

Mechanism for the Precipitation of Carbon on the surface of a Ni Catalyst

Tomoharu Tokunaga, Hiroki Tasugi, Natsuki Iwamoto, Katsuhiko Sasaki, Takahisa Yamamoto

Department of Quantum Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Aichi, 464-8603, Japan

Fuel cells (FCs), which use hydrocarbons and hydrogen as the fuel sources, provide an eco-friendly way to generate electricity [1]. FCs have attracted the interest of many researchers because they are believed to have the potential to alleviate many problems related to energy generation and usage, such as fuel shortages and environmental pollution. In particular, solid oxide fuel cells (SOFCs) made from various metals and ceramics have been studied [2], including those fabricated with desirable metals and ceramics such as Ni and yttria stabilized zirconia [3]. SOFCs provide reasonable and eco-friendly electricity generation, but they also have some disadvantages. For example, the power generation efficiency often decreases as the operating time increases. One of the reasons for such decreases in exchange efficiency is the deposition of carbon on the catalyst when hydrocarbons are used for fuel [4]. These challenges have yet to be addressed. Therefore, in this study, the mechanism for the precipitation of carbon on the Ni surface of the fuel electrode of a SOFC was observed using a high-resolution transmission electron microscope.

To precipitate graphite on the Ni surface, a Ni thin film was heated in a methane atmosphere. The Ni thin film was prepared from a thin Ni plate using an Ar ion thinning method. The fabricated Ni thin film was set on the stage of the heating holder, and then the heating holder was inserted into the sample observation chamber of the high-voltage transmission electron microscope (JEOL, JEM-1000KRS). An environmental chamber (EC) was next inserted into the sample observation chamber to cover the heating holder. Methane gas was flowed into EC, and the pressure of the EC was maintained at 1×10^2 Pa. After the pressure in the EC was stabilized, the Ni thin film was heated to 800 °C and observed.

In Fig. 1, a TEM image of the Ni thin film taken when the heating was started is shown. Lattice fringes corresponding to a distance of 0.20 nm were confirmed, which are consistent with the Ni (111) lattice. Then, the presence of terraces and steps on the Ni surface was confirmed. Two fringes with different distances to the Ni (111) lattice fringe were observed from the surface, and these corresponded to a distance close to that of graphite (001), 0.32 nm. Moreover, an electron energy loss (EEL) spectrum was acquired from an area of the Ni thin film surface near where the two fringes with different distances to the Ni (111) were observed, and the carbon K-edge was indeed confirmed. From these results, it is clear that these two fringes correspond to graphite (001). The graphite fringe signals continued to grow with heating time from the step to the right on the Ni (111) surface. The graphite fringes continued to increase in intensity when the graphite growth reached the step, and eventually the signal from the graphite fringes overwhelmed the Ni step signal (FIG. 2). Graphite growth continued on the Ni surface in this way. A catalyst growth model has usually been used to explain the graphite growth mechanism [5]. However, our results show that the catalyst growth model is applicable only for the initial growth of the graphite, and a new growth model

in which catalyst atoms and/or clusters that promote graphite growth are present on top of the graphite is proposed.

References

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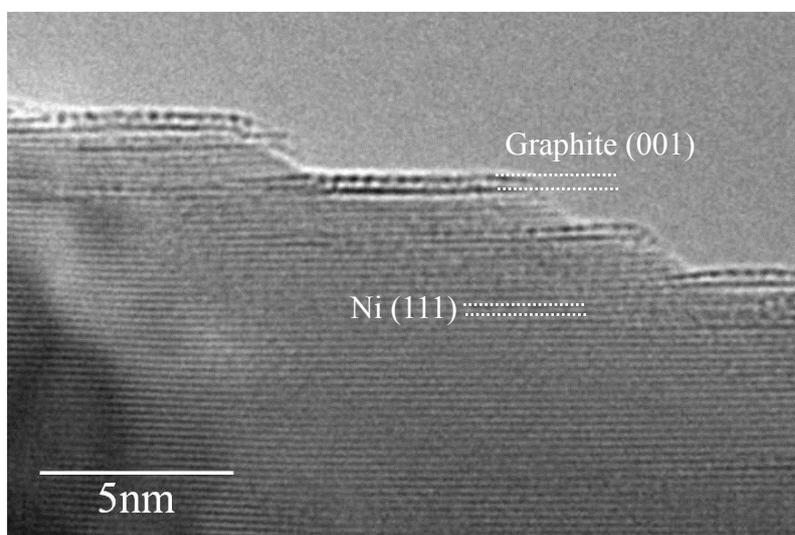


FIG. 1. TEM image of Ni thin film after heating was started in methane atmosphere

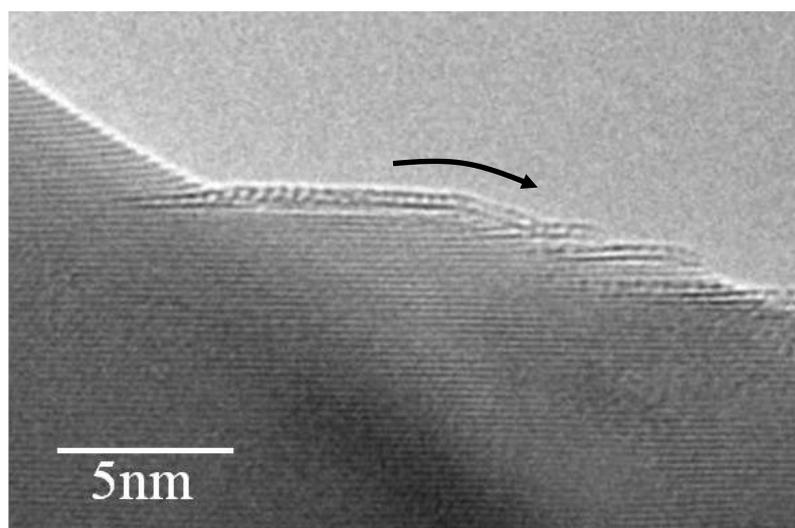


FIG. 2. TEM image of Ni thin film heated for a few minutes after heating was started