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Fabrication of Alumina Coating on Ni-Al Alloy Microchannel Wall for Catalyst Supporting

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Abstract

High-temperature oxidation of the inner wall of a microchannel has been examined in order to fabricate an oxide coating for catalyst supporting. The microchannel was produced in a nickel body by a powder metallurgical microchanneling process, and it was lined with a NiAl intermetallic alloy layer. By high-temperature oxidation, an alumina scale was fabricated on the surface of the microchannel lining layer. In some cases, the alumina scale had a needle-like structure on its surface.

Key words

Microreactor, Powder Metallurgy, NiAl, Oxide Coating, Catalyst Supporting

1. Introduction

Nowadays, the environmental issues become grave problems, and catalyst technology draws attention as one of the solutions of the problems. One of the important themes of catalyst technology is catalyst supporting. The catalyst support is required to have a high specific surface area and physicochemical stability.

A metallic microreactor is attracting attention for a chemical reactor suitable for high-temperature catalytic reactions. The metallic microreactor has a microchannel structure with a characteristic dimension from several to hundreds of micrometers. Its specific surface area is therefore very high. In addition, the high heat conductivity of the metallic material enable exact control of the temperature and reaction process in the microreactor. However, conventional microchanneling methods such as precision machining and photoetching require many operations and cost to produce three-dimensional microchannel networks.

Recently, some of the authors investigated a powder-metallurgical process to produce microchannels directly in metal bodies. [1] The concept for the process was based on the microscopic infiltration/diffusion phenomena that often occur during liquid phase sintering of a mixture of powder metals with different melting points. They used a metal with a higher melting point as a body metal, which is to compose the device body, and the other as a sacrificial-core metal, which is to flow out and give the shape of the microchannel. In their experiments, a body-metal powder compact containing a sacrificial core, a shaped sacrificial-core metal, was sintered at temperatures between the melting points of these metals. During sintering, molten sacrificial-core metal migrated to the body-metal powder region by infiltration and/or diffusion, and as a result, the microchannel was produced. An alloy layer lining the microchannel was also produced simultaneously.

This process can fabricate microchannels with simpler operations than the conventional methods. In addition, we can produce high-performance microreactors if the lining layers have various functions.

Some of the authors also found that a microporous NiAl lining layer formed when they used the combination of Ni and Al. [1] It is well known that NiAl forms thin alumina scale on its own surface when it is oxidized in a high-temperature air. Alumina is thermochemically stable and therefore suitable for the catalyst support for high-temperature reactions. In addition, it is reported that the structure of the alumina scale produced by high-temperature oxidation often exhibits micro hubbly structures. [2]

If such an alumina scale can be produced on the inner wall of the microchannel, we can produce a microreactor for catalyst reactions by a simple and easy method.

However, the previous oxidation study examined NiAl with only the stoichiometric composition, Ni-50mol%Al. The composition of the NiAl lining layer produced by the powder-metallurgical process varied depending the process conditions. [1] Possibly, oxidation behavior of the lining layer may be different from Ni-50mol%Al.

In the present study, we therefore examined the possibility of fabrication of the oxide coating on the surface of the NiAl lining layer.

2. Experimental Procedure

2.1 Fabrication of microchannel

13.9 grams of nickel powder with average particle size of 5 μm was used as the body-metal powder, and two or three aluminum wires with the diameter of 500 μm were used as the sacrificial core. The body-metal powder containing the sacrificial cores was uniaxially compressed under 460 MPa at room temperature. The shape of the resultant compact specimen was a cylinder 20 mm in diameter and 5 mm in height. The compact specimen was heated in an electric furnace at a constant rate of 0.2 K/s from room temperature to 1473K and then furnace cooled at 0.1 K/s under an argon atmosphere.

2.2 High-temperature oxidation

The sintered compact specimen was cut to thickness of 5 mm (see Fig. 1). After confirmed that a microchannel was formed, the sintered specimen was oxidized at 1473 K under an air atmosphere. Thermal histories for high-temperature oxidation are shown in Fig. 2. The symbol " τ " in the figure indicates the isothermal holding time.

2.3 Observation of the cross-sectional structure

The specimens were plated with copper to conserve the cross-sectional contour of the inner wall of the

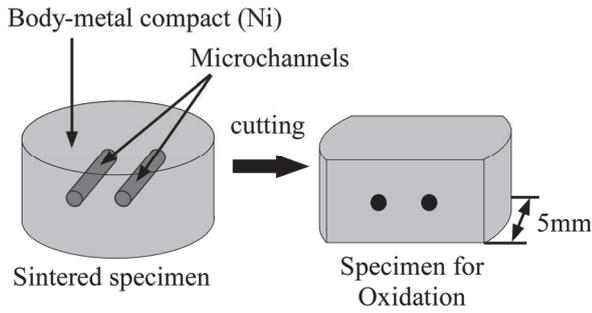


Fig. 1 Preparation of the specimen for high-temperature oxidation

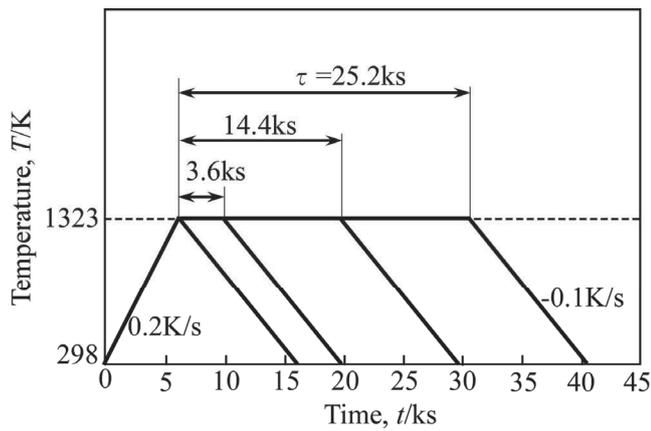


Fig. 2 Thermal histories of high-temperature oxidation

microchannel. A 0.63M $\text{CuSO}_4/0.50\text{M H}_2\text{SO}_4$ solution was used for electro plating of copper. After plating, the specimens were polished to remove the surface layer and then observed by using SEM.

2.4 Observation of the inner-wall surface of the microchannel

The oxidized specimens were cut along the microchannel to expose the inner-wall of the microchannel. The structure of the inner-wall surface was observed by using FE-SEM.

3. Results

3.1 Cross-sectional structures of the inner wall of the lining layer

Figure 3 shows a back-scattered electron image of the oxidized and copper-plated specimen ($\tau = 25.2$ ks). An open microchannel and a lining layer were observed. Similar structure was formed in every specimen prepared in our experiments. EPMA analysis shows that the composition of the lining layer near the oxide scale was $\text{Ni-}53(\pm 0.4)\text{mol\%Al}$. According to the Ni-Al binary alloy phase diagram (see Fig. 4), the corresponding phase is aluminum-rich NiAl.

Figure 5 shows the magnified structure near the inner wall of the microchannel in the oxidized specimen ($\tau = 25.2$ ks). For comparison, the structure of an unoxidized specimen is shown in Fig. 6. There was a black scale between the copper plate region and the lining layer in Fig. 5.

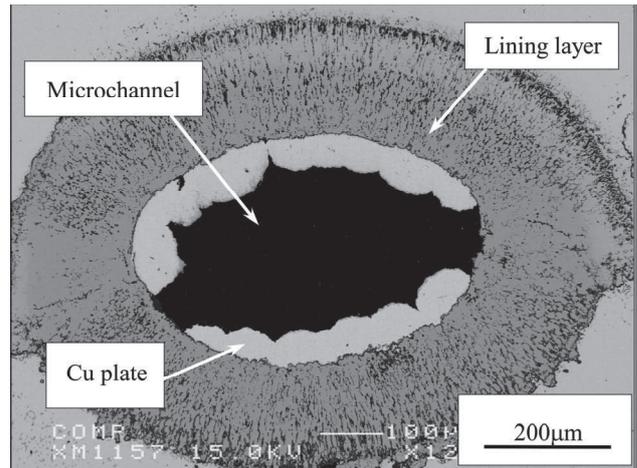


Fig. 3 Back-scattered electron image showing the microchannel, lining layer, and copper plate ($\tau = 25.2$ ks)

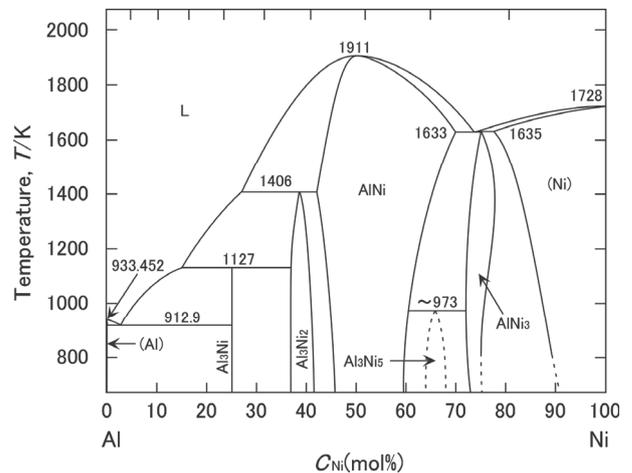


Fig. 4 Ni-Al binary alloy phase diagram [3]

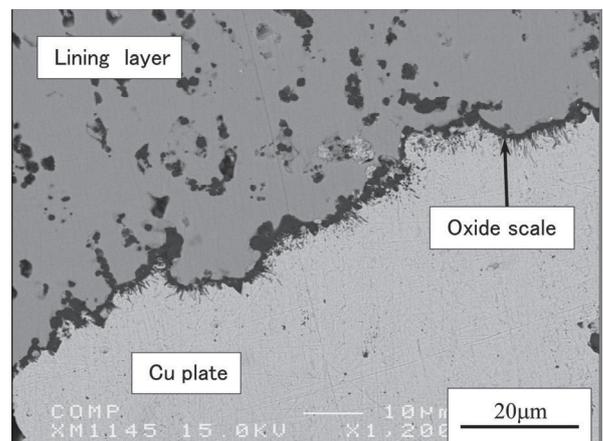


Fig. 5 Back-scattered electron image showing the magnified structure near the inner wall of the microchannel in the oxidized specimen ($\tau = 25.2$ ks)

On the other hand, no such structure was observed in the unoxidized specimen. This result suggests that the scale was formed by high-temperature oxidation.

EPMA analysis showed that the composition of the scale between the copper plate region and the lining layer was about Al-60mol%O. This composition corresponds to alumina (Al_2O_3). In addition, the aluminum concentration of the inner surface of the unoxidized lining layer was $57(\pm 1.5)$ mol% which was higher than that of the oxidized specimen. This result shows that aluminum near the inner surface of the lining layer was consumed by oxide scale formation.

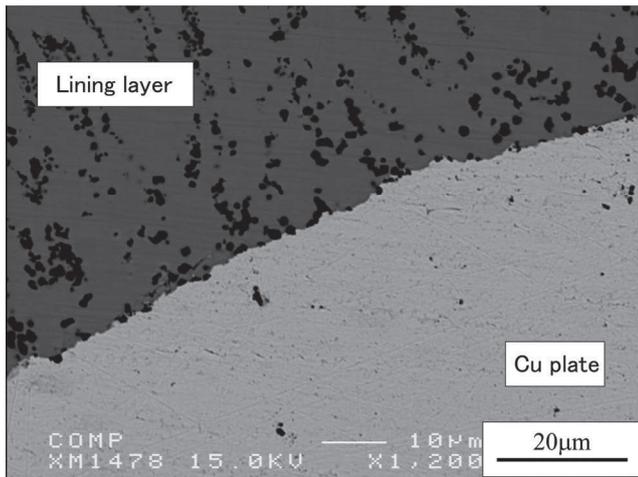


Fig. 6 Back-scattered electron image showing the magnified structure of the unoxidized specimen

3.2 Influence of the isothermal holding time on the thickness of the oxide film

Figure 7 shows the structures of four kinds of oxidized specimens produced with different isothermal holding times. In each specimen, an oxide film was observed. The oxide film in the case of $\tau = 0$ ks formed during the temperature rising and cooling steps. The phase of the oxide is probably α -alumina or θ -alumina referring to the previous reports [2, 4].

In this study, we defined the thickness of the oxide film, L , as that of dense layer part of the oxide film as illustrated in Fig. 8. Figure 9 shows the relationship between τ and the oxide film thickness, L .

The thickness of the oxide film increases with increasing isothermal holding time. On the other hand, the oxide growth rate decreases as the isothermal holding time increases. This tendency suggests a diffusion-controlling mechanism.

3.3 Surface structure of oxide scale

Figure 10 shows an FE-SEM image of the surface structure of the inner wall of the microchannel in an oxidized specimen ($\tau = 25.2$ ks).

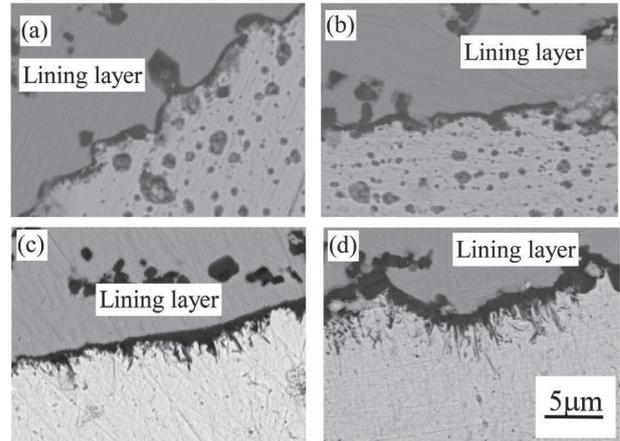


Fig. 7 Back-scattered electron images showing the magnified structures near the inner wall of the oxidized specimens. (a) $\tau = 0$ ks, (b) $\tau = 3.6$ ks, (c) $\tau = 14.4$ ks, (d) $\tau = 25.2$ ks

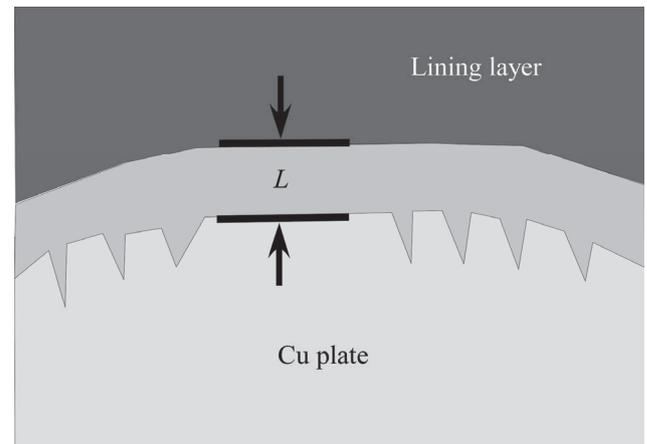


Fig. 8 Measurement of the oxide film thickness, L

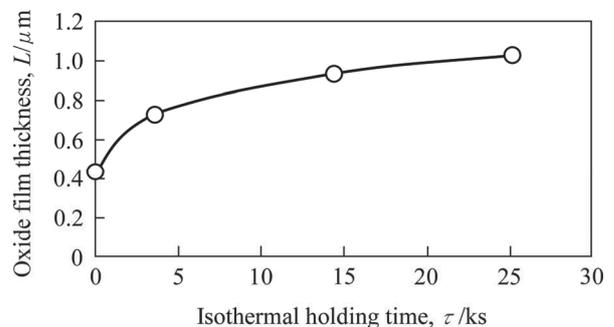


Fig. 9 Influence of the isothermal holding time on the thickness of the oxide film

In Fig. 10, needle-like asperities were observed. Such a surface structure tremendously increases the surface area of the inner wall of the microchannel.

The structure of the oxide scale is probably controlled by the lining layer composition and the oxidizing condition. The detail of those is a future subject.

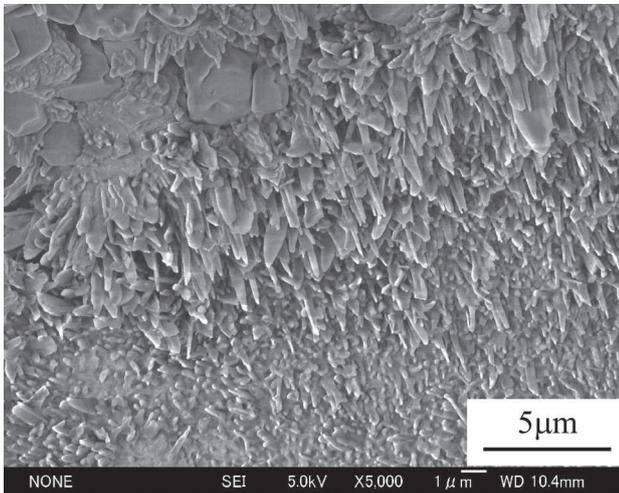


Fig. 10 FE-SEM image of the oxidized inner surface of the microchannel ($\tau = 25.2$ ks)

4. Conclusions

Fabrication of the oxide scale on the inner wall of the microchannel by high-temperature oxidation was examined. The results obtained are summarized as follows:

- (1) The alumina (Al_2O_3) scale was produced on the inner wall of the Ni-Al microchannel lining layer by high-temperature oxidation.
- (2) The oxide film thickness tended to increase with increasing oxidation time.
- (3) Needle-like structures formed on the surface of the oxide scale during oxidation. The result suggests that the possibility of tremendous increase of the surface area of the inner wall of the microchannel by controlling the surface structure of the oxide scale.

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