

Comparison between effects of aerial oxidation and electrochemical oxidation of Ni for Ni-YSZ cermets

Michiyoshi Sato¹, Tadashi Sakamoto¹, Kazuhisa Sato², Toshiyuki Hashida²

¹Graduate School of Environmental Studies, Tohoku University, Japan

²Fracture and Reliability Research Institute, Tohoku University, Japan

michiyoshi.sato@rift.mech.tohoku.ac.jp

Solid Oxide Fuel Cells (SOFCs) directly convert fuel chemical energy into electricity. SOFCs operate at high temperatures and represent an attractive and efficient technology for power generation. Ni-YSZ cermets have commonly been used as SOFCs anode mainly. Nowadays owe of, the main issues involve the improvement of their reliability and durability. It has been pointed out that the performances of SOFCs sharply reduced when the anode material (Ni-YSZ cermets) operates under alternatively oxidizing and reducing conditions at elevated temperature (redox cycles). Such redox cycles induce changes in microstructure of the anode, influencing mechanical and electrochemical properties. Oxidation of Ni has two cases, aerial oxidation by O₂ and electrochemical oxidation by ionic current O²⁻. It is necessary to understand the oxidation behaviors in order to improve the durability. The objective of this work is to examine aerial oxidation and electrochemical oxidation behavior of Ni-YSZ.

Experiments have been conducted using anode supported cells. All the samples tested were circular in shape with a diameter of 16 mm. The anode was composed of 60 wt% NiO and 40 wt% 8YSZ (ZrO₂ stabilized with 8% mol Y₂O₃) and diameter and thickness were 16 mm and 2.0 mm, respectively the electrolyte diameter was the same as the anode and thickness was ~15 μm. The cathode had a diameter of 10 mm and was centered on the electrolyte. This layer had a thickness of about ~30 μm. These samples were re-oxidized by air steam (aerial oxidation) or ionic current (electrochemical oxidation) at 800°C. In the case of aerial oxidation, the cells were completely oxidized by air steam during 12 h (re-oxidation). In the case of electrochemical oxidation, the cell was loaded to 0.5A/cm² and H₂ gas concentration had been reduced from $p_{H_2}=5\%$ to $p_{H_2}=2\%$ with measuring acoustic emission (AE) events, and Ni was oxidized by ionic current because of a shortage of H₂. And supplying H₂ to the anode side and air to the cathode, the cells were partially and fully re-oxidized by ionic current (10, 50, 150 mA/cm²) in order to evaluate changes in microstructure of anode. Cells re-oxidized were observed by scanning electron microscope (SEM).

After AE detection, OCV decreased from 1.07 to 0.99 V, and cell performance was dramatically reduced. Not only delamination between anode and electrolyte, but also cracks of the electrolyte and cathode were observed. In the optical observation of fracture cross-section of the cells partially re-oxidized by ionic current, these anodes had respectively two oxidized regions broadening from the electrolyte. It is considered that gray and green region respectively represent 1st and 2nd oxidation region. In the case of 10 mA/cm², the green region extended more widely and meagerly than 50 and 150 mA/cm². Because electrochemical oxidation in a high current density occurs near the electrolyte, the electrolyte and cathode are damaged because of the induced thermal stress. In the SEM observation of fracture cross-section of the anodes fully re-oxidized by air stream and ionic current, the morphology of NiO are “spongelike” texture and similar in both cases of oxidation. However the surface of NiO particles re-oxidized by ionic current was rougher than NiO particles re-oxidized by air stream because of grain boundary migration to reduce surface area in NiO/Air interface. Fracture cross-section of both NiO particles re-oxidized by air stream and ionic current had few micropores. It means that in the both aerial oxidation and electrochemical oxidation Ni²⁺ diffuse outward. And in the electrochemical oxidation, YSZ particles were observed to surround the NiO particles. It suggests that electrochemical oxidation proceeds along YSZ interface.

This work was partly supported by the JSPS Core-to-Core Program, A. Advanced Research Networks, “International research core on smart layered materials and structures for energy saving”.