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Oxygen-ion transfer between yttria stabilized zirconia single crystals under mechanical contact stress

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ABSTRACT

The present study concerns oxygen-ion transfer between yttria-stabilized zirconia (YSZ) single crystals under mechanical contact stress. Two YSZ single crystal plates were piled up between platinum meshes, and contact stress was mechanically applied. The interfacial conductivity as well as the bulk conductivity was successfully measured with this setup. The interfacial conductivity is greatly influenced by the contact stress, whereas the bulk conductivity is almost independent of the stress. The interfacial conductivity is significantly increased with increasing contact stress, especially from 0 to 5 MPa, and is saturated around 56 kΩcm^2 with the stress around 40 MPa. The interfacial capacitance increases with contact stress. The activation energy for the interface conductivity is equal to 105–111 kJ/mol, similar to that for the bulk, and appears to change slightly with stress.

1. Introduction

Yttria stabilized zirconia (YSZ) is known as an oxygen-ion conducting material and one of the common electrolyte materials for solid oxide fuel cell (SOFC) due to its good ionic conductivity as well as chemical and mechanical stabilities.

For polycrystalline YSZ, the oxygen-ion transport property is attributed to the oxygen ion conductivities of bulk (grain) and grain boundary [1–6], and it has been generally known that oxygen-ion conductivity in bulk is superior to that in grain boundary [1,2]. Nanocrystalline YSZ has a large specific area of grain boundary, thus the conductivity of grain boundary, including transports between the grains and also in/along the grain boundary, is critical [5–9], although the observed behaviors seem to be controversial, and possible microscopic stress has not been considered. On the other hand, the oxygen-ion conductivity of YSZ nano-films strained in a multilayer structure has been intensively studied [10–13]. Significant enhancement of the conductivity due to stress/strain has been observed, although the stress effect on grain boundary conductivity has been less discussed compared to that on other contributions such as conductivities of bulk and interface between substrate layers.

The oxygen-ion transport characteristics of the grain boundary in YSZ are normally extracted from the characteristics of polycrystalline samples, whereas it has been also evaluated using bicrystal or two single crystals in previous studies [14–16]. Dragoo et al. [14] evaluated the characteristics of the grain boundary by using YSZ bicrystal consisting of two single crystals and a *single* grain boundary and observed a large resistance of the grain boundary. Nakagawa et al. [15] confirmed a blocking effect of the grain boundary by measuring the oxygen-diffusion behavior of YSZ bicrystal. Fabry et al. [16] employed two YSZ single crystals mechanically contacting each other. A direct oxygen ion transfer between YSZ/YSZ involving no neutral oxygen atom was confirmed, although a large resistance due to the interface between YSZ/YSZ was obtained. The effect of the contact stress between two YSZ single crystals, however, was not considered in those studies.

Not only grain boundary, but also oxygen-ion transfer at every interface, e.g. between electrolyte/electrode in SOFC, is an important issue [17,18]. In most cases, an interface is subjected to contact stress (pressure); however it has not been quantitatively considered. For assessment of the oxygen-ion transfer at an interface under various contact stresses, a testing method should be established.

In the present study, the oxygen-transfer between YSZ single crystals was investigated under mechanical contact stress. A specimen configuration to apply contact stress of ∼40 MPa was proposed, and the effect of the contact stress on the interfacial resistance as well as on the interfacial capacitance was discussed. The proposed method can be used to evaluate effects of contact stress

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on interfacial characteristics between various materials and also to characterize grain boundary.

2. Experimental

13 mol%-yttria-stabilized zirconia single crystal plate (Dalian Optoelectronic Technology), a commercially available single crystal with a sufficient size, was used in the present experiments. The dimension of the original plate was 25 mm × 25 mm × 1.0 mm and the surfaces had (1 1 0) crystal orientation with a surface roughness of less than 1 nm. Various sizes of specimens were cut out from the plate using a diamond wheel saw.

For measuring impedance under contact stress, two different specimen configurations were employed, as illustrated in Fig. 1. In Config A shown in Fig. 1(a), which is similar to the configuration used in the literature [16], two small square plates (YSZ1 and YSZ2) with a size of 5.0 mm × 5.0 mm × 1.0 mm were piled up between platinum (Pt) meshes with attached Pt wires which were connected to a chemical impedance meter (3532-80, Hioki E.E.). Pt paste was applied to the bottom side of YSZ2. The whole Config A was placed inside a furnace of a material testing machine (1362, Instron). After a compressive load of 420 N (equivalent to 18 MPa of contact stress for Config A) was applied at room temperature, the specimen was heated up to 1073 K, where the Pt meshes were sufficiently compressed. The specimen was then cooled down to testing temperatures ranging from 597 K to 988 K. At each temperature, impedance was measured while unloading from 420 N to 120 N (i.e., 5 MPa). The test was also conducted during unloading from 420 N to 20 N (i.e., 0.8 MPa) at 597 K. For the impedance measurement, the two-terminal method was employed (terminals I and II in Fig. 1(a)) and the frequency ranged from 10 Hz to 1 MHz. A preliminary test verified that possible experimental error due to cables can be negligible when the measured impedance is greater than a few hundreds ohm. The load and the total displacement (shown as w in Fig. 1(a)) were also measured during unloading, where the measured displacement was calibrated [19].

Config B shown in Fig. 1(b) consisted of a small plate (YSZ3, 5.0 mm × 2.5 mm × 1.0 mm) and a large plate (YSZ4, 15 mm × 10 mm × 1.0 mm). YSZ4 with platinum paste on the bottom was placed on a dummy small plate (YSZ5) and a temporary plate (dashed line). The whole Config B was placed inside the furnace, the preload of 5 N was applied, and the temporary plate was removed. The preload was kept during elevating temperature up to 597–988 K. At each testing temperature, the load was increased to 405 N (equivalent to 37 MPa of contact stress for Config B), and the impedance measurement was conducted during unloading from 405 N to 5 N (i.e., 0.5 MPa) at each temperature. The impedance was measured using the terminals I and II for evaluation of interfacial characteristics, and also terminals I and III as a temperature reference. In addition, the impedances of a single plate of 5.0 mm × 5.0 mm × 1.0 mm with Pt electrodes and YSZ4 (I and III) were separately measured in an individual furnace for temperature calibration, since the thermo-couple was placed rather close to the stage (Fig. 1). Only the load was measured during the tests with Config B.

It should be noted that, in the measurement with Config A, a sum of the bulk impedances of YSZ1 and YSZ2 including the interfacial impedance between YSZ1 and YSZ2 was measured, whilst the bulk impedance of YSZ3, the *partial* impedance of YSZ4, and the interfacial impedance between YSZ3 and YSZ4 in Config B. All tests were carried out in air.

3. Results

3.1. Config A

Fig. 2 shows the impedance data (Nyquist and Bode plots) obtained during unloading from 18 MPa to 3 MPa at 597 K with Config A. Two semi-circles are clearly observed in the Nyquist plots for all cases, and the lower-frequency arc is always larger than the higher-frequency arc. During unloading, i.e., decreasing the contact stress, the lower-frequency arc becomes larger, whereas the higher-frequency arc remains almost unchanged. Below the stress of ~5 MPa, the higher-frequency arc almost cannot be separately observed because of the large lower-frequency arc. Two semi-circles have been reported in earlier studies similarly employing two single crystals [16] or bicrystal [14]; however, in those studies, mainly (or only) a huge lower-frequency arc was observed due to a lack of a sufficient contact stress. The higher-frequency arc can be assigned to the bulk response (YSZ1 and YSZ2), whereas the lower-frequency arc to the interfacial resistance between the two single crystals. The trail on the lower frequency side can be related to the electrode response, which will not be discussed in the present study. Note that the scatter at the lower frequency end, especially for lower stress, seems to be attributed to the very small current measured, and could be eliminated by increasing applied voltage.

Fig. 3 shows impedance data (Nyquist plots) obtained at different temperatures under contact stress of 18 MPa. At 597 K, as already shown in Fig. 2(a), two semi-circles are clearly observed. With increasing temperature from 597 K to 792 K, the size of the arcs decreases and also the higher frequency arc gradually. Above 889 K, only the electrode response is observed (not shown here).

Fig. 4 shows the variation of the interfacial resistance R_{intf} at 597 K with contact stress, which is calculated assuming that there

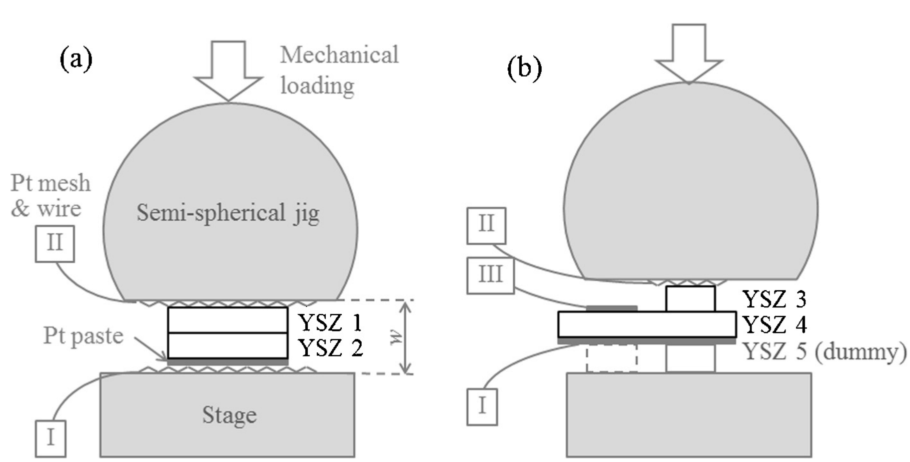

Fig. 1. Specimen configurations: (a) Config A, (b) Config B.