Formation of Rare Earth Zirconia Pyrochlores on Yttria-Stabilized ZrO₂ Single Crystals by Solid State Reactions

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At the interface of a high temperature solid oxide fuel cell (SOFC), the Sr-doped LaMnO₃ (LSM) cathode may react with the yttria-stabilized-zirconia (YSZ) electrolyte material at temperatures of 1000 °C, forming a La₂Zr₂O₇ (LZO) pyrochlore. This formation of a pyrochlore phase has been reported to play a significant role in degradation of YSZ-based high temperature SOFCs [1]. Therefore the principal mechanism of reaction between La₂O₃-vapour and YSZ(001)-single crystals was investigated [2]. At a temperature of 1100 °C the La₂O₃-vapour reacts with YSZ and forms LZO islands, with four or eight slightly tilted domains. We perform experiments with La₂O₃ and YSZ(001), respectively YSZ(110), single crystals. Specimens were fabricated by e-beam evaporation of La₂O₃ powder onto a heated YSZ substrate in a high vacuum chamber. Then the surface and morphology of the specimens were investigated at room temperature by atomic force microscopy (AFM). The relative orientation of the LZO lattice with respect to the YSZ lattice was determined by X-ray diffraction (XRD), and the LZO/YSZ reaction front was investigated by transmission electron microscopy (TEM).

During vapour-solid reaction at 1200 °C between La₂O₃-vapour and YSZ(001)-single crystals, islands with four or eight domains were formed, whereby four were tilted by 2.1° around <110> and on some specimens four other domains were found which were tilted by 0.9° around <100>. These results confirm the previous investigations [2]. The effect of tilted domains was explained by the assumption of active {101}-slip planes and Burgers vectors perpendicular to these slip planes. The Burgers vector component parallel to the interface accommodates the misfit of the pyrochlore islands to the YSZ substrate, and the perpendicular component causes the tilt. To prove this model, we apply TEM investigations using the g·b=0 criterion. After vapour-solid reaction at 1200 °C at a rate of 0.45 nm/min for 9 min between La₂O₃-vapour and YSZ(110)-single crystals, four domains were found by XRD pole figure measurements, two of which were tilted around [1-10] with a maximum at a tilt angle of 0.6° and the other two were tilted by 0.9° around [001]. AFM and TEM plan-view images show stripe-shaped islands with the long edge along [1-10] and the short edge along [001]. In addition to these vapour-solid reactions some experiments with solid-solid reactions were performed. In this case a deposition of La₂O₃ on YSZ single crystals was performed at a low temperature of approx. 100 °C and then the specimen was annealed in vacuum (pO₂=1.3·10⁻² Pa) at 1200 °C for 90 min. XRD pole figure measurements of the LZO(004) and phi-scans of LZO(440) and YSZ(220) planes revealed that for this solid-solid reaction of La₂O₃ and YSZ(001)-single crystals the relation (001)LZO k (001)YSZ; [100]LZO k [100]YSZ is valid without any systematic tilt (FWHM=0.5°).

Figure 1: Stereographic projections of a cubic crystal. We assume that \{101\} are active slip planes: (a) 001-orientation; (b) 110-orientation.

Figure 2: Deposition of 4 nm La$_2$O$_3$ on YSZ(001) at 1200 °C: (a) XRD pole figure of LZO(004) plane; eight tilted domains are visible; (b) AFM image; (c) TEM plan-view image.

Figure 3: Deposition of 4 nm La$_2$O$_3$ on YSZ(110) at 1200 °C: (a) XRD pole figure of LZO(440) plane; four tilted domains are visible; (b) AFM image; (c) TEM plan-view image.