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Decomposition of the ZrO_2 electrolyte in contact with Ni: Structure and chemical composition of the Ni–electrolyte interface

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The Ni/(ZrO_2 + 9.5 mol% Y_2O_3) interface was used as a model system to investigate decomposition reactions of a yttria-stabilized ZrO_2 electrolyte in contact with a metal at elevated temperature. In the present study, the sample was a diffusion-bonded symmetrical galvanic cell Ni|ZrO_2 + 9.5 mol% Y_2O_3|Ni. Various electron microscopy techniques were used to study the morphology and structure of the reaction products at the Ni–ZrO_2 electrolyte phase boundary after current flow. Below a critical oxygen partial pressure of approximately 10^{-27} atm, an intermetallic reaction layer formed at the Ni–electrolyte interface. Between the intermetallic layer and electrolyte a thin Y_2O_3 layer was present, which acted as a diffusion barrier for Zr and Ni, slowing down the overall chemical reaction. At several locations at the interface the Y_2O_3 layer broke up, leading to a morphological instability of the interface between electrolyte and Ni_5Zr, allowing further reaction. The thickness of the total reaction layer varied widely as a consequence of such an instability.

I. INTRODUCTION

Yttria-stabilized zirconia (YSZ) is widely used for solid electrolyte fuel cells and oxygen sensors operated at temperatures as high as 1300 K.[1] In fuel cells, metal–YSZ cermets are used as electrode materials at the anode.[1] An important requirement for electrode materials is that they degrade only slightly over several years. However, under reducing conditions the ZrO_2 electrolyte, which is in contact with a metal, can decompose forming intermetallic compounds, changing the electrical performance of the cell.[1] In addition, such reactions may degrade the mechanical properties of the metal–electrolyte interface. For this reason, it is of fundamental interest to study electrochemical reactions at metal–ZrO_2 interfaces. In particular, one can determine the influence of reaction phase composition and thickness on the adhesion between the metal and electrolyte. The thickness of such a reaction layer may be controlled precisely by applying an electrochemical method.

Recently, it was shown that at extremely low oxygen partial pressures the Ni–ZrO_2 phase boundary is thermodynamically unstable, and intermetallic phases Ni_xZr_y may form.[2,3] The present work was focused on the investigation of the very initial stages of this reaction process. Experiments were conducted with a symmetrical solid state galvanic cell Ni|(ZrO_2 + 9.5 mol% Y_2O_3)|Ni. Such an experimental setup can be used to investigate chemical reactions on the cathodic and anodic side of the cell simultaneously.[3] Our investigation was focused on the chemical reaction at the cathodic side of the cell, particularly on the behavior of the dopant Y_2O_3. Morphology and microstructure of the reaction products were studied by using conventional transmission electron microscopy (CTEM) and high-resolution transmission electron microscopy (HRTEM). Analytical electron microscopy (AEM) was used to analyze the composition of the reaction products and to determine the interdiffusion profiles. A detailed analysis of the very initial stages of the decomposition process of a ZrO_2 electrolyte in a low oxygen activity is given.

II. EXPERIMENTAL

Symmetrical galvanic cells were produced by diffusion bonding polycrystalline Ni plates (1 × 17 × 20 mm, 99.98% Ni) on both sides of yttria-stabilized (9.5 mol% Y_2O_3) single crystalline ZrO_2 crystals (2 × 17 × 20 mm). The bonding was performed in high vacuum (10^{-5} torr) at 1573 K. Details of the diffusion-bonding process are described elsewhere.[3] Electrochemical experiments were conducted under high-vacuum conditions in a quartz tube furnace at 1200 K. To lower the oxygen activity at the Ni–ZrO_2 interface a constant current density of 40 mA cm^{-2} was imposed for ~10 min, and the voltage

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drop across the cell was measured as a function of time. At the end of the experiment, the cell was cooled to room temperature at constant voltage. This procedure is necessary to suppress the decomposition of the reaction products that form during current flow.[3] To investigate the morphology and microstructure of the Ni–ZrO_2 interface (cathodic side of the cell, Fig. 1), cross-sectional transmission electron microscopy (TEM) foils were prepared by the preparation method described in Wagner *et al.*[3] and Strecker *et al.*[4] CTEM was conducted on a JEM 2000FX (JEOL) operated at 200 kV and high-resolution TEM on a JEM 4000EX (JEOL) operated at 400 kV. AEM was performed with a dedicated scanning TEM (STEM) VG HB501 UX, operated at 100 kV, equipped with an energy dispersive x-ray spectrometer. Linescans were performed perpendicular to the interface with a digital scan control.

III. RESULTS

A. Electrical characteristics of the symmetrical galvanic cell during current flow

After imposing a constant electrical current density of 40 mA cm^{-2} for 2 min on the galvanic cell, the measured cell voltage reached ~1.7 V. The total time of current flow was ~10 min. On the anodic side of the cell, formation of NiO took place, whereas on the cathodic side Ni_5Zr was formed under such reducing conditions (Fig. 1).[3] With the use of the Nernst equation,[5] for equilibrium conditions the open circuit voltage of the cell was calculated to be 0.93 V, which is much smaller than the measured voltage of ~1.7 V. Such a difference in voltage could be attributed to a strong polarization of the cell during current flow.[6,7] However, in the present study, it could not be determined whether the deviation of oxygen activity was caused by a polarization of the cathodic, anodic, or both sides. At the cathodic side, the oxygen partial pressure of the cell was at least as low as 10^{-27} atm, resulting in the formation of Ni_5Zr by the reaction $5Ni + ZrO_2 \rightarrow O_2 + Ni_5Zr$.[3] This pressure was calculated from the standard Gibbs free energies of the compounds Ni_5Zr and ZrO_2.

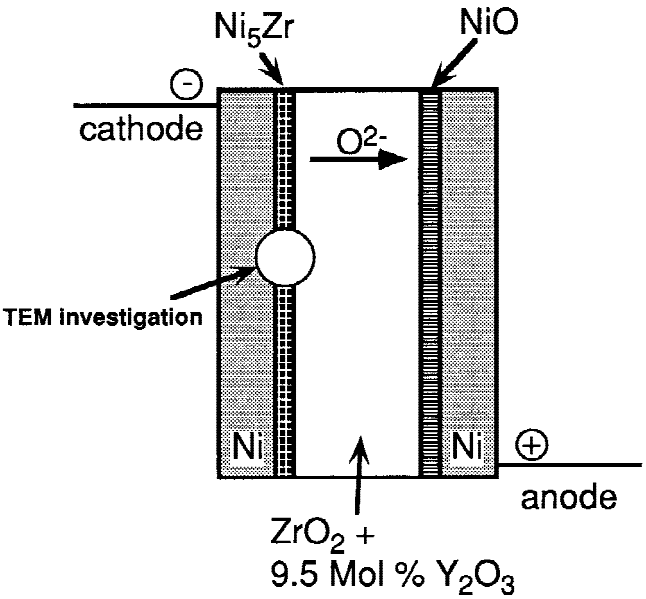

FIG. 1. Schematic of the galvanic cell. Oxygen ions are transported from the cathodic to the anodic side of the cell, decreasing the oxygen activity on the cathodic side.

B. Structural characterization

As shown in a recent publication, no chemical reaction products could be detected at the Ni–ZrO_2 interface after diffusion bonding.[3] Figure 2(a) shows a bright-field

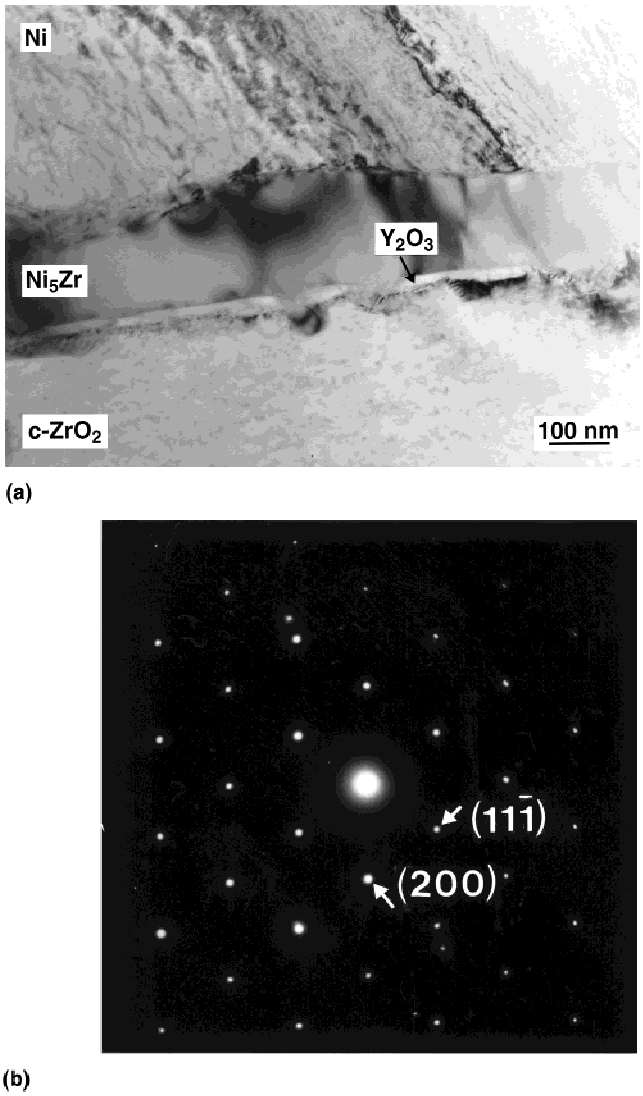

FIG. 2. (a) Bright-field image of the Ni–Ni_5Zr–electrolyte interface. A 10–20-nm-thick Y_2O_3 layer is present between electrolyte and Ni_5Zr. At a few locations, this layer is discontinuous, and the Ni_5Zr layer penetrates deeper into the electrolyte. (b) Selected area diffraction pattern of a single Ni_5Zr grain (electron beam parallel to [011]). The Ni_5Zr has no epitaxial orientation relationship to the single crystalline electrolyte or to the grains of the Ni electrode.

CTEM micrograph of the Ni–ZrO_2 electrolyte interface (cathode side) after current flow. A thin Ni_5Zr reaction layer formed between Ni electrode and electrolyte [Fig. 2(b)]. This reaction layer exhibited a uniform thickness of ~100 nm over large areas, but in some places it penetrated up to 300 nm into the electrolyte material, forming pockets that were sometimes >500 nm wide (Fig. 3). These pockets were separated by ridges composed of ZrO_2.

Furthermore, as can be seen in Fig. 2(a), an almost continuous film with a thickness of ~10–20 nm covered the electrolyte substrate at such locations, where no pockets were present. Convergent-beam electron diffraction (CBED) investigations were used to show that this layer is Y_2O_3 [Fig. 4(a)]. The Y_2O_3 layer had an epitaxial orientation relationship with the ZrO_2 electrolyte [Fig. 4(b)]: (001) Y_2O_3 || (001) ZrO_2 and [010] Y_2O_3 || [010] ZrO_2. The Y_2O_3 layer was also present on the ZrO_2 ridges between the pockets (Fig. 5).

The structure of the epitaxial Y_2O_3 layer was investigated by HRTEM in more detail. Figure 6 shows an HRTEM micrograph of the ZrO_2–Y_2O_3 interface in the [001] ZrO_2 zone axis. The interface between ZrO_2 and Y_2O_3 consisted of steps and dislocations and was not atomically smooth. Misfit dislocations were present in the interfacial region accommodating the lattice mismatch $f = 3\%$[8,9] between electrolyte and Y_2O_3. The dislocation spacing varied locally along the interface. This may be caused by the roughness of the ZrO_2–Y_2O_3 interface. The Burgers vector component parallel to the interface was determined as $\mathbf{b}_{\parallel} = a/2\langle 001\rangle$ where a is the lattice parameter of Y_2O_3.

C. Chemical composition of the reaction phases

Energy dispersive x-ray spectroscopy (EDS) was performed to analyze the chemistry of the reaction layer. While the electron beam, with a diameter of ~2 nm, was scanned step by step perpendicular across the reaction layer, spectra were taken at each pixel. With use of the Cliff–Lorimer equation, the spectra were quantified, and chemical profiles were calculated. Figure 7 shows a chemical profile with a stepsize of 7 nm perpendicular to an undisturbed (not broken up) reaction layer [Fig. 2(a)]. Clearly, one could distinguish between the ZrO_2, Y_2O_3, Ni_xZr, and Ni layers. The Ni_xZr layer consisted of approximately a 40-nm-thick layer of Ni_5Zr and a 50-nm-wide interdiffusion zone. The error in the Ni:Zr ratio (4.5 ± 0.5) is relatively large because of surface oxidation and the use of standardless k factors, not because of the statistics of the spectra. Linescans with a higher spatial resolution (stepsize 3 nm) showed that the Y_2O_3 layer

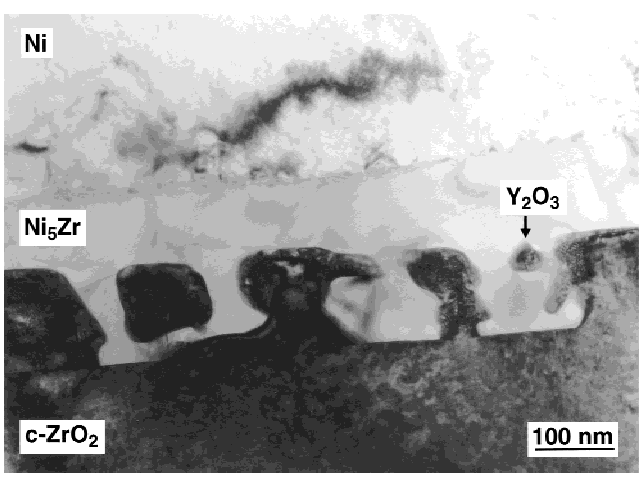

FIG. 3. Bright-field TEM micrograph of the reaction layer. The interface between electrolyte and Ni_5Zr shows a morphological instability that leads to a variation in reaction layer thickness.

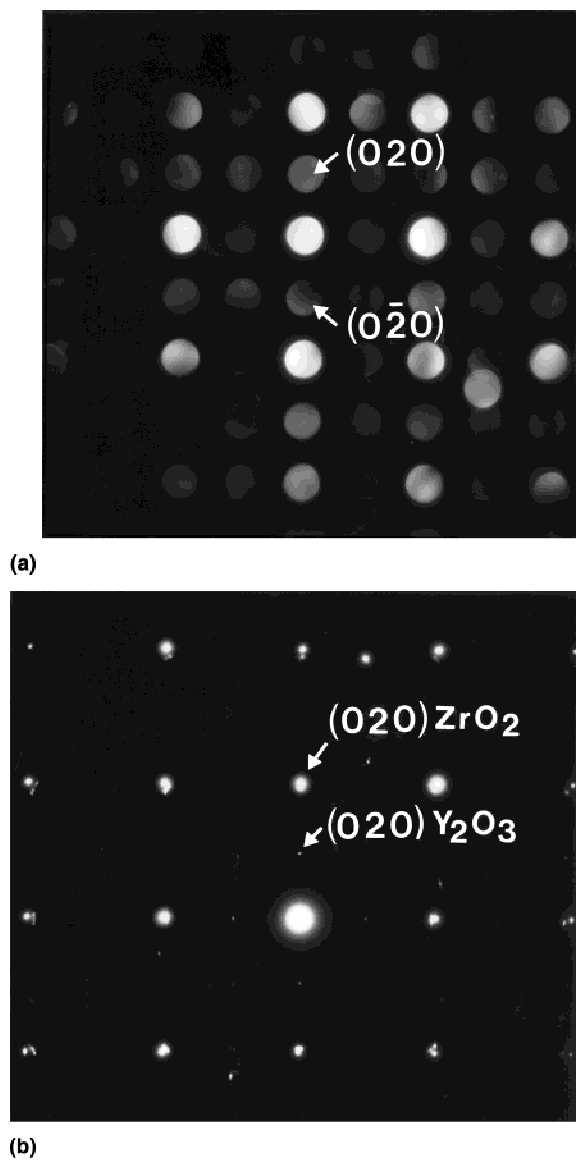

FIG. 4. (a) CBED pattern of the Y_2O_3 film (electron beam parallel to [001]). (b) Selected area diffraction pattern of the electrolyte and Y_2O_3 film. The Y_2O_3 film is oriented epitaxially to the electrolyte.

was ~10–20 nm wide. Thus, the width of the reaction layer as revealed from AEM corresponds to the results obtained by CTEM. Unfortunately, the diffusion profile of Zr into the Ni layer cannot be interpreted, because the interface between Ni_5Zr and Ni might be tilted and not be edge on.

IV. DISCUSSION

A. Formation of reaction phases

The diffusion bonded Ni–ZrO_2 electrolyte interface was investigated recently by Wagner *et al.*[3] As expected from thermodynamics, no reaction products formed at the Ni–ZrO_2 interface during bonding in high vacuum at 1573 K.

The solid-state reaction between the Ni and ZrO_2 electrolyte was triggered by the electrical current and resulted in the formation of Ni_5Zr and a thin Y_2O_3 layer that was in contact with the electrolyte (Fig. 3). Under the assumption that the electrolyte reacted with Ni fully to Ni_5Zr and Y_2O_3, the ratio $r = d(Ni_5Zr)/d(Y_2O_3)$ can be calculated as $r = 13$, where $d(Ni_5Zr)$ and $d(Y_2O_3)$ are the corresponding layer thicknesses. With use of measured values of the reaction layer thicknesses, a mean value $r_{ex} = 14 \pm 3$ was calculated. The good agreement of both values shows that the chemical reaction at the cathodic side of the cell could be written as (~10 mol% Y_2O_3 doping of electrolyte)

$$4\ Ni + Zr_{0.8}Y_{0.2}O_{1.9} = 0.1\ Y_2O_3 + 1.6\ O + 0.8\ Ni_5Zr. \quad (1)$$

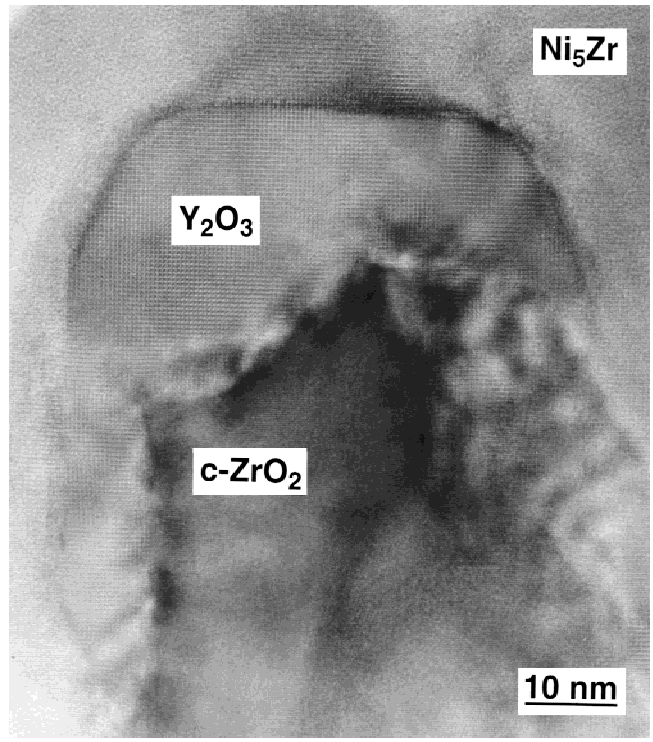

FIG. 5. HRTEM micrograph of one of the ridges separating the pockets shown in Fig. 3. The incident electron beam is parallel to [001]. The Y_2O_3 layer covers the top of the ridges fully and their sides partially.

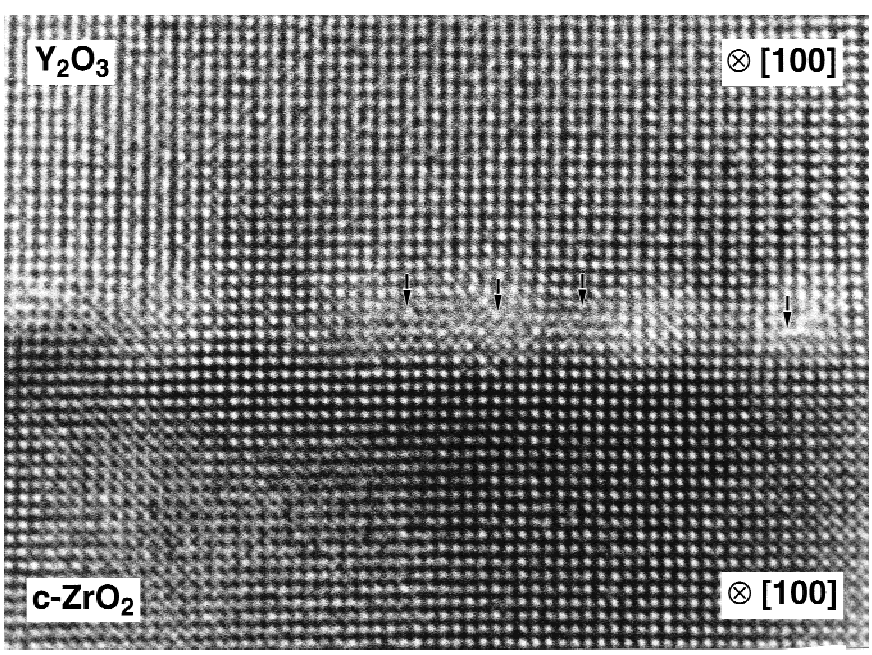

FIG. 6. HRTEM micrograph of the region around the Y_2O_3–electrolyte interface. The interface is not atomically abrupt, and misfit dislocations (compare arrows) are present. The misfit dislocations have a Burgers vector component $\mathbf{b}_{\parallel} = a/2\langle 100\rangle$ that is parallel to the interface.

Both reaction products, Y_2O_3 and Ni_5Zr were identified by TEM and AEM investigations.

In a simplified picture, the very initial reaction at the cathode between Ni and electrolyte can be described as follows. The electrolyte was depleted in Zr and oxygen. The Zr diffused into the Ni, forming Ni_5Zr, and the oxygen ions released during the reduction process were transported through the electrolyte toward the anodic side of the cell. This process led to a continuous increase of the Y concentration at the original Ni–electrolyte interface. The oxygen activity was fixed by the experimental conditions and was obviously not low enough to dissociate Y_2O_3. The formation of Y_2O_3 was accompanied by a reorganization of the remaining Y^{3+} and O^{2-} ions. Y_2O_3 has a cubic C-type oxide structure and can be described as a modified fluorite phase having one anion in four missing to balance the trivalent cationic charge with a slight readjustment of the positions of the remaining ions.[10] Thus, after the Ni and oxygen depletion of the electrolyte, this readjustment leads to the formation of Y_2O_3. Furthermore, the Y_2O_3 layer had an epitaxial orientation to the ZrO_2 electrolyte. Such an orientation relationship is favored by the similarities of the crystal structures and by the low lattice mismatch between both ceramics. The lattice mismatch between Y_2O_3 and electrolyte was accommodated by misfit dislocations (Fig. 6), revealing that the interface is semicoherent.

Figure 8 shows the reaction process schematically. In the very initial stage of reaction, a ultrathin Y_2O_3 layer

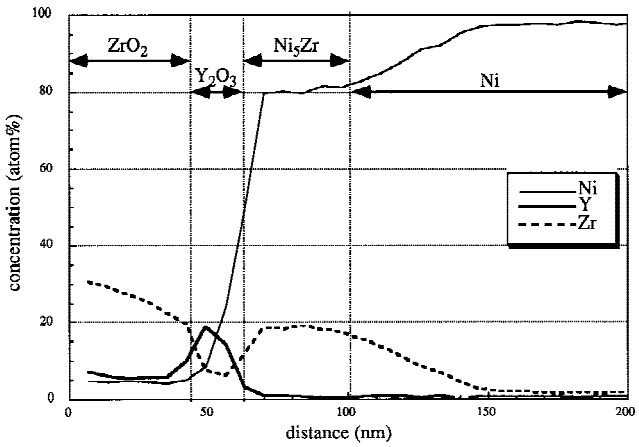

FIG. 7. Chemical profile across the undisturbed reaction layer as calculated from a EDS linescan. Clearly visible are the three regions of ZrO_3, Y_2O_3, Ni_5Zr with an interdiffusion layer, and Ni.

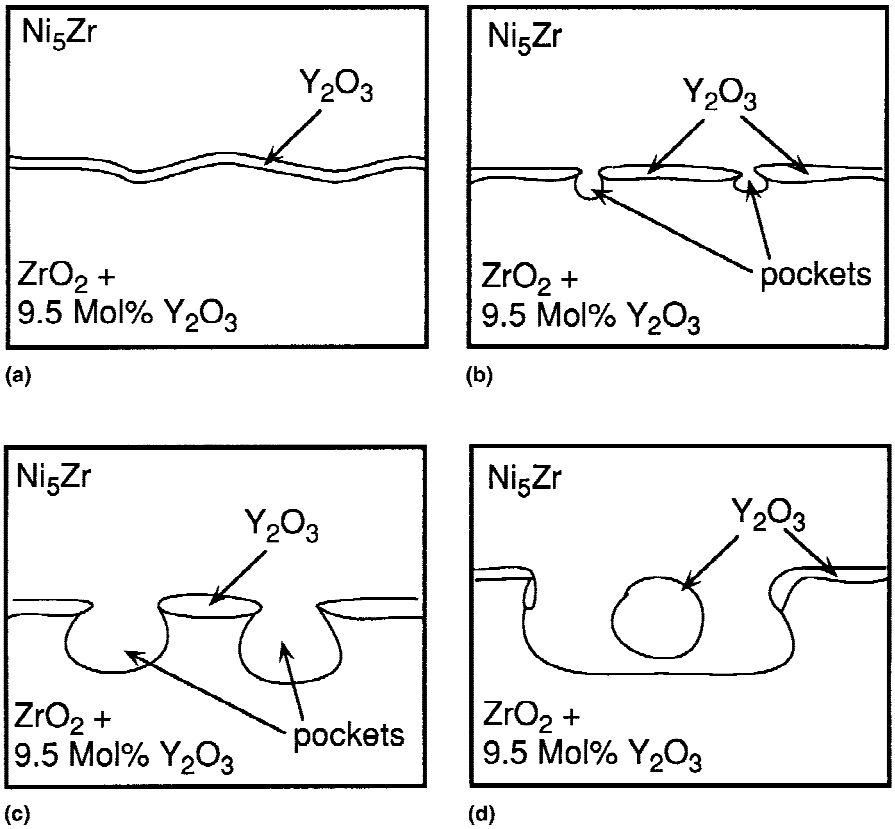

FIG. 8. Simplified schematic of the reaction phase formation at the Ni–electrolyte interface. (a) Formation of a continous Y_2O_3 layer between Ni_5Zr and electrolyte. (b) The Y_2O_3 layer breaks up into islands, and the formation of pockets that are filled with Ni_5Zr just started. (c) The pockets grow deeper into the electrolyte, forming ridges between each other. (d) The ridges are transformed into Ni_5Zr and Y_2O_3, leaving Y_2O_3 particles behind.

may have formed, which covered the electrolyte continuously [Fig. 8(a)]. The Y_2O_3 layer may have acted as a diffusion barrier for Ni and Zr slowing down the overall reaction. At a certain thickness of the Y_2O_3 layer, the layer broke up and exposed the electrolyte locally [Figs. 3 and 8(b)]. In these places the diffusion process was fast enough for a more rapid formation of Ni_5Zr. This resulted in a local variation of the thickness of the intermetallic. Thus, a fast interdiffusion of Zr and Ni was still possible at these locations, resulting in the formation of pockets in the electrolyte surface that were filled with Ni_5Zr [Fig. 8(c)]. Between these pockets, ridges that were partially covered with Y_2O_3 remained. However, with further growth of the reaction phase, part of the sides of the ridges reacted to Ni_5Zr and Y_2O_3 and finally resulted in the isolation of Y_2O_3 particles from the electrolyte [Fig. 8(d)]. Isolated Y_2O_3 particles embedded in Ni_5Zr were observed experimentally for longer reaction times.[3]

The formation of the pockets described above is only possible when the Y_2O_3 film broke up, forming a discontinuous film. Such a process may be stimulated by high-growth stresses during reaction layer formation. Growth stresses could be caused by the volume decrease of ~15%, which is accompanied by reaction (1).

V. CONCLUSIONS

The decomposition process of an Y_2O_3-doped ZrO_2 electrolyte was strongly influenced by the formation of the appropriate reaction layers. The reaction layer consisted mainly of Ni_5Zr. However, the decomposition resulted in the formation of a thin epitaxial Y_2O_3 layer that covered most of the electrolyte. At some places, the Y_2O_3 layer broke up and uncovered the electrolyte again. This may be caused by high-growth stresses that were present during reaction layer formation. The Y_2O_3 layer itself acted as a diffusion barrier for Ni and Zr, slowing down the Ni_5Zr formation. Thus, the reaction layer was inhomogeneous in thickness, because of the faster reaction between electrolyte and Ni at those locations, where the Y_2O_3 layer did not cover the electrolyte surface.

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