Effect of Aluminum Titanate (Al_2TiO_5) Doping on the Mechanical Performance of Solid Oxide Fuel Cell Ni-YSZ Anode

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Abstract

The mechanical behavior of un-doped and 1-10 wt% aluminum titanate doped NiO-YSZ anodes was evaluated in the oxidized and reduced state of the material. Sample bars 25x5x2 mm were fabricated and tested in a three-point bending apparatus and statistical analyses of the collected data were performed. A remarkable enhancement of the flexural strength was found both for the reduced and oxidized state of the material when compared to the un-doped samples. In both cases, the development of a secondary phase was observed proportional to the doping amount of aluminum titanate. Morphological analyses along with preliminary phase identification and suspected mechanisms for strength enhancement are presented and discussed.

Keywords: Ceramics, Doping, Electron Microscopy, Mechanical Properties, Solid State Reactions

1. Introduction

A solid oxide fuel cell (SOFC) is an energy conversion device that electrochemically oxidizes a fuel in order to produce electrical power and heat. For several decades, research effort focused on

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improving the performance of SOFCs to justify its existence and competitiveness within the renewable energy market. With SOFC technology becoming mature, materials selection is an increasingly significant challenge due to the need to find candidates able to offer high performance and durability under operative conditions, while maintaining cost effectiveness and ease of fabrication. In comparison with the electrolyte supported design, anode supported SOFC design is better suited for operation at lower temperatures because lesser ohmic loss and better interface contact can be realized. Recently, there has been growing interest in anode supported SOFCs with excellent single cell performance [1–7]; however, to produce significant power, planar SOFC units must be stacked in electrical series. To maximize the contact between adjacent single cell units, stacks are subjected to high clamping pressures e.g., 65–70 kPa [8,9]. For anode-supported cell, the anode substrate provides the mechanical strength of the stack but in contrast to the vast amount of data available on their electrochemical properties, little fundamental data on the mechanical performance of these systems exist. Due to the inherent brittleness of the dense ion-conducting ceramic membranes, the reliability and robustness of SOFCs depends critically on the thermo-mechanical properties of their components such as coefficient of thermal expansion, elastic behavior and fracture characteristics.

Therefore, it is fundamental to address their mechanical integrity before any stack operation can be undertaken. Despite active search for alternatives, Ni–YSZ composites are widely used as anode components [10,11]. For this reason, a strong YSZ framework able to support the mechanical load under operative conditions is necessary. Several promising substrate materials have been well studied so far [12–20]; however, new compositions require further investigations. The mechanical properties of ceramics are strongly sensitive to variations in materials chemistry and processing methods. The introduction of a second phase, which does not compromise the sintering and electrochemical performance of the anode, has been proven as a successful approach to manipulate the material microstructure enhancing its mechanical performance [6,7,21,22]. A common ceramic manufacturing technique is mechanical mixing of precursor powders with selected particle size followed by an appropriate sintering process. This process easily allows for production of customized formulations, namely the introduction of second phase constituents, without requiring any additional processing.

Previous research reported that appropriate doping level of Al_2O_3 shows a beneficial effect on the sintering behavior as well as on the electrical and mechanical properties of YSZ electrolytes [6,21,23–25]. TiO_2 addition was found to have a similar effect [7,26–30]. Previous research [31–34] has observed that the addition of aluminum titanate $Al_2TiO_{5,}$ (ALT) to the Ni/YSZ system stabilizes SOFC performance in terms of slow degradation rates and high power output. Since there is little fundamental data on the mechanical strength and fracture mechanism of ALT doped systems, this study aims to complement the electrochemical benefits offered by Al_2TiO_5 doping investigating its effect on the mechanical performance of NiO/YSZ and Ni/YSZ anodes.

2. Experimental

Nickel Oxide (NiO) powder (4 μm, Alfa Aesar) and 8 mol% Yttrium Stabilized Zirconium (8YSZ), powder (300 nm, Tosoh) and Aluminum Titanate (ALT) powder (25 nm, Sigma Aldrich) were used for sample manufacturing. Powders, in the ratio of 34 wt% YSZ, 66 wt% NiO and 0-10 wt% ALT, were mechanically mixed for 24 hours with binder (5 wt% Polyethylene Glycol, Alfa Aesar) and deionized water and subsequently placed in a freeze drier under a vacuum for at least 48 hours to allow sublimation of the water.

Rectangular 25 x 5 x 2 mm samples were manufactured pressing 1.5 grams of powder in a uniaxial hydraulic press under a force of 22 kN for 1 minute. This procedure was developed to produce defect-free samples required for reliable mechanical testing. Thermolysis of pressed samples was performed for 2 hours in ambient air heating at 2°C/min up to 450 °C in a box furnace (Thermolyne, 1300). Sintering was conducted with a heating/cooling rate of 5°C/min up to 1400°C and a dwell time of 5 hours (Zircar, Hot Spot 110). Reduction was performed in a tube furnace (Thermo Scientific, Lindberg Blue M) flowing 5% H_2 and 95% N_2 gas, at 800°C for a time sufficient to convert 97 wt% of NiO into metallic nickel. The percentage reduction was evaluated with a Radwag XA 82/220.R2 microscale. Time required for the reduction process varied proportionally to the doping amount of ALT.

Un-doped and 1, 5 and 10 wt% ALT doped batches of 30 oxidized and reduced samples were loaded at a rate of 0.2 mm/min in a three-point bending apparatus (Pasco Scientific 8236) as per ASTM C1161-13 standard. Fracture strength, effective volume V_{eff}, scaled characteristic strength σ_0', Weibull modulus (m) with normalized upper and lower bounds, and porosity, by alcohol immersion method, were evaluated. Field Emission Scanning electron microscopy (FE-SEM, Zeiss Ultra) microstructural characterization and preliminary Scanning Auger NanoProbe (PHI 710) analyses were conducted to determine the nature of the developed phases and their contribution to the material mechanical strength.

3. Results and Discussion

3.1 Mechanical properties

Tables 1-3 summarize the results for all the tested batches. ALT enhanced the mechanical strength of the material in both the oxidized and reduced state. Pertinent literature reports an average fracture strength between 80 and 130 MPa [20,35] and a Weibull modulus between 5 and 7 [36] for undoped anodes. Most of the values recorded for ALT doped samples fall above these ranges. When compared to the undoped, the oxidized samples showed, for the 5 wt% ALT doped sample, an increase up to 71% of the scaled characteristic strength while for the reduced samples, an increase up to 55% was found for the 10 wt% ALT doped sample.

Measurement of the fracture strength of bulk ceramic suffers big scatter in the results and must be determined using statistical analyses based on Weibull approach. The reason for this is that mechanical failure is recognized to be microstructure sensitive, and the weakest spot under stress determines the strength of a brittle material. Figure 1 shows Weibull plots for both the oxidized and reduced sample batches while Table 1 summarizes the Weibull modulus values calculated as the slope of the Weibull plots. The normalized upper and lower bounds on the maximum likelihood estimate of the Weibull modulus (90% confidence interval) has been determined per ASTM C1239 – 13 for batches of 30 samples [37–39]. The Weibull modulus indicates the nature, severity and dispersion of flaws and is used for statistical comparison of the relative quality of two or more test data sets to predict the probability of failure [9,35,40]. A high Weibull modulus is desirable for all materials since it indicates an increased homogeneity in the flaw population and a more predictable failure. On the contrary, a low Weibull modulus is indicative of a large spread within the group and a less predictable failure behavior.

Basing on these assumptions, the 10 wt% ALT doped samples seems to offer the best mechanical performance in both the oxidized and reduced state.

The Weibull approach considers that the weakest spot under tension determines the strength of the sample. Thus, the measured strength is larger if the tested volume is smaller, giving a wrong impression of a stronger material. Therefore, it is important to account for the effective volume V_{eff} while analyzing the results because the probability to apply stress to a flaw increases if the tested volume under tension is larger [35,41–44]. The effective volume is defined by Equation 1 while Equation 2 defines the scaled characteristic strength [41].

$$V_{eff} = \frac{lwh}{2(m+1)^2} \tag{1}$$

$$\sigma_0' = \sigma_0 \left(\frac{V_{eff}}{1\ mm^3}\right)^{\frac{1}{m}} \tag{2}$$

Where l is the distance between support points, w and h are the width the height of the sample, m is the Weibull modulus, and σ_0 is the characteristic strength corresponding to ~63% probability of failure.

Table 2 compares the strength results scaled to the same effective volume of 1 mm^3. When compared to the undoped, the oxidized samples showed, for the 5 wt% ALT doped sample, an increase up to 71% of the scaled characteristic strength while for the reduced samples, an increase up to 55%. The strength of ceramic is dependent on the porosity distribution within the material [19,20,37,42,43] since the presence of one or more pores in the loaded volume will result is a more fragile material. Table 3 summarizes the porosity values measured for all of the tested batches. For the oxidized samples, despite the fact that changes in the scaled characteristic strength and m were observed, a constant value of the porosity ~1.8% was found. Previous findings [45] reported that, for samples with a porosity lower than 10%, any discontinuation in the bulk material, as processing induced flaws and/or presence of secondary phases, play a more important role in the failure of the material rather than pores. Variations of size, shape and orientation of these flaws result in a large scatter of the strength data [46]. Due to the nature of the doped material, formation of secondary phases with mechanical properties and composition different from the undoped material and dependent on the ALT amount, is most probably responsible for the increased strength and will be discussed later.

Reduced samples reflect these observations having a porosity between ~12% and 25%, a Weibull modulus between 6 and 11 and a scaled characteristic strength between 120 and 186 MPa. Fan et al. [45] found that ceramic materials with porosity between 10 and 55% resulted in Weibull modulus values in the range between 4 and 11 with a medium to high scatter in the fracture strength regardless of the composition, grain size, testing techniques or surface finish of the specimens. The failure of these kind of materials has been linked to the pore evolution during sintering process. Since the reduction time of the doped samples, when compared to the undoped, was found to be dependent on the amount of ALT; it is thought that, in addition to second phase formation and evolution, the kinetics of the reduction process, where the oxygen release is responsible for the pore formation, plays a fundamental role in defining the ultimate mechanical strength of the material.

Basing on the above discussion there is a clear need to correlate microstructure, Weibull modulus and scaled characteristic strength to define which material is the most reliable in terms of mechanical performance. The highest Weibull modulus was calculated for 10 wt% ALT doped samples both in the oxidized and reduced states of the material; however, the highest characteristic strength was measured for the 5 wt% ALT doped samples in the oxidized state. Weibull modulus data is limited in the literature and the correlation between the porosity and fracture properties is not clear because of different sensitivity to local features of the crack field geometry [37,47,48].

Figure 1 Weibull plots present a medium to high scatter in the fracture strength data for most of the materials, which will result in the need to include high safety factors in their designs. The 5 wt% ALT doped samples present the lowest strength data scattering both in the oxidized and reduced state suggesting this material as the most reliable one.

The investigation of the reduced materials, showed that a decrease in the porosity corresponds to an increase in the scaled characteristic strength; however, it should be noted that reduction in porosity will reduce the anode catalytic activity. Therefore, investigation of the dependence of fracture stress on other factors, such as pore shape and size is needed and will be of great significance.

3.2 Microstructural analyses

Field Emission Scanning Electron Microscopy (FE-SEM) was performed on samples' surface and cross sections. Cross section morphologies confirmed trans-granular fracture for all batches and can be seen in Figures 2 and 3. Figure 4 a-d shows the surface microstructure of the NiO-YSZ samples with 0, 1, 5, and 10 wt% ALT. It can be observed (circled areas of Figure 4b-d) that a secondary phase, here defined as the "rough phase", developed proportionally to the doping amount of ALT. A similar microstructure defined as "undulated" was found for TiO_2 doped YSZ material [7].

Figure 5 a-d shows the surface microstructure of the Ni-YSZ samples with 0, 1, 5, and 10 wt% ALT. The presence of the "rough phase" is confirmed however, a new phase starts to develop as small particles (circled in Figure 5c) in the 5 wt% ALT doped sample and its amount is increased (circled in Figure 5d) in the 10 wt% doped ALT sample. To relate the comparison of the new phases with the increased mechanical strength, preliminary Scanning Auger Nanoprobe analyses were performed on samples' surface. Figure 6 shows the Auger map collected on the same area with two different element overlays for a Ni-YSZ + 10 wt% ALT sample. Figure 6b shows that the nickel particles, about 1 μm in size (blue areas), are decorated with a layered structure specifically, an immediately adjacent titanium based layer followed by an aluminum based layer; also, the small particle phase is revealed to be nickel clustered on an aluminum substrate. The “rough phase” is indicated to be titanium preferentially distributed within the zirconium which is found to fill the area between the nickel particles (Figure 6c).

In the presented manufacturing conditions, ALT spontaneously decomposes to Al_2O_3 and TiO_2 [31,34,49–51]. Part of the Al_2O_3 initially reacts with NiO to form $NiAl_2O_4$ [6,33,34,43,52] proportionally to the amount of Al_2O_3 made available through ALT doping. For the oxidized samples, an enhancement of the scaled characteristic strength was observed for all of the ALT doping amounts. $NiAl_2O_4$ is expected to have a positive impact on the material strength due to its higher stiffness than YSZ [43,53]. Previous research showed that the threshold amount of Al_2O_3 doping to enhance the flexural strength was 3 wt% [6] which corresponds to ~6 wt% ALT doping. This well relates to the difference in the calculated scaled characteristic strength where the highest and lowest values were found for the 5 wt% (~2.5 wt% Al_2O_3) and the 10 wt% (~5 wt% Al_2O_3), which are respectively below and above the defined threshold. In the oxidized state, the anode material is a composite where NiO, YSZ, Al_2O_3, and $NiAl_2O_4$ have different thermal expansion coefficients; which, at a microstructural scale, will cause internal residual stresses contributing to a decrease in strength of the support [43,53].

TiO_2 is thought to react with YSZ enhancing its sintering characteristics [7,33,34] and leading to the formation of a solid YSZ framework [7] here defined as the “rough phase”, which enlarges proportionally to the amount of ALT. Tetragonal domains in the cubic phase were found for TiO_2

doping [7,34,54] and have been confirmed for ALT doping [34]. In addition to second phase formation, the enhanced mechanical strength, could also be related to the volume change resulting from a tetragonal to monoclinic stress-induced phase transformation [7] caused by the discussed thermal expansion mismatch. Further research is needed to quantify residual stresses and clarify the relationship between second phase development and YSZ phase transformation.

Figures 4 and 5 show almost no morphological difference in the Ti-YSZ framework (rough phase) before and after reduction; thus, it is thought that it persists without modification. The differences observed in the scaled characteristic strength are; therefore, to be correlated with the reduction of NiO and $NiAl_2O_4$. The reduction of NiO to Ni is expected to increase the mechanical strength because of added ductility into the ceramic system. Despite Ni formation, the scaled characteristic strength for undoped reduced samples, when compared to the corresponding oxidized ones, is decreased due to quick reduction time (~3 hours) and associated porosity development (Table 3).

Previous research has shown that $NiAl_2O_4$ at 800°C in reducing atmosphere has very low reaction kinetics and cannot be reduced during short times (less than 10 hours) [43]. In the 1 wt% ALT doped samples, the scaled characteristic strength is increased when compared to the undoped samples due to $NiAl_2O_4$ forming and persisting upon reduction (~5 hours); however, this value is lower than that calculated for the oxidized sample due to high porosity. The formation of $NiAl_2O_4$ depletes the system of available NiO for reduction resulting in a lower porosity when compared to the undoped samples. Under long term exposure, $NiAl_2O_4$ could progressively be reduced into Ni and Al_2O_3 at 800°C [43]. The decrease in porosity from 23.1% (1 wt% ALT) to 12.5% suggests that for the 5 wt% ALT doped samples, the amount of $NiAl_2O_4$ is largely increased. The reduction process of the 5 wt% ALT doped samples required ~12 hours which could allow for initial reduction of $NiAl_2O_4$. Figure 5 supports this, showing that small particles are developing on the sample surface and are believed to be Ni nanoparticles [6,43,55]. Despite the decreased porosity, the scaled characteristic strength is found to be lower than for the 1 wt% ALT doped samples; this can be explained by the fact that the reduction of $NiAl_2O_4$ is accompanied by a theoretical volume shrinkage of ~18% that can generate residual stresses detrimental to the system [56].

The reduction for the 10 wt% ALT doped samples was achieved after ~40 hours. This drastic increase in the reaction time is to be correlated with the partial reduction of $NiAl_2O_4$. Figure 5d shows a substantial increase in the small particle phase and Figure 6 confirms the presence of Ni nanoparticles within an Al_2O_3 matrix. The Al_2O_3 layer observed in Figure 6b-c around the nickel particles is also probably generated during this process. The nature of the Ti layer immediately adjacent to the nickel particles is yet to be identified. The slight increase in porosity is related to the increased oxygen release while the highest scaled characteristic strength is due to the increase in nickel acting either as crack deflector or stopping the crack propagation due to its ductility [43,55–57]. Experimental measurements showed that the volume decrease during the reduction of $NiAl_2O_4$ is between 3 and 9% instead of the theoretical 18% indicating that the system, if given enough time, finds a mechanism to avoid generating large volume changes and relaxes the stresses associated with the reduction reaction [56]. This phenomenon can be explained with the interface between the Ni particles and Al_2O_3, withstanding large stresses from a large coefficient of thermal expansion mismatch, while the interface between the unreduced $NiAl_2O_4$ and the two-phase mixture of Ni and Al_2O_3 withstanding large volume changes [55].

Despite this work demonstrating the enhanced mechanical strength and reliability of ALT doped materials, the authors understand that further research is needed for the optimization of the system in fuel cell operative conditions including the evaluation of electrochemical properties and redox cycling.

4. Conclusions

This study has demonstrated that ALT doping can enhance the mechanical properties of Ni-YSZ systems. Despite the uncertainty of the Weibull modulus falling within the range of those for the other compositions, the Weibull plots showed that the 5 wt% ALT doped samples present the lowest strength data scattering both in the oxidized and reduced state suggesting this material as the most reliable one. The enhanced scaled characteristic strength resulting from ALT addition has been related to the development of secondary phases: Al_2O_3 reacts with NiO to form $NiAl_2O_4$ while TiO_2 preferentially reacts with YSZ to form a solid YSZ framework defined as the “rough phase”, which enlarges proportionally to the amount of ALT and persists upon reduction. The mechanical behavior of the reduced samples has been related to the presence of $NiAl_2O_4$ and its partial reduction leading to the formation of Ni nanoparticles within an Al_2O_3 matrix. This work has highlighted the need for further investigation of relationship between mechanical properties and microstructural factors, such as pore shape and size as well as on the quantification of residual stresses and clarification of their effect on second phase development and transformations. Despite this work demonstrating the enhanced mechanical strength and reliability of ALT doped materials, the authors understand that, for the materials to be optimized, more testing in fuel cell operative conditions, including the evaluation of electrochemical properties and redox cycling, is needed.

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Table 1: Weibull modulus of anode material

	0% ALT	1% ALT	5% ALT	10% ALT
Oxidized (NiO/YSZ)				
m	5.1	3.5	6.9	7.7
90% Confidence Interval	3.8-6.2	2.6-4.3	5.2-8.4	5.8-9.4
Reduced (Ni/YSZ)				
m	7.5	5.6	8.6	10.6
90% Confidence Interval	5.6-9.1	4.2-6.9	6.5-10.5	8.0-12.9

Table 2: Mechanical properties of anode material

	0% ALT	1% ALT	5% ALT	10% ALT
Oxidized (NiO/YSZ)				
Average strength σ/MPa	100	136	226	150
V_{eff}/mm^3	1.8	3.2	1.1	0.9
Scaled Characteristic strength σ_0'/MPa	137	213	234	156
Strength Increase/%	N/A	55	71	14
Reduced (Ni/YSZ)				
Average strength σ/MPa	120	151	164	187
V_{eff}/mm^3	0.9	1.5	0.7	0.5
Scaled Characteristic strength σ_0'/MPa	120	175	168	186
Strength Increase/%	N/A	46	40	55

Table 3: Porosity of anode material

	0% ALT	1% ALT	5% ALT	10% ALT
Oxidized (NiO/YSZ)				
Porosity/%	1.8	1.8	1.9	1.8
Reduced (Ni/YSZ)				
Porosity/%	25.3	23.1	12.5	13.9

Figure 1: Weibull plots of NiO-YSZ (oxidized) and Ni-YSZ (reduced) samples

Figure 2: FE-SEM cross sectional image of NiO-YSZ + (a) 0 wt%, (b) 1 wt%, (c) 5 wt%, and (d) 10 wt% ALT

Figure 3: FE-SEM cross sectional image of Ni-YSZ + (a) 0 wt%, (b) 1 wt%, (c) 5 wt%, and (d) 10 wt% ALT

Figure 4: FE-SEM surface image of NiO-YSZ + (a) 0 wt%, (b) 1 wt%, (c) 5 wt%, and (d) 10 wt% ALT

Figure 5: FE-SEM surface image of Ni-YSZ + (a) 0 wt%, (b) 1 wt%, (c) 5 wt%, and (d) 10 wt% ALT

Figure 6: Auger elemental map of Ni-YSZ + 10 wt% ALT sample surface: (a) details of mapped areas, (b) Nickel-Blue, Titanium-Red, Aluminum-Green, and (c) Zirconium-Blue, Titanium-Red, Aluminum-Green