3) The fine copper structure disappeared during the excessive alkali leaching.

References

- [1] Jamelyn, D. H., Yong, W. and Evan, J.: Review of Developments in Portable Hydrogen Production Using Microreactor Technology, *Chemical Reviews*, **104**-10 (2004), 4767-4790.
- [2] Lioubov, K. M. and Albert, R.: Microstructured reactors for catalytic reactions, *Catalysis Today*, **110** (2005), 2-14.
- [3] Tonkovich, A. Y., Zilka, J.L., LaMont, M. J., Wang, Y. and Wegeng, R. S.: Microchannel reactors for fuel processing applications. I. Water gas shift reactor, *Chemical Engineering Science*, **54** (1999), 2947-2951.
- [4] Ingrid, A., Torbjørn, G., Hilde, V., Oliver, G., Peter, P., Marcus, F., Anders, H. and Klaus, S.: Catalytic conversion of propane to hydrogen in microstructured reactors, *Chemical Engineering Journal*, **101** (2004), 93-99.
- [5] Ohmi, T., Hayashi, N. and Iguchi, M.: Formation of Porous Intermetallic Thick Film by Ni-Al Microscopic Reactive Infiltration, *Materials Transactions*, **49**-11(2008), 2723-2727.
- [6] Ohmi, T., Kodama, T. and Iguchi, M.: Formation Mechanism of Microchannels and Lining Layers in Sintered Iron Powder Compacts with Copper Sacrificial Cores, *Materials Transactions*, **50**-12 (2009), 2891-2896.
- [7] Kobayashi, K., Ohmi, T., Sakairi, M. and Iguchi, M.: Dealloying of Cu-Zn Alloy Microchannel Lining Layers for Producing Microporous Catalyst, *J. JSEM*, **11**-Special issue (2011), SS280-SS283.
- [8] Saitoh, Y., Ohmi, T., Sakairi, M. and Iguchi, M.: Alkali Leaching of Ni-Al Alloy Microchannel Lining Layers, *J. JSEM*, **11**-Special issue (2011), SS276-SS279.
- [9] Smith, A. J., Tran, T. and Wainwright, M. S.: Kinetics and mechanism of the preparation of Raney® copper, *J. Appl. Electrochem.*, **29** (1999), 1085-1094.
- [10] Qi, Z., Zhao, C., Wang, X., Lin, J., Shao, W., Zhang, Z. and Bian, X.: Formation and Characterization of Monolithic Nanoporous Copper by Chemical Dealloying of Al-Cu Alloys, *J. Phys. Chem. C*, **113** (2009), 6694-6698.
- [11] Massalski, T. B., Okamoto, H., Subramanian, P. R. and Kacprzak, L.: Binary Alloy Phase Diagrams, *The Materials Information Society*, ASM International (1986), 142-14.
- [12] Sato, M. and Ohta, N.: Decrease of the Surface Area of Raney-type Catalysts in the Aluminium dissolution Process, *Bull. Chem. Soc. Japan*, **28**-3 (1955), 182-185.
- [13] Schofield, E.: Anodic routes to nanoporous materials, *Transactions of the Institute of Metal Finishing*, **83**-1 (2005), 35-42.