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Catalyst enhancing aluminum titanate for increasing strength of nickel-zirconia cermets

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ABSTRACT

Aluminum titanate (ALT), a catalyst-enhancing phase in nickel-zirconia SOFC anodes, has been observed to have the secondary benefit of increasing flexure strength. Ni-YSZ cermet discs doped with 5 wt% ALT exhibit 150% of stress at failure of non-doped samples in equibiaxial flexure tests. Also observed is a ~25% increase in toughness, which may be related to the localized introduction of tetragonal zirconia, or alternatively, that the sintering enhancement effect of ALT yields modified flaw geometry at cermet interfaces. Comparison of non-doped and doped Ni-YSZ $\sigma_{50\%}$ values indicates that the thickness of ALT enhanced anodes could be reduced by ~20% while maintaining the flexural strength of an unmodified anode.

1. Introduction

Traditional two-phase cermets represent an unsurpassed balance of cost, performance, stability, scalability, and durability in SOFC anode fabrication. In spite of the ubiquity and in-depth study of this anode material, the nature of these anodes has remained largely unchanged for the last decade or so.

Recent work targeted at catalyst enhancement through reducing coarsening induced degradation has also suggested improved mechanical properties of Ni-YSZ cermets [1–4]. Although anode-supported cells are capable of producing high power densities, the necessary porosity and two phase mixture limits the mechanical strength requiring additional thickness to support the cell [5]. Further, the mechanical strength requirements of anode supported cells dictate anode thicknesses greater than the thickness required for sufficient electrochemical activity [6]. A Ni-YSZ cermet strength increase could provide a route to reduced anode thickness and increased porosity allowing for: reduced weight, reduced material cost, and increased performance from improved fuel diffusion. This letter examines flexure strength enhancement of Ni-YSZ cermets by ALT additions through dilatometry, electron microscopy, and equibiaxial flexure testing.

2. Experimental

2.1. Materials processing

Anodes were fabricated with ~4μm NiO (Alfa, Stock #12359), and 8 mol% Y_2O_3 stabilized ZrO_2 specified at $7 \pm 2\ m^2/g$ and 300 nm (Tosoh Inc., 8YS Grade) in a 66:34 wt% ratio, respectively. ALT (Aldrich, Stock #634131, <25 nm) was added at 5 wt% in the Ni-YSZ [1–4]. Mixtures were ball milled for 48 h in an aqueous suspension with 5 wt% PEG (Alfa, Stock #42635) as pressing binder and flash frozen by liquid nitrogen submersion. Anode powders were uniaxially pressed in a 38 mm die at 35 MPa. Two sintering profiles were used for the non-doped powders: (1) 5 °C min^{-1} to 1400 °C for 10 h (P-1400C-10h), and (2) 5 °C min^{-1} to 1550 °C for 5 h (P-1550C-5h). ALT-doped samples were sintered according to (1) (A-1400C-10h). After sintering, but prior to flexure testing (all series), NiO was reduced under flowing 5% H_2 forming gas at 900 °C for 6 h.

2.2. Dilatometry & microstructural examination

Pellets of 6.35 mm diameter were sintered in a Linseis L75 dilatometer to 1400 °C in air. Compositions ranged from 0 to 10 wt% ALT in NiO-YSZ. After large sample flexure testing, fracture surfaces of reduced samples were examined with scanning electron microscopy (Zeiss, Supra 55-VP). Images were collected at 1 kV with a working distance of 4mm.

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2.3. Equibiaxial flexure testing

From each sample series, 20 samples were tested using monotonic equibiaxial flexure testing (ring-on-ring) in a manner consistent with ASTM Designation C1499-09 [7]. The custom aluminum fixture was machined with load and support ring diameters of 8 mm and 20 mm, respectively. The fixture was used in an Instron 5543 load frame with a loading rate of 500 N min^{-1}. Flexural strength was calculated according to Eq. (1) [7].

$$\sigma_f = \frac{3F}{2\pi h^2} \cdot \left\{ (1+v) * \frac{D_S^2 - D_L^2}{2D^2} + (1+v) \ln \frac{D_S}{D_L} \right\} \quad (1)$$

F is the maximum load reported by the Instron, h the sample thickness, v Poisson's ratio, D_S diameter of the support ring, D_L load ring diameter, and D sample diameter. Flexure strength values were subjected to Weibull analysis and standard ANOVA.

3. Results and discussion

3.1. Densification & microstructure

Dilatometry and SEM microstructural characterization established the validity of strength comparison for varying treatments. On first consideration, it seems that processing of ALT-enhanced and non-doped specimens be identical outside of the ALT addition. However, ALT is an effective sintering aid in NiO-YSZ, yielding greater density prior to reduction and therefore influencing flexure strength through porosity mismatches. Thus, a second set of non-doped specimens was sintered to increase density towards that of the ALT doped samples.

Densification curves for NiO-YSZ compositions doped up to 10 wt% ALT are shown in Fig. 1. With a 5 °C min^{-1} ramp to 1400 °C with no dwell, 5 wt% ALT affected the greatest change in relative density.

Iterative sintering runs were performed with the pure NiO-YSZ to achieve a density greater than the doped specimen to validate that flexure strength benefits are not solely density dependent. As such, the pure material was sintered at 1550 °C for 5 h. Archimedes' density established that while P-1400C-10h (5.3 g cm^{-3}) was indeed less dense than A-1400C-10h (5.8 g cm^{-3}), P-1550C-5h density exceeded the doped samples at 6.1 g cm^{-3} On the basis of porosity and flaw distribution, this would indicate that P-1550C-5h should exceed the strength of the doped specimens. Fracture surfaces following reduction and flexure-testing are shown in Fig. 2. The left panel highlights the additional porosity present in the P-1400-10h sample series corresponding to decreased cermet strength shown in Table 1. These images indicate mixed mode fracture consistent with literature reports [5,8].

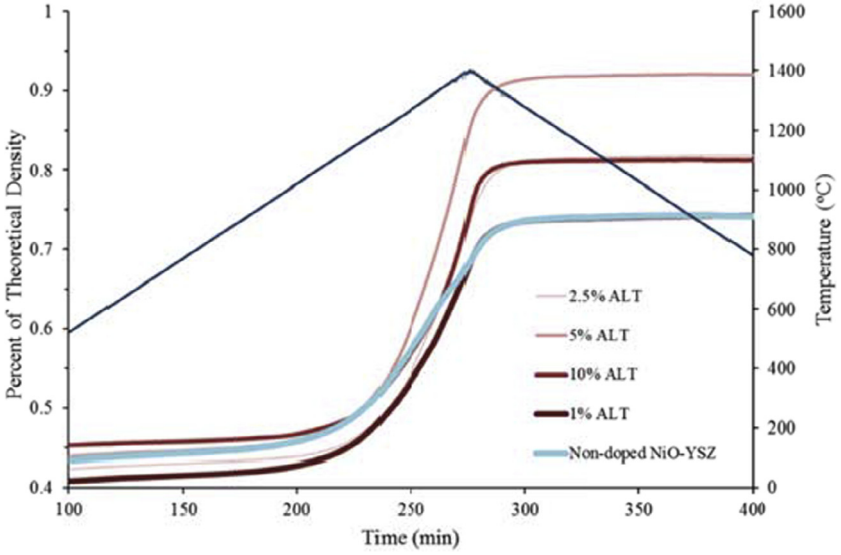

Fig. 1. Dilatometry results for uniaxially dry-pressed pellets of NiO-YSZ doped with ALT at 0–10 wt%. The trace with two linear portions represents the sintering profile (right-hand axis).

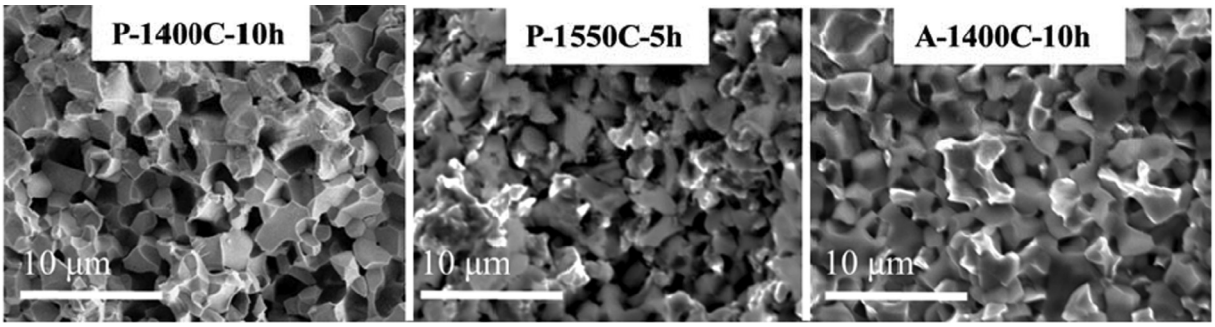

Fig. 2. SEM micrographs selected as representative of each series. Views are of fracture surfaces after reduction (where porosity is generated from the NiO–Ni reduction process) and flexure testing.