In situ TEM observation of solid-gas reactions

K Kishita,1,3 T Kamino,2 A Watabe,2 K Kuroda3 and H Saka4
1 Material Analysis Department, Material Engineering Division, Vehicle Engineering Group, Toyota Motor Corporation, 1 Toyota-cho, Toyota 471-8572, Japan
2 Hitachi High-Technologies Corporation, 11-1 Ishikawa-cho, Hitachinaka, Ibaraki 312-0057, Japan
3 Department of Quantum Engineering, Nagoya University, Nagoya 464-8603, Japan
4 HVEM Facility, Ecotopia Science Institute, Nagoya University, Nagoya 464-8603, Japan

Abstract. Under a gaseous atmosphere at high temperatures, almost all the materials (metal, catalysts, etc.) change their structures and properties. For the research and development of materials, it is of vital importance to clarify mechanisms of solid-gas reactions. Recently an in situ TEM system combined with an environmental holder, which has a gas injection nozzle close to a specimen-heating element, has been developed. The gas injection nozzle permits gas to flow around the specimens sitting on the heating element made of a fine W filament. The newly developed in situ TEM has a differential pumping system; therefore, the pressure in the specimen chamber is maintained in the range of higher than 1 Pa, while the pressure in the electron gun chamber can be kept in the range of 10⁻⁵ Pa. This system was applied to in situ observation of chemical reactions of metals with gases: Observation of oxidation and reduction under a gas pressure ranging from 10⁻⁵ Pa to 1 Pa at high temperatures (room temperature to ~1473 K) were successfully carried out on pure metal and rare metal catalysts at near-atomic resolution. This in situ environmental TEM system is promising for clarifying mechanisms of many solid-gas and liquid-gas reactions that take place at high temperatures under a gas atmosphere.

Introduction
Under a gaseous atmosphere at high temperatures, almost all the materials (metal, catalysts, etc.) react with gas and change their structures and properties. For the research and development of materials, it is of vital importance to clarify mechanisms of solid-gas reactions. In situ experiment in TEM is a powerful method for this purpose, and various environmental TEMs have been developed [1][2].

In this study, for the purpose of observing detailed processes of solid-gas and liquid-gas reactions of material at high temperatures at high resolution, we have developed an in situ TEM system, which is composed of a side-entry specimen holder with a heating element and a gas injection nozzle, a TEM column with a differential pumping system and an inlet gas control system. Using the in situ TEM system, structural changes of some materials were observed under a gaseous atmosphere at high temperatures at near atomic resolution level.
Development of hardware

1.1. Specimen holder
A specimen holder equipped with a gas injection nozzle and a heating system has been developed for TEM observation of gas-solid reactions at high temperatures [3]. The holder is shown in figure 1. The gas injection nozzle was built in the specimen-heating holder originally developed by Kamino and Saka [4]. A spirally wound tungsten wire of 25 µm in diameter was used as a heating element. A gas injection nozzle with the inner diameter of 0.5 mm was built in near the heating element at a distance of about 1 mm. A schematic illustration of the gas injection nozzle and the heating element is shown in figure 2. The gas injection nozzle permits gas to flow around specimens sitting on the heating element. Specimens in the order of micrometers in dimension are directly mounted on the heating element, which was heated by a direct electric current via a power supply unit driven by batteries. This holder allows one to observe phenomena that happen at temperatures up to 1473 K. The gas flow rate was controlled using a gas control system connected to the holder with a tube outside the column of the TEM.

![Figure 1](image1.png)

Figure 1. Specimen holder (a) Whole image (b) enlargement of the tip.

![Figure 2](image2.png)

Figure 2. Schematic illustration of heating element and gas injection nozzle.

1.2. TEM
The particular TEM developed is shown in figure 3. The TEM is based on a Hitachi H-9500 (Acc.Vol. 300kV). Spherical aberration co-efficient (Cs) and chromatic aberration co-efficient (Cc) of the microscope are 0.6 mm and 1.4 mm, respectively. The TEM has a newly developed differential pumping system consisting of three 260 l/s turbo molecular pumps and a 60 l/s ion pump. When gas was introduced using the gas injection nozzle, the pressure at the specimen chamber was maintained at the range of higher than 1 Pa, while the pressure of the electron gun chamber could be kept in the range of $10^{-3}$ Pa. This allows observation of high resolution TEM images using a LaB$_6$ cathode at the accelerating voltage of 300 kV.

![Figure 3](image3.png)

Figure 3. TEM and Gas control system
AMT ERB high resolution digital imaging CCD camera system was attached to the TEM and used for recording TEM images of dynamic behaviour of the specimens. For analysis, EDX (EDAX: Genesis XM2) and EELS (Gatan: Tridiem) systems were also attached.

1.3. Gas control system
The gas inlet equipment has been developed to control gas atmosphere in the TEM. Different kinds of gases (H₂, O₂, Air, Ar, N₂, etc.) could be introduced to the TEM. This system controls the pressure, flow rate and kind of gas introduced; it takes only a few minutes to change gas kinds and gas pressure and the gas the pressure was maintained for several hours. Using this system, observations of oxidation and reduction with high reproducibility are made possible with precise pressure adjustment.

Experimental results

1.4. Silicon system
Figure 4 shows reduction of a natural oxide layer on a Si particle and re-oxidation of the fresh surface of the Si particle. In this experiment, EELS analysis was used. The Si particle observed was covered with a 1.5 nm thick natural oxide layer at room temperature (figure 4a) and the oxygen K-edge is evident in the EELS from the surface layer. Figure 4b shows the silicon surface heated at 773 K in a vacuum of 10⁻⁵ Pa. The oxide layer was reduced (figure 4b) and the oxygen K-edge is not evident from the surface layer. Then, on introducing oxygen gas to the specimen chamber of the microscope, an oxide layer grew again (figure 4c) and the oxygen K-edge is also evident. It was confirmed that this reduction and oxidation is quite reversible.

1.5. Platinum on Al₂O₃
Figure 5 shows the behaviour of Pt particles on Al₂O₃ under a pressure of 1 Pa in oxygen atmosphere. Under oxygen atmosphere, some Pt particles started to move about on the Al₂O₃ surface (figure 5b). Furthermore, the Pt particles coagulated with each other (figure 5c).
Conclusion

The developed in situ TEM system has the capability and stability high enough for high resolution observation and analysis to be carried out under in situ conditions (temperature and gas atmosphere). Our system has the potential to clarify many kinds of phenomena under pressure ranging from $10^{-5}$ Pa to 1 Pa and temperature ranging from room temperature to 1473 K. Hereafter, we will elucidate many processes of the automotive catalyst, fuel cell materials, metals and so on.

References

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