

binding molecular dynamics method.¹⁷ They also find the substitutional Ni in a CNT with Ni-C distance 2.03–2.08 Å: The distances are much longer than our result where Ni-C distance=1.83 Å. Consequently, the Ni substitution model is the most plausible structure of the Ni species which strongly interact with the graphene sheet.

E. XANES application to nanomaterials in combination with multiple scattering analysis

In this work we determine the location and structure of Ni species in the CNF by XAFS and multiple scattering analyses. We also evaluate the sensitivity of XANES to Ni-C distance and Ni charge. We find that we can determine the Ni-C distance within the precision of ± 0.1 Å. The distance error bar of XANES is one order bigger than that of EXAFS. Thus the combination of EXAFS and XANES must be necessary. The charge and valence state of metal species can often be inferred from XANES. The edge shift is corresponding to the chemical shift in XPS and the L_2, L_3 white line peaks are related to the density of d vacancy.

We also check how the curvature of the CNT affects the XANES spectra by using multiple scattering theory. We postulate CNTs with 14 Å in diameter as shown in Fig. 11. We set one Ni atom both outside (a) and inside (b) the tube. Comparing the XANES for the Ni on a graphene sheet with the XANES for the Ni outside the CNT with 14 Å, we can see that the curvature has only small influence on the XANES spectra. However, the “inside” model gives much weaker peaks at 7 eV and 16 eV. This may be because the different distances to carbon atoms in next nearest neighbors affect the XANES spectra in these models. This result is quite interesting because any other experimental tools cannot provide such information. Some theoretical simulations support the “outer” models considered here.^{14,16,17} The question about the metal location inside or outside of a CNT can be answered based on the XANES analyses.

Thus the XANES in combination with multiple scattering method will provide a new and unique structural tool to study nanomaterials.

F. Comments on the application of CNTs and CNFs prepared from Ni catalysts

Nanotoxicology is a new terminology to evaluate the toxicological hazard to human body and environment.⁵² Nano-

technology is revolutionarily developing and is changing our daily life. But the assessment of toxic effects of the nanomaterials is not fully accomplished and nobody knows how the nanomaterials damage ourselves and our environment. One can understand the situation easily in the example of asbestos. Our XAFS analyses that show the presence of strongly bound Ni in a CNF and the facts that Ni is a toxic element suggest that the CNTs and CNFs produced from Ni catalysts should not be used for biomaterials.

V. CONCLUDING REMARKS

In this paper we investigate the local Ni structures before and after the purification of CNFs by EXAFS and XANES. Ni atoms are dominantly in Ni particles together with small amount of Ni oxide before the purification. After the purification they are in Ni monomer species substituted in the graphene sheet to form strong Ni-C bonds.

We have few reliable characterization techniques for small amount of residual species. This work demonstrates the remarkable usefulness of the XAFS (XANES+EXAFS) techniques combined with multiple scattering calculations. In particular XANES can give a detailed stereochemical structures of the Ni species, although it is not so sensitive to the bond distance. In contrast, EXAFS is sensitive to the bond length to nearest neighbors within 0.01 Å. A combination of these two techniques should be a powerful tool for the studies of nanosciences.

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Development of Environmental Cell for Gas Reaction of Nano-size Particles

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Abstract. “Environmental cell” microscopy was applied for surveying gas reaction of hydrides in magnesium base alloys, which are candidates for hydrogen storage materials in advanced hydrogen energy systems. In order to clarify the mechanism of hydrogenation process, in-situ experiment has been carried out by using a 200 kV transmission electron microscope (TEM) equipped with a newly developed environmental cell, which is capable to 0.1 MPa in the temperature range between R.T. and 200°C. When hydrogen gas reacted with magnesium powders, straightening of surface steps (60~70 nm in height) was observed, indicating that volume expansion occurred. In addition, the formation of MgH₂ was indicated in selected-area-diffraction patterns (SADP). The precise study on this in-situ experiment, as well as its improvement, will be continued, with using transparent films.

Introduction

The hydrogen storage alloy attracts attention as one of the hydrogen storage materials. Although many studies have been done for development of better materials, microscopic observation of the hydrogen absorption reaction process aiming at evaluation or control of material has not been performed. TEM observation and *in-situ* XRD analysis are carried out to understand effects of microstructures and temporal structure changes. (e.g. reference [1],[2]). Although these ways are very effective for understanding of material properties, it isn't able to observe successive microstructural changes with hydrogenation. We thought the environmental cell enables to observe them and it is useful to the development of advanced hydrogen storage materials.

Environmental cell is a technique for *in-situ* observation in TEM. In the past study, *in-situ* observation of the oxidation process of Ni-Cr alloy was performed using the HVEM which is the acceleration voltage of 1.2 MV (2.4-2.8 kPa, 500 °C) [3]. In the catalytic reaction, P. L. Gai *et al.* are performing *in-situ* observation for the catalytic reaction of molybdcic acid bismuth which is a heterogeneous catalyst on 100 Torr and 400-500 °C conditions using C₃H₆ gas [4]. As an example of the *in-situ* observation of crystal growth, cryostat is introduced in a microscope and *in-situ* observation of crystal growth process of sulfur hexafluoride (SF₆) is performed at 50 Torr and below 150 K [5]. As the multiple usages with open-type environmental cell other than heating, there is a case which is doing the tensile test pouring hydrogen gas, and the interaction of hydrogen and a rearrangement is observed [6].

Although the above cases of application of environmental cells were reported, the environmental cell had not been used for the hydrogen storage alloys. In this study, therefore, an environmental cell capable to build gas environment in a column without converting a TEM body was manufactured in order to perform *in-situ* observation of a hydrogen absorption reaction. As the first report of *in-situ* observation of the hydrogenation reaction process, magnesium was investigated using the manufactured environmental cell.

Experimental

The scheme of the newly manufactured environmental cell. The holder manufactured was a modified holder of a general-purpose type TEM (JEOL JEM-2010). The environmental cell holder is mainly made of aluminum, and the acroteric is brass. The stainless steel pipe with a valve, which is for the path of gas, is located in the inside of this holder. The schematic view of the nose of a holder is shown in figure 1. This environmental cell is a closed (window) type and airtightness is kept by three O-rings about 0.2 mm in thick and the grid of two upper and lower sides by which the film was covered. The narrow tunnel is extended toward the acroteric hollow and gas flows through this. Moreover, this narrow tunnel is connected with the stainless steel pipe in a holder. Figure 2 is a photograph of a gas-control part of an environmental cell, and a schematic view of a gas-control system. The tube extended from the inside of a holder is connected with the gas-control part which has a rotary pump and a gas cylinder. By this gas-control part, arbitrary gas can be introduced from several pascals to 0.1 MPa. Figure 3 is a schematic view of a grid. The grid is made of copper with the carbon film (50 nm in thick), which is stabilized with the triacetyl cellulose (TAC) film (20 nm in thick). The TAC is stable against accelerated electron beam [7], so that observation can be carried out without breaking vacuum in column. A single hole grid is used as a spacer when using a powder sample.

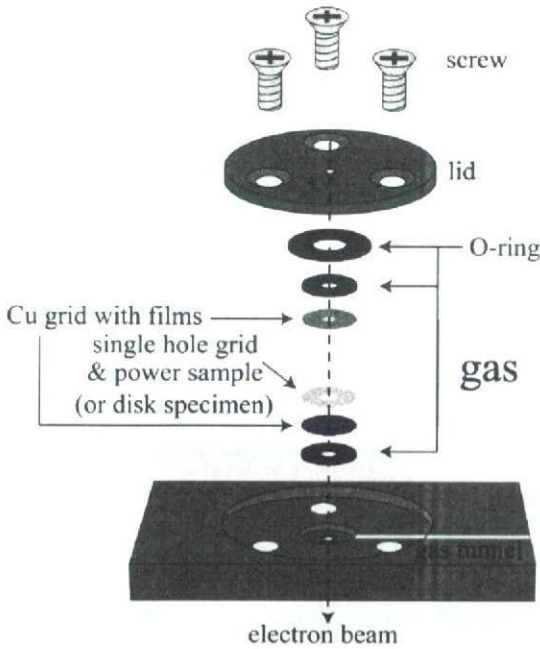


Figure 1. The schematic view of the nose of environmental cell holder

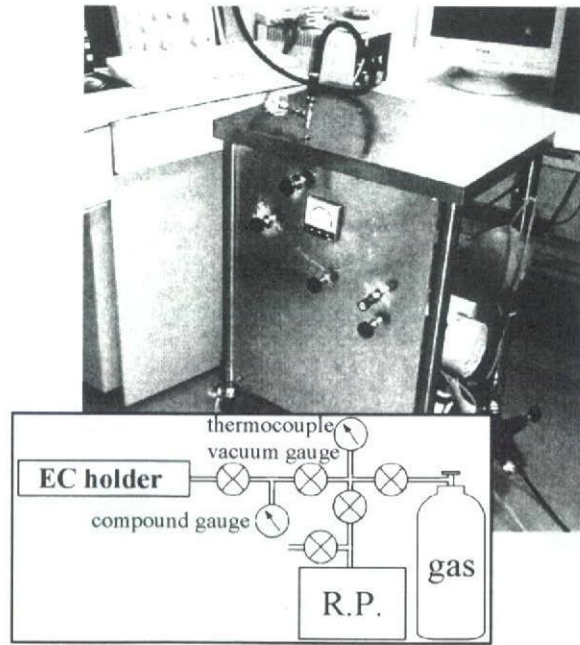


Figure 2. Photograph of the gas-control part and schematic view of a gas-control system

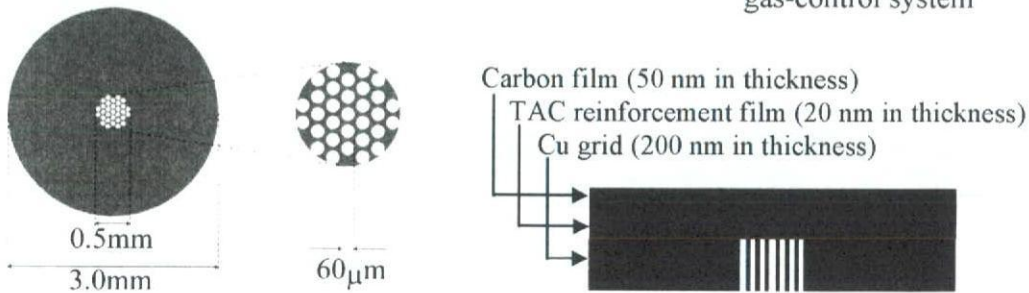


Figure 3. The schematic view of an electron-transparent grid

Sample preparation and loading. The powder of magnesium hydride (MgH_2 , Alfa Aesar) packed into the quartz tube with a valve was heat-treated at about 250°C for 1 hour in electric furnace with a diffusion pump for degassing. This dehydrogenated Mg powder was used as a Mg sample.

Primarily, the head of the environmental cell holder was cleaned by ethanol with ultrasonic. In order to remove the ethanol, which might adhere into a holder line, bake-out was carried out with a pre-evacuation device at 55°C for 1 hour. For preventing oxidation and keeping surface activity, the holder was loaded with the sample within the globe box in argon atmosphere. Firstly, O-ring, Cu grid, two sheets of single hole grid and paper lid are attached to the head of a holder in the air. The edge of upper single hole grid is folded so that it may be easy to remove. This single hole grid is for making powder covers only the center of grid. Then, the valve of the environmental cell holder was opened, so that it might be easy to flow through gas. After these steps were completed, a stereoscopic microscope, an environmental cell holder, a sample and tools were put in the glove box. A stereoscopic microscope is used for precise specimen setting. The inside of a glove box is evacuated using a rotary pump, and it is filled up with the argon gas at an atmospheric pressure. This process has done twice. And the following processes were carried out within a glove box.

When Mg powder was picked with tweezers and dropped on the grid, the holder was set upside-down struck it lightly, and then, big powders that might break films were dropped. Small powder only remained on the film of a grid by this process. After carrying a sample, the paper lid and the folded single hole grid tend to be dismantled, so that the lid with two O-rings was stabilized with screws. The TEM disc was set instead of it. Finally, the valve of the environmental cell holder was closed and it took out from the glove box.

The holder loaded with the sample was inserted in TEM (JEOL JEM-2010). In observation of magnesium, bright field images and selected-area-diffraction patterns were taken before hydrogen introduction. The argon gas in an environmental cell holder was evacuated with the rotary pump after photographing. Subsequently, H_2 gas of 0.1 MPa was introduced, and some images were taken in the same manner.

Result and discussion

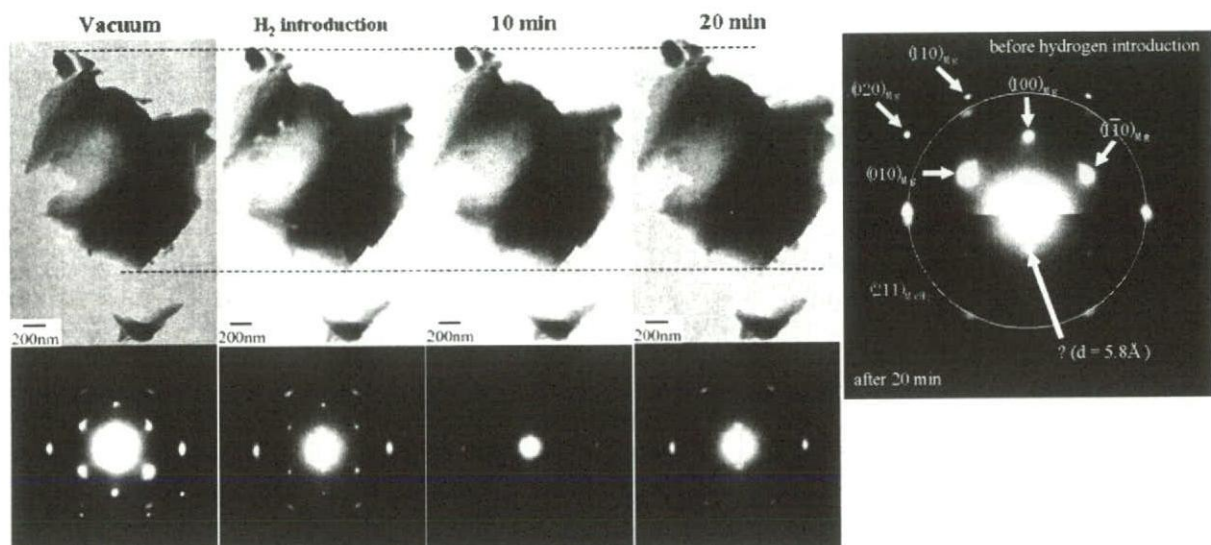


Figure 4. BF and SADP of Mg particles before and after introducing hydrogen.

Figure 4 shows the bright field (BF) images and SADP of Mg grains before and after hydrogen introduction. The broken line shows the grain size before hydrogen introduction. As shown in a figure 4, grains were expanded slightly after introducing hydrogen. In the photograph before hydrogen

introduction and after introduction for 20 minutes, maximum width of grains was increased about 10 % and the cross-sectional area seemed to be increased about 28 %.

Moreover, it assumed that the measured cross-sectional area was equivalent to the cross-sectional area of a sphere, and the rate of volume increase was calculated. It seems that the volume of the grains hydrogen-introduced for 20 minutes increased about 40 %. From the crystal structure and the lattice constant of Mg and MgH₂, it is expected that the ideal cubical expansion by hydrogenation is about 30 %, suggesting that the assumption used this time for the estimation of volume expansion was not appropriate.

A right viewgraph in figure 5 is the comparison of SADP before and after introduction for 20 minutes. The spacing of lattice planes corresponding to a spot is calculated from the following formula: ($d = \lambda L/R$). Where λ is wavelength of electron beam (=0.0251 Å at 200 kV), L is camera length (=80 cm) and R is the distance between a spot and center. With R measured from the film, the spacing of lattice planes, d , can be calculated. Furthermore, the value of the spacing of lattice planes, d , and the calculated value from JCPDS card (Mg, Mg oxides, and MgH₂) were compared, and also Miller indices were determined. There is a spot disappeared in 20 minutes after hydrogen introduction. It is probably a pattern from Mg because the Mg sample used this time was simple substance. Moreover, there is a firm ring-like pattern before and after hydrogen introduction, and this is considered to be a pattern from MgH₂. There is a possibility that the dehydrogenation of MgH₂ is incomplete. Although dehydrogenation was carried out at 250 °C, unless MgH₂ might be heated up to 600 K, dehydrogenation does not fully occur. Therefore, it is almost certain that MgH₂ exists at the time before the hydrogen introduction in this experiment.

Although diffraction spots showing $d=5.8$ Å were observed in this experiment, we could not identify what they resulted from.

Summary

Using the environmental cell newly manufactured for the *in-situ* observation of the hydrogenation reaction process, magnesium was observed. It seems that the manufactured environmental cell was a powerful tool for investigation of a hydrogenation reaction.

The *in-situ* observation of magnesium indicated grain expansion due to introducing hydrogen. Besides, disappearing of diffraction spot during hydrogenation reaction was observed. The spacing of lattice planes of the spot was quite larger than Mg and its compound was also seen, however, what it is a pattern resulting from had unknown.

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