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Catalytic properties of Ni_3Al/Ni two-phase alloy foils for methane steam reforming

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We for the fist time investigated the catalytic properties of Ni_3Al/Ni two-phase alloy foils for methane steam reforming in the temperature range of 873-1173 K. It was found that the flat foils show a catalytic activity above 1023 K in spite of their low surface area and the activity increases with reaction temperature. SEM and XRD analyses revealed that metallic Ni particles and aluminum oxide Al_2O_3 were produced on the foil surface during the catalytic reaction. These Ni particles are considered to contribute to the observed activity for methane steam reforming.
Key words: Ni_3Al/Ni two-phase alloy, thin foils, catalytic activity, methane steam reforming.

1. INTRODUCTION

Ni_3Al intermetallic is known as high-temperature structural material, because of its excellent high-temperature strength and good oxidation/corrosion resistance [1-3]. The brittleness at room temperature used to be a big problem which restricted its practical application. Recently we have overcome this problem and successfully developed thin foils of Ni_3Al intermetallics by cold rolling without boron addition [4].

Up to now, the catalytic properties of Ni_3Al intermetallics have attracted no attention. However, we have recently found a high catalytic activity on the Ni_3Al foils for hydrogen production such as methanol decomposition and methane steam reforming in spite of their low surface area [5-9]. The cause of the activity is attributed to the fine Ni particles on the foil surface which are produced in the reaction condition or by chemical pretreatment. Considering the excellent high-temperature structural properties, the foil catalysts can be used as both catalysts and structural materials in the micro reactor for hydrogen production.

Ni_3Al/Ni two-phase alloy is superior to Ni_3Al single-phase alloy in structural performance such as creep properties and workability. But its catalytic properties have never been studied yet. It is thus interesting to examine whether Ni_3Al/Ni two-phase alloy foils exhibit catalytic activity for hydrogen production or not. In this study, we for the first time investigated their catalytic properties for methane steam reforming.

2. EXPERIMENTAL

2.1 Sample preparation

Ni_3Al/Ni alloy foils of 32 μm in thickness were fabricated by cold rolling the single crystalline plate with the composition Ni-18at%Al. The Ni_3Al/Ni two-phase structure was confirmed after cold rolling.

2.2 Catalytic reaction

Methane steam reforming was performed in a conventional fixed-bed flow reactor at ambient pressure. The foils were reduced by hydrogen at 773 K for 1 hour before the reaction. The reactants of CH_4 and H_2O (molar ration of CH_4 and H_2O = 1) were introduced into the reactor at a gas hourly space velocity of 0.00027 $m^3h^{-1}m^{-2}$. Catalytic reaction was measured in the temperature range of 873 K to 1173 K in stepwise heating manner at an interval of 50 K. After holding at each temperature for 30 minutes, the outlet gaseous composition was analyzed by gas chromatography (GL science, GC-323 equipped with thermal conductivity detectors). The total flow rate of the outlet gases was measured except steam by a soap bubble meter just after gas analysis.

2.3 Sample characterization

The surface morphologies and composition of the foils were determined by scanning electron microscopy (SEM: JEOL, JSM-7000F) along with an X-ray energy dispersive spectroscopy (EDS) after the catalytic reaction. The crystal structures of the foils were characterized by X-ray diffraction (XRD) using a Cu Kα source (Rigaku, RINT2500)

3. RESULTS AND DISCUSSION

3.1 Catalytic reaction

Figure 1 shows the methane conversion as a function of reaction temperature. The methane conversion increased with temperature above 1023 K, and finally reached 74 % at 1173 K, while no obvious conversion was detected below 973 K. The result demonstrates that the Ni_3Al/Ni two-phase alloy foils have a catalytic activity for methane steam reforming above 1023 K.

Figure 2 plots the production rates of the outlet gases products as a function of reaction temperature. The production rates of H_2 and CO increased with reaction temperature above 1073 K, having a molar ratio of approximately 3:1. The results indicate that the methane steam reforming (equation 1) occurred over the foil surface of the Ni_3Al/Ni two-phase alloy.

$$CH_4 + H_2O \Leftrightarrow 3H_2 + CO \quad \Delta H^0_{298} = +206 \text{ kJ/mol} \quad (1)$$

In contrast, the production rate of CO_2 was much lower than those of H_2 and CO. It remained low even at 1173 K, indicating that the water-gas shift reaction (equation

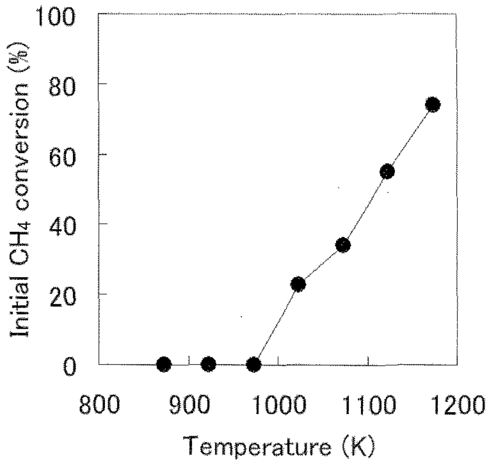

Fig.1 Methane conversion as a function of reaction temperature

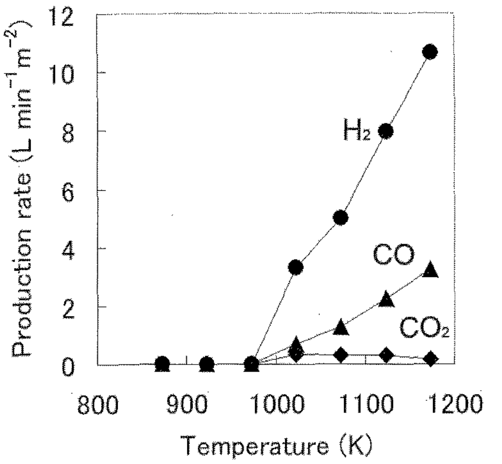

Fig.2 Production rate of H_2, CO and CO_2 as a function of reaction temperature

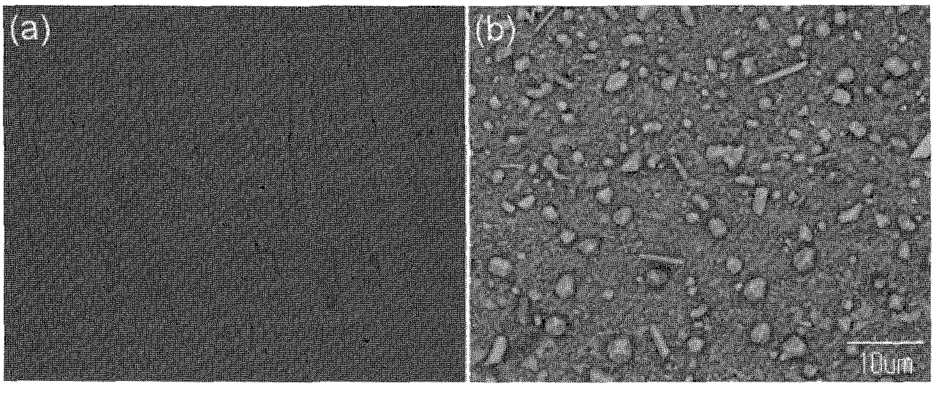

Fig.3 SEM back scattered electron image on foil surface (a) before the reaction and (b) after the reaction

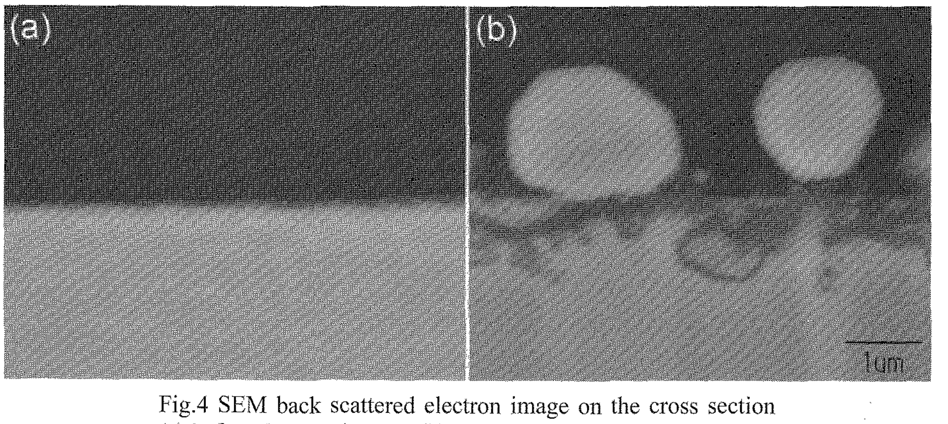

Fig.4 SEM back scattered electron image on the cross section (a) before the reaction and (b) after the reaction

2) was considerably suppressed over the foil surface of the Ni_3Al/Ni two-phase alloy. This behavior is different from that in common Ni catalysts where the water-gas shift reaction is accompanied by the methane steam reforming [10].

$$CO + H_2O \Leftrightarrow H_2 + CO_2 \quad \Delta H^0_{298} = -41 \text{ kJ/mol} \qquad (2)$$

3.2 Surface morphologies after the catalytic reaction

Figure 3 shows the SEM backscattered electron images on the foil surface before and after the reaction. Before the reaction, the foil surface was flat, having a weak contrast of band structure along the horizontal direction as shown in Fig. 3a. This band structure was formed during cold rolling process before the reaction as

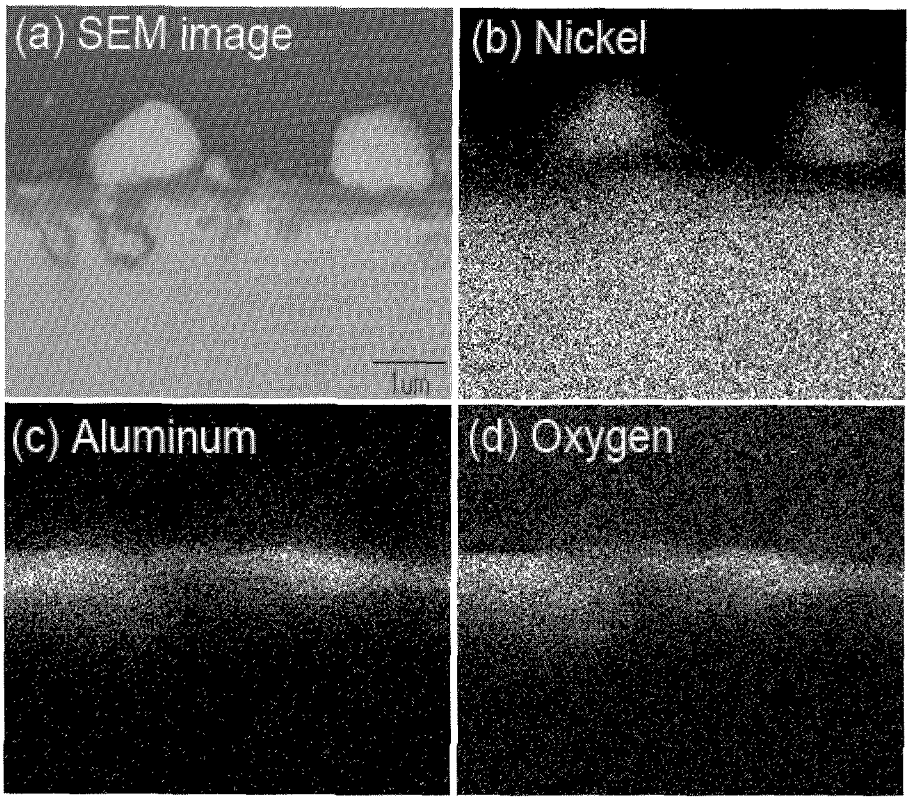

Fig.5 Elemental mapping on the cross section after the reaction
(a) SEM image, (b) nickel, (c) aluminum and (d) oxygen

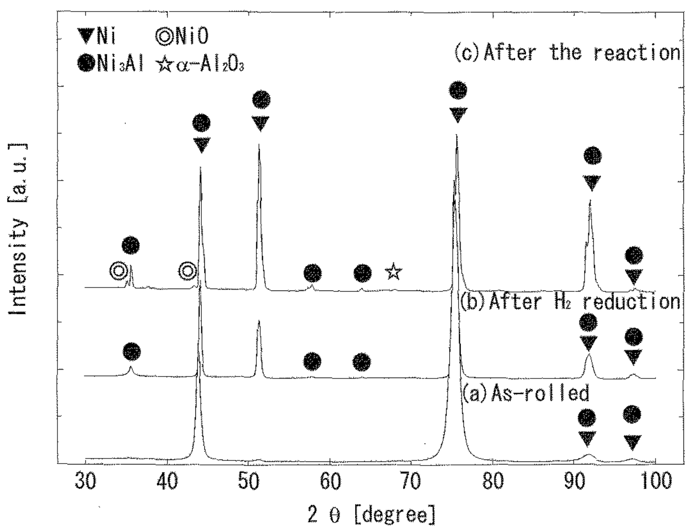

Fig.6 XRD diffraction pattern
(a) as-rolled, (b) after H_2 reduction and (c) after the reaction

previously reported [11]. After the reaction the band structure disappeared and many bright spherical phases were observed. The diameters of these bright spherical phases were found in a wide range from 200 nm to 3 μm.

Figure 4 shows the SEM images backscattered electron images on the cross section of the foils before and after the reaction. Before the reaction, the foil showed a very flat surface, having a very thin top layer of native Al oxides which were barely detectable by XPS. After the reaction, many spherical particles, which were are the same one in Fig. 3b, were observed on the foil surface, being accompanied with a thin layer below them.

Figure 5 shows the elemental mapping on the cross section of the foil after the reaction. It shows that the spherical particles mainly consist of nickel and the thin layer consists of aluminum and oxygen.

The crystal structures of the above-mentioned surface products were characterized by XRD and were compared before and after the reaction, as shown in Fig.

6. Only Ni and Ni_3Al, which are the starting component phase, were identified in the XRD profiles of the as-rolled foil and the foils after H_2 reduction. After the reaction, Al_2O_3 and NiO were confirmed in addition to Ni and Ni_3Al. It is noticed in Fig. 6 that the relative intensity of Ni peak at high 2-theta increased after the reaction, indicating the production of Ni on the foil surface during the reaction.

The SEM, EDS and XRD results indicate that fine metallic Ni particles were produced on the foil surface during the reaction, being accompanied with the formation of Al oxides layer between the Ni particles and the substrate foil. It is known that metallic Ni can serve as effective catalysts for methane steam reforming. We consider that the high catalytic activity is due to these fine Ni particles produced during the reaction.

4. CONCLUSION

Methane steam reforming was carried out over the surface of the Ni_3Al/Ni two-phase alloy foils in the temperature range of 873-1173 K. The main results are summarized as follows:

(1) Ni_3Al/Ni two-phase alloy foils demonstrated a high catalytic activity for methane steam reforming above 1023 K. The activity increased with the reaction temperature.

(2) Ni particles and aluminum oxide Al_2O_3 were produced on the foil surface during the reaction. The high catalytic activity is attributed to the spontaneous formation of these Ni particles.

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