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Dynamic Gas Environmental System Development for *in situ* Real-time SEM Imaging under Atmospheric Pressure

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In situ scanning electron microscopy (SEM) has become an increasingly important tool for materials characterization. It provides key information on the structural dynamics of materials technologies, including automotive exhaust catalytic converters, fuel cell degradation due to humidified air and micro structural evolution of hydrogen storage materials. To date, environmental SEM and environmental static cell techniques have been applied to these fields. However, pure hydrogen gas requires a special pumping system due to its fast gas diffusion. In addition, in situ quantitative experiments by well-defined quantitative gases are challenging in the case of gas injection systems without a cell. A closed cell system would allow us to use pure hydrogen atmosphere and liquid observation. Hence dynamical studies on gas species dependency are structurally difficult. [1] Here, we demonstrate a dynamic study in gaseous environment at atmospheric pressure. The use of MEMS technology and a sophiscated gas in/outlet system allowed us to perform a quantitative and dynamic gas study at atmospheric pressure. In addition, this experimental platform allows us to use a conventional SEM (SEM /FIB) system via a simple modification. It is therefore known that MEMS membranes can be used for liquid observation [2] and composition analysis [3], this experimental platform provides future opportunities of dynamical *in-situ* composition analysis under high pressure gas / liquid atmosphere. In this report, a brief *in situ* SEM observation was performed under argon / hydrogen gas atmosphere at atmospheric pressure. Figure 1 shows an overview and a schematic diagram of the bespoke SEM stage. Two gas lines underneath the stage are connected using smart tube connectors. This is essential in order to ensure stable performance at high- resolution without vibration from the gas line. These also aid installation into a conventional SEM specimen chamber, which generally allows only 25 mm height and 50 mm diameter (e.g. FEI, Holland).

The introduced gas species is enclosed by a Si_3N_4 membrane, which is penetrated by the electron beam. The specimen is attached to a membrane aligned inside the cell. The window size of the membrane is 50 μm square.

The specimen used in this proof-of-concept experiment is a hydrogen storage material, $LaNi_5$-based alloy with the commercially used composition $MmNi_{3.6}Al_{0.3}Co_{0.7}Mn_{0.4}$ (Mm denotes ‘‘misch metal’’, which is composed of some rare earth elements) was prepared in a purified argon atmosphere by induction melting from element constituents (99.9 % purities). By uncoupling the gas inlets, specimen was enclosed in the cell with Ar gas as reference state. This was then replaced by H_2 gas Figure 2 shows an environmental SEM image under (a) Ar gas (b) H_2 gas at 100 k Pa (implication of atmospheric pressure) . By measuring these particle sizes, 9 % volume expansion is confirmed. The previous reports and estimated value on maximum hydrogen storage capacity suggests ca. 20 % of volume expansion. [4]

However, this difference can possibly imply grain size and surface oxidization dependence which couldn't studied by microscopic method. Grain size expansion in the presence of H_2 is successfully revealed without significant morphological change. This kind of hydrogen storing is sensitive to the surface state. In our previous experiments without first performing bake-out, and after exposure to humidity in the lab didn't show any expansion. In practice, our enclosable cell system with gas in and outlet would provide easy access to the surface sensitive materials. In conclusion, we have developed a gas environment system with dynamically switchable gas atmosphere. This *in situ* microscopy can allow observation at high pressure of 100 k-Pa. We demonstrate its unique capability by using conventional SEM to study the micro scale mechanism of hydrogen uptake behavior at high pressure. Expansion was observed in the hydrogen storage material to the hydrogen intercalation. This experiment suggests broad opportunities for liquid-based electron microscopy studies relevant to energy storage. In particular, the possibility of measuring the dynamic behaviour under operating gas atmosphere, or even 100 k-Pa on conventional SEM, is now anticipated.

References:

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Fig.1

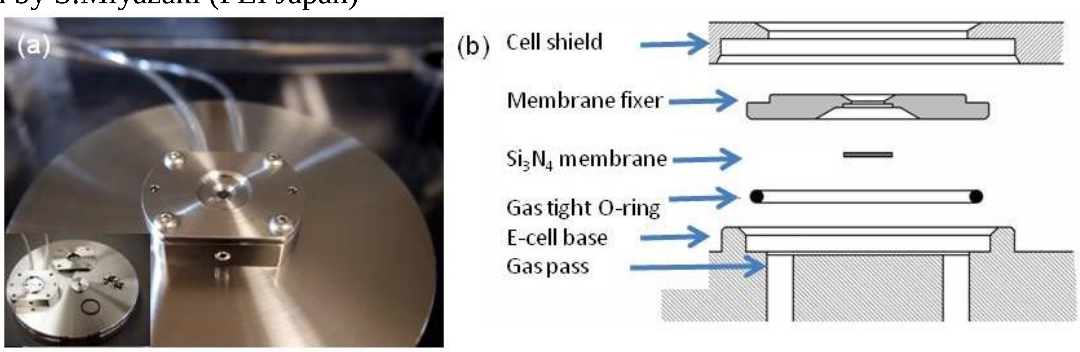

Fig.2

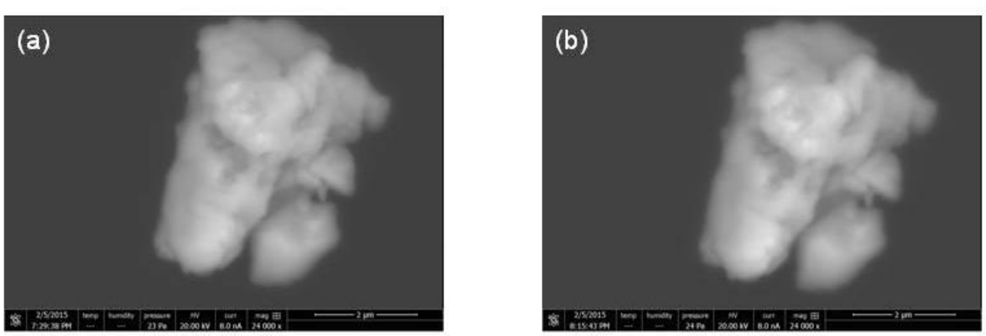

Figure 1 (a) Photograph and (b) schematic diagram of the specially designed SEM stage.

Figure 2 *In situ* observation SEM photograph under (a) Ar gas and (b) H_2 gas conditions. The gas pressure is 100 k-Pa.