Application of Sputter Deposition Technique to the Preparation of Amorphous Alloy-Derived Catalysts for NO Decomposition

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Sputter deposition technique has been applied to the preparation of amorphous alloy precursors of catalysts on a fine oxide powder, in order to overcome the low surface area of the catalysts prepared from melt-spun amorphous alloy precursors. Amorphous Ni-Ta-Pd alloys have been sputter-deposited onto the γ-alumina powder with a high surface area, and then pre-oxidized at 1023 K in a 0.5% NO atmosphere. During the preoxidation, the amorphous alloys have been converted to palladium catalysts supported on the NiTaOx double oxide. The BET areas of the catalysts thus prepared (sputter-deposited catalysts) are approximately 50 times higher than those prepared from a melt-spun Ni-40Ta-1Pd alloy precursor (melt-spun catalyst). The catalytic activity of the sputter-deposited catalysts for NO decomposition becomes about twice as high as that of the melt-spun catalyst. Furthermore, the selectivity of nitrogen formation is also improved compared with the melt-spun catalyst. Accordingly, the application of sputtering technique is quite suited for preparing amorphous alloy catalyst precursors with a high surface area.

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1. Introduction

Since the first report of amorphous alloy catalysts in 1980(1), the catalytic properties of various amorphous alloys have been studied for a range of chemical reactions. The catalytic properties of amorphous alloy-derived catalysts, which have been mostly prepared by oxidation or oxidation-reduction treatment of amorphous alloys, have also examined. Due to their unique structure and morphologies, the amorphous alloy catalysts and the amorphous alloy-derived catalysts have often shown specific catalytic properties, compared with conventionally prepared catalysts. For instance, the activity of the catalyst, prepared in situ from an amorphous Pd-Zr alloy, for methanation of carbon dioxide is about one order of magnitude higher than that of Pd/ZrO2 catalyst prepared by wet impregnation(2). The selectivity of the products for hydrogenation of carbon monoxide has also been reported to be different on the amorphous and corresponding crystalline iron-nickel base alloys(3). Further, the Rh/ZrO2 catalyst prepared from amorphous alloys possesses longer durability for the hydrogenation reaction of carbon dioxide than the conventionally prepared catalyst(4).

In spite of these superior catalytic properties of amorphous alloy catalysts and amorphous alloy-derived catalysts, one of the disadvantages to use amorphous alloys as catalysts and catalyst precursors is the small surface area of the catalysts. The amorphous alloys for catalysts and catalyst precursors have been mostly prepared so far by the melt spinning method. The surface areas of the melt-spun amorphous alloy ribbons are relatively low, even after activation treatments, compared with conventionally prepared supported catalysts. Therefore, for the practical use of amorphous alloy catalysts and amorphous alloy-derived catalysts, the surface roughening of the catalysts is required.

In this study, we applied a sputter deposition technique to prepare amorphous alloy-derived catalysts having high surface area. Amorphous alloys were deposited onto fine powder of γ-alumina with BET surface area of about 95 m²·g⁻¹ and the catalytic property was examined for the decomposition of nitrogen monoxide (NO) after oxidation pretreatment.

Nitrogen monoxide, emitted into atmosphere by oxidation of nitrogen during combustion of fossil fuels, is well known to induce acid rain and urban smog as well as to be harmful for human being. Thus, the decomposition of nitrogen monoxide have been studied extensively. At present, the nitrogen monoxide, emitted from gasoline vehicles and from fuel-burning plants, have been practically decomposed using three-way catalysts and using a selective reduction method with ammonia, respectively. However, the most feasible reaction to remove nitrogen monoxide is its direct decomposition, expressed as

\[ 2\text{NO} \rightarrow \text{N}_2 + \text{O}_2. \] 

(1)

Although nitrogen monoxide is formed by the reverse reaction of eq. (1) at high temperatures more than 1200
K, nitrogen monoxide can be decomposed thermodynamically to nitrogen directly at lower temperatures. However, the reaction (1) does not proceed easily due to high activation energy of the reaction even under the presence of catalysts examined so far. The direct decomposition has been studied since the beginning of the 20th century. In particular, after the report that Cu/ZSM-5 catalysts show high catalytic activity even at relatively low temperatures\(^{59(60)}\), attention has been focused on the catalytic direct decomposition\(^{59(60)}\). Various catalysts have been studied, but no catalysts with sufficient activity for practical use have been developed.

Some of the present authors have reported that the catalysts prepared from melt-spun amorphous nickel-valve metal-palladium alloy ribbons by HF immersion and subsequent oxidation treatment show high activity at 773 K and higher temperatures\(^{19}\). The HF immersion leads to selective dissolution of valve metals and nickel with a consequent enrichment of palladium on the ribbon surface, together with surface roughening\(^{19}\).

Among them the catalysts derived from amorphous Ni-Ta-Pd alloy ribbons show high activity even without HF treatment\(^{11}\). Further, the activity was enhanced after transformation of NiO and Ta\(_2\)O\(_5\), formed during oxidation at 773 K, to a double oxide of NiTa\(_2\)O\(_5\) during oxidation at higher temperatures\(^{39}\). However, the activity was limited due to small surface areas of the catalysts. Accordingly, in the present study amorphous Ni-Ta-Pd alloys were selected to prepare amorphous alloy-derived catalysts with high surface area by sputter deposition. The catalytic properties of the alloy after oxidation have been examined and compared with the catalyst, of similar composition, prepared by the melt spinning method.

II. Experimental

1. Catalyst preparation

An amorphous Ni-63 at% Ta-3 at% Pd alloy was prepared on γ-alumina powder using a dc magnetron sputtering apparatus shown in Fig. 1. About 2 g of γ-alumina powder (Marumoto Kogyo Co. Ltd.), nominally of 6 mm diameter, was agitated on the rotating drum, which is water cooled, during sputter deposition. The target was composed of 99.9% pure tantalum disc of 47 mm diameter and 3 mm thickness, in the sputter erosion region of which 99.95% pure nickel disks of 8 mm diameter and 99.9% pure palladium discs of about 4 mm diameter were fixed symmetrically. After evacuating the chamber to the order of 10\(^{-3}\) Pa, sputter deposition was carried out for 20, 60 or 120 min. The composition of the alloy/γ-alumina powder was determined by electron probe microanalysis (EPMA). For comparison, amorphous Ni-40 at% Ta-1 at% Pd alloy ribbons were prepared by a single roller melt spinning method. The melt-spun amorphous alloy specimens were oxidized in air at 1023 K for 3 d and the sputter-deposited alloy specimens were oxidized under the catalytic conditions, described later, at 1023 K for 5 h prior to measuring the catalyst performance.

2. Catalytic reaction

The catalytic reaction was carried out using a fixed bed continuous flow reactor. In the center of a quartz tubular reactor 8 mm in inner diameter and 500 mm in length, 1.0 g of the catalysts were fixed at the length of about 40 mm. A reactant gas mixture of 0.5% nitrogen monoxide in helium was passed at a flow rate of 30 mL·min\(^{-1}\).

The catalytic activity and selectivity were measured at temperatures ranging from 823 to 1173 K. The gas composition after the catalytic reaction was analyzed using gas chromatograph-mass spectrometer (Shimadzu GCMS-QP300EX). Oxygen, nitrogen and nitrogen monoxide were separated by Molecular Sieve 5A, and nitrous oxide (N\(_2\)O) was separated using Porapack Q. The steady-state activity and selectivity were measured at each temperature from 823 to 1127 K at 50 K intervals.

3. Characterization of catalysts

BET surface areas of the alloy specimens after the catalytic reaction were measured by the Belsorp 28SA automatic gas adsorption apparatus using nitrogen physisorption at 77 K. Structural changes of the specimens by oxidation and catalytic reaction were determined using X-ray diffraction with Cu K\(_α\) radiation. Further, a transmission electron microscope (JEOL JEM-3010) was used to examine the structure in detail. An analytical TEM (JEOL 2000FX with EDX facilities) was also used to clarify the distribution of alloy deposits on the γ-alumina powder after the catalytic reaction.

III. Results and Discussion

1. Characterization of precursor alloys and catalysts

Figure 2 shows the X-ray diffraction patterns of the sputter-deposited Ni-25Ta-5Pd alloy and melt-spun Ni-40Ta-1Pd alloy. The melt-spun alloy shows a halo typical of an amorphous structure. In the X-ray diffraction pattern of the sputter-deposited alloy, reflections of γ-alumina can be seen clearly. Besides the reflections of γ-alu-
mina a halo pattern is observed at the diffraction angle slightly higher than that of the melt-spun alloy, indicating that the sputter-deposited alloy is also amorphous. The shift of the halo position is possibly due to the difference of alloy composition. After the pre-oxidation and subsequent catalytic reaction, the amorphous alloys are transformed to a double oxide of NiTa2O6, supporting palladium metal (Fig. 3). NiO is also formed for the melt-spun catalyst and the sputter-deposited Ni–25Ta–5Pd catalyst. However, the formation of NiO is not clearly detected in the X-ray diffraction pattern of the sputter-deposited Ni–63Ta–3Pd catalyst. The atomic ratio of nickel to tantalum in the latter catalyst is almost equal to that in the double NiTa2O6 oxide. On the other hand, the former two catalysts contain excess nickel, with respect to the atomic ratio of the double NiTa2O6 oxide. This should be a main reason why NiO is formed for the melt-spun catalyst and the sputter-deposited Ni–25Ta–5Pd catalyst, but not for the sputter-deposited Ni–63Ta–3Pd catalyst. The reflections of palladium metal in the X-ray are relatively weak, due to the low content of palladium in the precursor alloys.

Oxidation of melt-spun amorphous alloy ribbons under the catalytic reaction conditions proceeded with 100% decomposition of nitrogen monoxide at the initial stage. After the complete oxidation of the alloys, steady-state catalytic activity was obtained. The time required for the complete oxidation was more than 20 h. Similarly, when the sputter-deposited alloy specimens were exposed under the catalytic reaction condition at 1023 K, 100% decomposition of nitrogen monoxide was initially observed. In this period, no oxygen formation was detected and the sputter-deposited alloy was oxidized. Therefore, nitrogen monoxide was decomposed initially by oxidizing the sputter-deposited alloys as follows:

\[ \text{NO} + x \text{M} \rightarrow \frac{1}{2} \text{N}_2 + \text{M}_2\text{O}_x. \]

The oxidation of the alloy specimens sputter-deposited for 120 min was completed within 5 h, and the steady-state activity for the direct decomposition reaction (eq. (1)) was achieved.

A transmission electron micrograph of the sputter-deposited Ni–63Ta–3Pd catalyst, after the catalytic reaction up to 1173 K and the EDX spectra at the positions indicated in the micrograph, are shown in Figs. 4 and 5, respectively. Fine particles composed of mainly γ-alumina are observed at the bottom-left side of this micrograph, although thin alloy film has been deposited on these particles. Darker particles, shown at the right side of the micrograph, indicate that thicker alloy films are deposited. This is confirmed from EDX spectra shown in Fig. 5. Clearly, the particles in region A are composed mainly of alumina. The intensities of tantalum and nickel are rather low. On the other hand, in region B the tantalum peak is most intense and palladium peak is also detected, while the aluminum peak is relatively weaker than that in region A. Thus, it is clear that the thicker alloy is deposited in region B and that the thin alloy is deposited in
Fig. 4 A transmission electron micrograph of the specimen after oxidation and subsequent catalytic reaction of the Ni-63Ta-3Pd alloy sputter-deposited onto γ-alumina powder for 120 min.

Fig. 5 EDX spectra from the regions A and B indicated in the transmission electron micrograph of Fig. 4.

Table 1 The BET surface area and palladium content of the catalysts prepared from sputter-deposited and melt-spun alloys.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sputtering time (min)</th>
<th>Palladium content (mass%)</th>
<th>BET surface area (m²·g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sputter-deposited</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-25Ta-5Pd/Al₂O₃</td>
<td>120</td>
<td>1.0</td>
<td>77.2</td>
</tr>
<tr>
<td>Ni-63Ta-3Pd/Al₂O₃</td>
<td>20</td>
<td>0.2</td>
<td>86.5</td>
</tr>
<tr>
<td>Ni-63Ta-3Pd/Al₂O₃</td>
<td>60</td>
<td>0.8</td>
<td>63.8</td>
</tr>
<tr>
<td>Ni-63Ta-3Pd/Al₂O₃</td>
<td>120</td>
<td>1.0</td>
<td>55.7</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0</td>
<td>—</td>
<td>94.5</td>
</tr>
<tr>
<td>Melt-spun</td>
<td></td>
<td>1.0</td>
<td>1.2</td>
</tr>
<tr>
<td>Ni-40Ta-1Pd</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

diameter has the BET surface area of about 95 m²·g⁻¹. The surface area of the sputter-deposited Ni-63Ta-3Pd catalyst decreases with increasing sputtering time. This indicates that the deposited alloy, transformed to palladium catalysts supported on NiTa₂O₆, possesses a low surface area as compared with γ-alumina. However, the surface area of the catalyst prepared by sputter deposition for 120 min is still about 50-fold higher than that of the catalyst prepared by the melt spinning method. This fact clearly reveals that amorphous alloy-derived catalysts with high surface areas are prepared by the sputter deposition of alloys on fine powder supports.

The sputter deposition technique to produce metal-coated powder has been developed by Takeshima et al. They have sputter deposited various metals onto the powder of several tens of micrometer diameter, which is much larger than the γ-alumina used in the present study, and this technique has been practically used for the preparation of novel hard materials, pigments, heat sink materials and so on. In the present study, the sputter deposition technique is applied for the first time to the preparation of catalysts with high surface area.

2. Catalytic properties

The activity and selectivity of the catalysts prepared from sputter-deposited alloys have been examined for direct decomposition of nitrogen monoxide. Figure 6 shows the conversion of nitrogen monoxide to nitrogen on the Ni-63Ta-3Pd catalysts, sputter deposited for 20, 60 and 120 min, as a function of reaction temperature. On all the catalysts the conversion increases almost linearly with reaction temperature. Further, the catalysts prepared for longer sputter deposition time show the higher conversion at each temperature. The conversion is particularly enhanced when the sputter deposition time is elongated from 20 to 60 min. Further elongation of the sputter deposition time from 60 to 120 min leads to only a slight increase in the conversion, suggesting that most of the γ-alumina surface is covered by the alloy during the initial sputtering for 60 min and the number of surface palladium atoms, which may be the active sites for the reaction, increases only slightly after sputtering for 60 min.
The conversions of the catalysts prepared by sputter deposition for 120 min and by melt spinning are shown in Fig. 7. Clearly, the conversion of nitrogen monoxide to nitrogen on the sputter-deposited Ni-25Ta-3Pd and Ni-63Ta-5Pd catalysts is similar and is approximately twice as high as that on the melt-spun catalyst. Since the catalytic activity only appears when palladium is added as an alloying element\cite{16}, surface palladium atoms should be active sites for the present reaction. The weight percentage of palladium in the bulk of the sputter-deposited catalysts, including alumina, is similar to that in the melt-spun catalyst, as shown in Table 1. However, the activity of the sputter-deposited catalysts is significantly higher than that of the melt-spun catalysts. The activity of the melt-spun catalysts increased with increasing palladium content of catalysts\cite{16}, but even for the melt-spun Ni-40Ta-10Pd catalyst the activity is lower than that of the present sputter-deposited catalyst. Therefore, the sputter deposition technique for the preparation of the amorphous alloy-derived catalysts is quite useful to enhance the activity without increasing the content of noble palladium metal. The activity enhancement by using sputter deposition technique could be mainly due to the enhanced surface roughness of the sputter-deposited catalysts. The surface roughening should result in the increase in the number of surface palladium atoms. However, in contrast to the about 50-fold higher BET surface area of the sputter-deposited catalysts with respect to the melt-spun Ni-40Ta-1Pd catalyst, the activity of the sputter-deposited catalysts is only about twice higher than the melt-spun catalyst. This fact may suggest that an increase in the number of surface palladium atoms, that is, the active sites for the catalytic reaction, in the catalysts by sputter deposition is fairly less than the increase in the surface roughness of the catalysts, although the differences in dispersion, grain size and interaction with oxide support between the sputter-deposited and melt-spun catalysts should be considered. It is, however, clear from the practical point of view that the sputter deposition of amorphous alloys on fine oxide powder is suitable for producing highly active amorphous alloy-derived catalysts.

During the catalytic reaction nitrous oxide (N₂O) is also produced as well as nitrogen. The selectivity of nitrogen formation is also improved by preparing the catalysts using the sputter deposition method. Figure 8 shows the selectivity of the products on the sputter-deposited and melt-spun catalysts. At temperatures more than 973 K, nitrogen is formed exclusively and almost no nitrous oxide is produced on all the catalysts examined. At lower temperatures, however, nitrous oxide is also formed and the amount of nitrous oxide formed increases with a decrease in reaction temperature. In particular, at 823 K almost equal amounts of nitrogen and nitrous oxide are formed on the melt-spun catalyst. On the other hand, the selectivity of nitrogen on the sputter-deposited catalysts is remarkably higher than that on the melt-spun catalyst. Even at 823 K nitrogen is formed with more than 95% selectivity on the sputter-deposited Ni-63Ta-3Pd catalyst, although the selectivity of nitrogen formation on the sputter-deposited Ni-25Ta-5Pd catalyst is slightly lower than that on the high tantalum catalyst prepared by sputter deposition at lower temperatures. The selectivity of nitrogen formation on the Ni-63Ta-3Pd catalysts sputter-deposited for 20 min is
slightly higher at relatively low temperatures, compared with the catalysts sputter-deposited for longer time, as shown in Fig. 9.

The factors affecting the selectivity of products are not presently well known. It was reported that the oxidation of the melt-pun Ni-40Ta-1Pd alloy at 823 K led to the formation of a mixture of NiO and Ta₂O₅ on which palladium was supported²⁰. The selectivity of nitrogen on the catalyst is relatively low at 923 K or lower temperatures, but the selectivity becomes higher after the mixture of the oxides is transformed to the NiTa₂O₆ double oxide⁶⁰, indicating that palladium supported on the double oxide has higher selectivity of nitrogen formation than that on the mixture of NiO and Ta₂O₅. For the present sputter-deposited Ni-63Ta-3Pd catalyst, the oxide present in the catalyst is mainly the NiTa₂O₆ oxide, in contrast to the presence of NiO with the double oxide in the Ni-25Ta-5Pd catalyst. Therefore, the exclusive formation of this double oxide from the sputter-deposited alloy could be one of the reasons for the higher selectivity of nitrogen on the sputter-deposited Ni-63Ta-3Pd catalyst than on the Ni-25Ta-5Pd catalyst.

The selectivity of nitrogen formation on the sputter-deposited catalysts is significantly higher than that on the melt-spun catalyst at relatively low temperatures. It has been reported that a wet impregnated Pd/Al₂O₃ catalyst shows higher selectivity for nitrogen formation than the melt-spun Ni-40Ta-1Pd catalyst²⁰. Furthermore, other metal catalysts supported on alumina have been reported to show relatively high selectivity for nitrogen formation²⁵, although the catalytic activity is not high. Therefore, it is expected that alumina has a crucial role in the catalytic properties of the present sputter-deposited catalysts. In order to confirm the role of alumina in the present Pd/NiTa₂O₆(-NiO)/Al₂O₃ composite catalysts, further precise characterization of the sputter-deposited catalysts and the mechanistic study of the catalytic reaction are in progress.

IV. Conclusions

Using a sputter deposition technique highly active amorphous alloy-derived catalysts, with higher surface area compared with the melt-spun amorphous alloy-derived catalysts, have been prepared for the first time. The sputter deposition of amorphous Ni-Ta-Pd alloys onto the γ-alumina powder and the subsequent oxidation lead to the formation of a palladium supported on double NiTa₂O₆ oxide/γ-alumina catalyst (sputter-deposited catalyst), the BET surface areas of which are more than 50 m²·g⁻¹, being approximately 50-fold higher than that of the catalyst prepared from the oxidation of the melt-spun Ni-40Ta-1Pd alloy (melt-spun catalyst). The catalytic activity of the sputter-deposited catalysts, deposited for 60 min or more, for direct decomposition of nitrogen monoxide is about twice higher than that of the melt-spun catalyst. Further, the selectivity of nitrogen formation at 923 K and lower is remarkably improved on the sputter-deposited catalysts, compared with that on the melt-spun catalyst. The higher surface area, which leads to the higher active sites for the catalytic reaction, and the exclusive formation of the double oxide without NiO by the oxidation of the sputter-deposited alloy should be responsible for the higher activity and selectivity for the
decomposition of nitrogen monoxide to nitrogen and oxygen.

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