The function and benefits of a multifunctional heating holder developed for use with conventional high resolution analytical TEMs

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Abstract. Specimen heating holder consisting of a gas injector and two sets of heating element has been developed for use with conventional high resolution analytical TEMs. One of the heating elements is used for specimen heating and the other for metal deposition. Both heating elements are made of fine wire of tungsten. The specimen holder allows high resolution in-situ TEM observation of a process of gas-solid reaction followed by a metal deposition on the reactant product. The microscope used in the study was a standard TEM equipped with EDX detector and TV camera system. Thanks to the high speed pumping system and well designed column, the pressure of the electron gun area was kept at 5x10⁻⁵Pa or lower for more than 5 hours while the specimen chamber was gas injected to the pressure of 10⁻¹Pa. Oxidation of Al to synthesize Al₂O₃ carrier, deposition of AuPd catalyst on the Al₂O₃ carrier and behaviour of the deposited AuPd nano-particles at high temperatures in the air injected environment were successfully observed at atomic resolution.

1. Introduction
We developed a specimen heating holder equipped with an evaporator and a gas injector for use with conventional TEMs. The purpose of the development of the specimen heating holder is shown in figure 1. Composites materials are produced, characterized and property measured. Firstly, composites material “A” is produced in a gaseous atmosphere. Then, the structural and compositional analyses of the composite “A” is carried out. Secondly, composite “B” is deposited on the composite “A” in gaseous atmosphere or in vacuum. After the characterization of composite “B”, property of the composites “A+B” will be measured in the gaseous atmosphere at elevated temperatures.

Figure 1. A flow chart of procedure for synthesis, characterization and property measurement of the composites using the developed specimen heating holder.

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In this paper, we report on a method to synthesize catalyst and observation of the behaviour of the synthesized catalyst at elevated temperatures in gaseous atmosphere. Process of the synthesis and the structural changes of the catalyst are observed at atomic resolution.

2. Method

External view of the specimen heating holder is shown in Figure 2. A heating element located in the center of the holder is used for specimen heating. An heating element used as the metal evaporator and gas injector are allocated beside the heater. Spirally wound tungsten wires of 0.025mm in diameter are used as the heating elements of the specimen heater and the evaporator.

![Figure 2. External view of the specimen heating holder equipped with an evaporator and a gas injector.](image)

The thickness of the specimen heating holder is designed within 2mm so that the use of the holder in an even narrow-gapped high resolution objective lens pole-piece is possible without any modification to the specimen chamber. The microscope used in the study was Hitachi H-9500 analytical TEM equipped with an LaB6 filament operated at 300kV. Spherical (Cs) and chromatic aberration coefficient(Cc) of the objective lens are 0.6mm and 1.4mm, respectively, and the point-to-point resolution is 0.18nm. The specimen chamber of the microscope is evacuated with a turbo molecular pump of the pumping speed of 260l/s. There are 0.3mm and 1.0mm apertures above and below specimen chamber as a support of differential pumping of specimen chamber during gas injection to the specimen area. The reactive gas is directly introduced to the specimen area via gas injector of 0.5mm in inner diameter. Safety valve, separating electron gun chamber and the lower part of the column in case of emergency, is equipped in the intermediate chamber. Maximum gas pressure available in the specimen chamber under the condition of high magnification TEM image observation using the LaB6 filament is in the range of 10\(^{-1}\)Pa and the highest heating temperature of about 1700K is available in this atmosphere.

3. Application to a synthesis and in-situ observation of catalyst

A catalyst of nanometer-sized AuPd on Al\(_2\)O\(_3\) carrier has been synthesized in the conventional 300kV TEM and the behaviour of the catalyst in a gaseous atmosphere was dynamically observed at elevated temperatures at atomic resolution. Al particle of 500nm in diameter was used as the raw material of Al\(_2\)O\(_3\) carrier and a sub-millimeter sized particle of AuPd alloy was used as a source of nanometer-sized AuPd catalyst. Al particles were heated to 673K in the air atmosphere of 2.5x10\(^{-3}\)Pa to synthesize Al\(_2\)O\(_3\) carrier. High resolution TEM images observed at the early stage (a) and final stage (b) of oxidation of Al particle are shown in Figure 3. At the final stage of oxidation, crystal lattice fringes with the distance of 0.45nm and 0.42nm in demonstration of the formation of Al\(_2\)O\(_3\) carrier are observed on the whole particles. Thus, the end of solid-gas reaction, oxidation in this case, can be directly confirmed by the observation of high resolution TEM images and the structure of the reaction product can be precisely characterized by the observation of crystal lattice fringes.
Figure 3. High resolution TEM images of Al particle at early stage (a) and final stage of oxidation (b). Structural changes of the specimen can be characterized by the observation of crystal lattice fringes.

After the production of Al₂O₃ carrier, the specimen chamber was evacuated to the vacuum of 10⁻⁴ to 10⁻⁵Pa. Then, nano-particles of AuPd were in-situ deposited by an evaporation of AuPd alloy. The sequence of the growth of the AuPd nano-particles on the Al₂O₃ carrier was continuously observed at high magnification until the AuPd nano-particles has grown to 2-5nm in diameter (Figure 4). The growth speed of the particles was about 0.3nm/s (Arrows in the figures).

Figure 4. A dynamic observation of an in-situ deposition of AuPd nano-particles on the in-situ synthesized Al₂O₃ carrier.

The deposited AuPd nano-particles were characterized by TEM and EDX analysis. After the characterization of the AuPd nano-particles, air was injected to the specimen chamber and the specimen was heated to 693K in the air atmosphere of 1.5x10⁻³Pa. High resolution TEM image was dynamically observed during the heating in the air atmosphere. The AuPd nano-particles became active and showed various kind of structural changes such as phase transformation, coalescence and
separation. Figure 5 shows one of the excentric phenomenon observed during the experiment. A small particle of about 1nm in diameter separated from the AuPd particle of about 4nm in diameter. Although temperature and atmosphere were kept constant, a facet of the AuPd nano-particle raised and the raised area continued to grow until the small particle completely separate from the mother particle (Indicated by arrows) in about 20 seconds.

![Figure 5](image)

Figure 5. Separation of a AuPd particle at 693K in the air atmosphere of 1.5x10^{-3}Pa.

4. Concluding remarks
The feature of the newly developed multifunctional specimen heating holder and its application to a synthesis, characterization and observation of behaviour of the in-situ synthesized catalyst has been discussed. This is the first attempt to carry out an in-situ synthesis of metal oxide carrier and a nano-catalyst deposition in a conventional TEM. The proposed technique provides unexampled capabilities to investigate the behaviour of a structure and elements controlled materials under various gas pressures at elevated temperatures even in a standard TEM laboratory.

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