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Effect of water vapor and hydrogen treatments on the surface structure of Ni_3Al foil

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ABSTRACT

We have developed a water vapor treatment followed by hydrogen reduction to modify the surface structure of Ni_3Al foils in order to obtain high catalytic activity. The Ni_3Al foils were heat treated in water vapor at 873 K for 1 h followed by H_2 reduction at 873 K for 1 h. The effects of the water vapor treatment and the H_2 reduction on the surface structure of the Ni_3Al foils were investigated by means of scanning electron microscopy and synchrotron radiation X-ray photoemission spectroscopy. Both Ni and Al in the surface layer of the Ni_3Al foil were oxidized during the water vapor treatment; fine NiO particles with a high density were formed on the outermost surface, accompanied by the formation of oxide layers of $Al(OH)_3$ and $NiAl_2O_4/Al_2O_3$ beneath the NiO particles. The NiO particles were reduced to metallic Ni and the $Al(OH)_3$ was decomposed to Al_2O_3, whereas the $NiAl_2O_4$ and Al_2O_3 remained unchanged during the subsequent H_2 reduction, forming a Ni-enriched porous structure on the surface layer of $NiAl_2O_4/Al_2O_3$.

1. Introduction

The Ni_3Al intermetallic compound is known as a promising high-temperature structural material because of its excellent high-temperature strength and corrosion/oxidation resistance [1–3]. However, its poor room-temperature ductility has been a serious problem. We have overcome this problem and successfully developed thin foils of Ni_3Al with a thickness of less than 30 μm by cold rolling unidirectionally solidified ingots [4–6]. Recently, we investigated the catalytic properties of the Ni_3Al foils for methanol decomposition in the temperature range from 513 to 793 K and found that such flat foils show high catalytic activity and selectivity for methanol decomposition into H_2 and CO, despite the small surface area of the foils, demonstrating that the Ni_3Al foils can be used as plate type catalysts [7], and thus serve both functionalities of catalytic and structural materials, by which one can make a more efficient reactor for hydrogen production [8,9]. The high catalytic activity for methanol decomposition was attributed to the formation of fine Ni particles on the foil surface through a selective oxidation and/or hydroxylation of Al by the small amount of H_2O produced during the reaction [9,10]. This result suggests that water vapor oxidation is effective for modifying the surface morphology and enhancing the catalytic activity of Ni_3Al foils.

Many studies have been carried out on the oxidation of Ni_3Al in air or pure O_2 [11–17], whereas there have been very few studies on the oxidation of Ni_3Al in water vapor [18,19]. Schumann et al. [18] studied the oxidation behavior of Ni_3Al single crystals under low oxygen partial pressure realized by exposing the Ni_3Al in a flowing H_2/H_2O mixture at 1223 K. Fine Ni particles were observed on the surface of the Ni_3Al after being exposed for 1 min, accompanied by formation of a continuous thin γ-Al_2O_3 oxide scale. Continued oxidation resulted in thickening of the γ-Al_2O_3 scale and coalescing of the Ni particles. However, they did not report the effect of water vapor at temperatures lower than 1223 K and at high water vapor partial pressures. Garza et al. [19] studied the interaction of an oxide film on Ni_3Al with the water vapor, and they revealed that the water vapor can significantly affect the oxide film even at low H_2O pressures. However, they did not mention the oxidation behavior of Ni_3Al caused by water vapor.

In this study, we carried out a water vapor treatment of Ni_3Al foils at 873 K, followed by H_2 reduction at 873 K, which is commonly used as a pre-reduction process for Ni_3Al catalysts [20,21]. The effect of the water vapor treatment and H_2 reduction on the surface structure of the Ni_3Al foils was investigated by means of

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scanning electron microscopy (SEM) and synchrotron radiation X-ray photoemission spectroscopy (SR-XPS).

2. Experimental

2.1. Foil sample preparation

Ni_3Al (Ni-24 at% Al) foils with a thickness of 30 μm were fabricated using 98% cold rolling of single crystals [5,6]. Samples for SR-XPS measurement were cut into 7 mm × 7 mm squares and then mechanically polished to get a surface roughness height of less than 0.5 μm. After polishing, the samples were washed with ethanol and de-ionized water in an ultrasonic bath.

2.2. Water vapor and H_2 reduction treatments

Water vapor and H_2 reduction treatments were carried out in a conventional fixed-bed flow reactor composed of a quartz tube (internal diameter 8 mm) in an electric furnace connected with gas and liquid supply units [7,8]. The samples were first heated up to 873 K in flowing N_2 (30 mL/min) and then water vapor was introduced using a micro-pump at a liquid flow rate of 50 μL/min for 1 h with continually flowing N_2 (101 kPa total pressure). The partial pressure of the water vapor in the reactor was 68 kPa during the water vapor treatment. After the water vapor treatment, the H_2 reduction was carried out at 873 K for 1 h in a flow of mixed H_2 (30 mL/min) and N_2 (5 mL/min). After the treatments, the samples were cooled down to room temperature in flowing N_2 (30 mL/min). Then the samples were taken out and preserved in a desiccator at room temperature for several days until SEM and SR-XPS analyses.

2.3. SR-XPS analysis

The SR-XPS measurements were performed on the samples in the as-polished state, after the water vapor treatment, and after the H_2 reduction using monochromatic synchrotron radiation with a photon energy of 1486.6 eV at the high-energy resolution soft X-ray beam line BL23SU at the synchrotron radiation facility SPring-8 (Japan). A detailed description of the BL23SU and the experimental station used can be found in previous reports [22,23]. The base pressure of the analysis chamber was maintained below 5×10^{-8} Pa during the measurements. The core level spectra of Ni 2p, Al 2p, Ni 3p, O 1s, and C 1s were measured for each sample. In order to obtain the depth profile of the surface structure, the measurements were carried out at different take-off angles (TOA) from 0° to 60° with respect to the surface normal. The photon energy scale was calibrated by using the peak position of the Au $4f_{7/2}$ core level at 84.0 eV [24].

2.4. Surface morphology analysis

The morphology of the surface and cross section of the foils in the as-polished state, after the water vapor treatment, and after the H_2 reduction was examined by means of scanning electron microscopy (SEM) (JEOL, JSM-7000F) with a field emission gun. The chemical composition of the surface products was analyzed by an energy dispersive X-ray spectroscopy (EDS) system equipped in the SEM. The cross-sectional samples were prepared by means of an argon ion beam cross-section polisher (JEOL, SM09010).

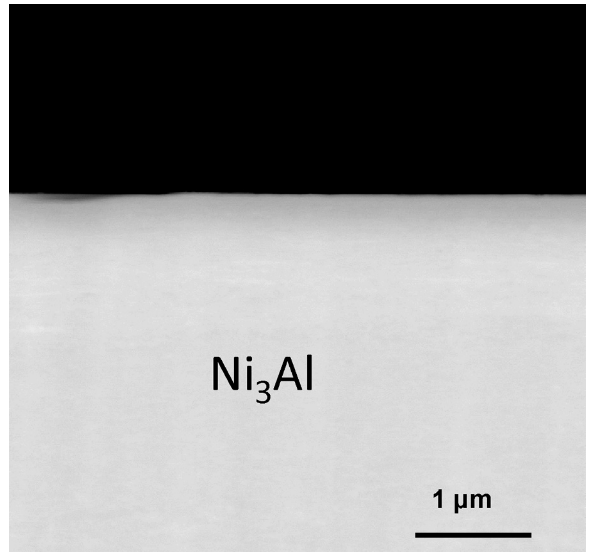

Fig. 1. Backscattered electron image of the cross section of as-polished Ni_3Al foil.

3. Results and discussion

3.1. As-polished samples

Fig. 1 shows the SEM backscattered electron (BE) image of the cross section of the as-polished foil. The surface of the foil was macroscopically smooth. No particles or precipitates were observed near the surface. The image contrast shows no obvious change from the surface to the depths of the foil, indicating a uniform elemental composition across the cross section of the foil.

Fig. 2 shows the Ni 2p (Fig. 2a), Al 2p and Ni 3p (Fig. 2b) SR-XPS spectra obtained at TOA = 0°, 40°, and 60° for the as-polished foil. At TOA = 0°, a Ni $2p_{3/2}$ peak at a binding energy of 853.6 eV and a Ni $2p_{1/2}$ peak at 870.8 eV were detected; they were accompanied by satellite peaks. These peaks correspond to metallic Ni [24]. With increasing TOA, the shape of the satellite peaks changed, and the spectral intensity ratio of the satellites relative to the main Ni 2p peaks increased. This change matches the features of Ni oxides [11,19,24], indicating that a small amount of Ni oxide was formed near the surface even though the oxides were not detected by SEM observation. The Ni 3p spectra in Fig. 2b also show a shape change with the increase of TOA. At TOA = 0°, a Ni 3p main peak is observed at a binding energy of 67.0 eV with a shoulder on the high binding energy side, which agrees well with the Ni 3p spectra of metallic Ni [10,12]. However, the intensity of the shoulder relative to the main Ni 3p peak increased with the increase of TOA, becoming even larger than the main Ni 3p peak at TOA = 60°, which is typical of Ni oxides [14]. This result is in agreement with that of Ni 2p, indicating the formation of Ni oxides on the surface. These Ni oxides are thought to be native Ni oxides (NiO_x) formed during polishing or exposure to air at room temperature.

The Al 2p core level showed two chemical states, as shown in Fig. 2b. The major peak located at 73.0 eV corresponds to metallic Al, whereas the minor peak at around 74.5 eV corresponds to Al oxide, probably a native amorphous AlO_x [10,14]. With increasing TOA, the intensity of the AlO_x peak relative to the metallic Al peak increased, indicating the presence of AlO_x on the surface.

3.2. Samples after water vapor treatment

Fig. 3a shows the SEM secondary electron (SE) image of the Ni_3Al foil surface after water vapor treatment. A high density of fine particles on the surface was observed. Most of the particles were