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The mechanical properties of tubular solid oxide fuel cells

N. M. SAMMES
Department of Mechanical Engineering, University of Connecticut, Storrs, CT 06269, USA
E-mail: sammes@engr.uconn.edu

YANHAI DU
Connecticut Global Fuel Cell Center, University of Connecticut, Storrs, CT 06269, USA
E-mail: ydu@engr.uconn.edu

The mechanical strength of solid oxide fuel cell (SOFC) components is one of the key issues for determining their performance and reliability. A minimum strength is required for the handling of these components in manufacturing, namely in relation to the application of the electrode or electrolyte coatings, the application of the current collection metals and the construction of the stack. Small tubular SOFCs have been found to have excellent thermal shock properties and low-cost of fabrication through traditional extrusion techniques. The mechanical integrity of the small, thin walled, tubular ceramics could be tested using traditional 3 or 4-point bending techniques, however these techniques are liable to cause failure by crushing the tube wall. Thus, a more reliable method for realizing the strength of small thin walled tubes is to pressurize the inside volume and obtain the strength value at which the tube bursts under the internal pressure. A custom burst-test instrument was constructed to obtain the average strength value of differing types of small ceramic tubes. The mechanical properties of 8 mol% yttria-stabilized zirconia (8YSZ) and NiO-YSZ tubes were investigated and are discussed. An average burst strength of 97 ± 28 MPa was observed for 8YSZ electrolyte tubes and 72 ± 23 MPa and 70 ± 16 MPa for as-sintered and reduced anode support tubes, respectively. © *2003 Kluwer Academic Publishers*

1. Introduction

For fuel cell elements to be handled without breakage during fabrication, stack assembly and survive during operation, it is imperative that at least one of the material components, for example the anode, cathode, or the electrolyte, must be of sufficient thickness and mechanical integrity to provide the structural support. The strength of a zirconia electrolyte material is superior to that of typical anode and cathode materials (compare values in Tables I and II), by approximately one order of magnitude. However, using a thick electrolyte decreases the cell performance by increasing the ohmic contribution of the cell. The preferred choice is to decrease the cell resistance through decreased electrolyte thickness, and the retention of cell strength is via the use of either an anode or cathode support. Cathode-supported SOFC's, such as those used in the Siemens-Westinghouse design, typically consists of doped lanthanum manganite materials, however, lanthanum manganite can be relatively expensive and exhibits a lower strength compared to Ni/YSZ anode material. Therefore, the relatively inexpensive anode material (Ni/YSZ) is the obvious alternative for the support system. Fung *et al*. [1] investigated the mechanical properties of Ni-YSZ and Ni-TZP materials as sheets. These workers found that a flexural strength of 120–140 MPa was obtained for 50–70 vol% NiO (ca. 37 vol% to 58 vol% Ni)-8YSZ. Several workers have studied the mechanical properties of anode cermet materials, and these are summarized in Table I. In Table I, the mechanical strengths of Ni-YSZ anode materials are collated from the literature and compared to values reported for 8YSZ tubes, rods and bars. The mechanical strength data reported on thin walled tubular zirconia is sparse consisting mainly of the work by Prica *et al*. [2] and Du *et al*. [3]. It can be seen that the mechanical strength values obtained for the zirconia tubes, are comparatively low compared to those observed by Prica *et al*. [2]. However, a large percentage of micro-porosity was observed with the specific batch of extruded tubes, therefore there was likely a large number of defects in these tubes. The pressurized burst test used by Sammes *et al*. [4] consisted of a hand pumped hydraulic fluid system with the tube adhered to tubular end-caps using an epoxy adhesive. This system proved to give sufficient results. However, as problems occurred with the end-caps and often tubes would burst close to the adhesive end-cap interface, likely erroneous results occurred with the end-cap, and often effects. Typically, breakage greater than a tube diameter from the end-cap is considered to be a successful rupture. A better system was required for more reliable testing to

TABLE I Mechanical strength values of 8YSZ and NiO-YSZ ceramics for various test methods

Sample composition and type	Test technique (at room temperature, unless otherwise stated)	Mechanical strength (MPa)	Reference
8YSZ extruded tubes at 50 mm length, 2.4 mm diameter and 200 μm wall thickness	Hydraulic pressure test	115	[6]
8YSZ extruded tubes, 2.4 mm diameter and 200 μm wall thickness	3-point bend test	407	[2]
8YSZ extruded rods, 0.56 mm diameter	3-point bend test	734	[2]
8YSZ bars	4-point bend test	245	[7]
NiO-YSZ 75 mol% NiO-8YSZ (31% porosity)	4-point bend test	56	[8]
37 vol%Ni-YSZ (20.7% porosity)	Flexure strength of bars	120	[1]
47 vol%Ni-YSZ (24.8% porosity)	Flexure strength of bars	130	[1]
58 vol%Ni-YSZ (24.8% porosity)	Flexure strength of bars	140	[1]
40 vol%Ni-8YSZ	3-point bend on bars	80–120	[5]
40 vol%Ni-8YSZ	3-point bend on bars @ 500°C	80–200	[5]
Ni/8YSZ (Coat-Mix®) reduced anode	4-point bend test	60–80	[9]
NiO/8YSZ (Coat-Mix®)	4-point bend test	80–120	[9]
Ni	Metal bar	317	[10]
Ni-3YSZ support/Ni-8YSZ anode/8YSZ	Tensile strength, of planar half cells after sintering at 1300/12 h	154	[11]

TABLE II Young's modulus, Poisson's ratio and modulus of rupture (MOR) for typical fuel cell materials

Material	Young's modulus (GPa)	Poisson's ratio	MOR (MPa)	Reference
8YSZ (<2% porosity)	215	0.32	377	[8]
8YSZ single crystal	220.45	0.315		[12]
NiO-YSZ 75 mol% NiO-8YSZ (86-92% density)	161	0.317	180	[8]
NiO-YSZ 75 mol% NiO-8YSZ (31% porosity)	55	0.17	56	[8]
LSM (33% porosity)	35	0.25	46	[8]
LSM			~50	[10]
NiO-YSZ 75 mol% NiO-8YSZ (31% porosity)	207.13	0.327		[8]
Ni	205	0.299	317	[10, 12–14]
NiO	277			[5]

minimize end-cap influence and produce a more reproducible test.

2. Experimental

Tubular electrolytes, 8 mol% yttria stabilized zirconia (8YSZ) of ca. 4 mm OD and 250 ~ 250 μm wall thickness, with length of 65 mm, were fabricated using the process developed from our previous study [3]. Anode-support tubes were prepared using a plastic extrusion process. Anode powder was characterized before the extrusion process to determine the chemical compositions (NiO/YSZ = 50:50 vol%), particle size distribution, and surface area. The cermet powder was mixed with organic binders in a high shear blade mixer to form a plastic mass. This plastic mass was then rheologically studied to optimize the formulation, materials and the mixing process. Extrudable dough was extruded through a die to form a hollow tube. After drying in air in a sample tube holder, the extrudates were fired in a furnace at temperatures from 700 to 1650°C for 2 h. Fig. 1 shows a photograph of the anode support tubes fired at describing temperatures. It can be seen that the tube coloration changes through a light region to a darker color with higher temperature firing producing a denser tube. The electrolyte and anode tube densities and porosities are summarized in Table III. Significant porosity is produced in the anode tube after reduction (ca. 29%); this will lead to a decrease in the strength of the material due to an increase in the defects, however the reduction of the NiO to Ni metal is a shift to a stronger material and is an offset to the increased porosity as interpreted by Fung *et al*. [1]. Tube samples fired at 1475°C were used for mechanical testing. The anode support tubes fired at 1475°C had dimensions of ca. 5.5 mm outside diameter and 0.5 mm wall thickness. Reduction of the fired anode tubes was achieved at 650–900°C for 4 h in a pure H_2 atmosphere.

Modulus of rupture (MOR) of the anode tubes fired at different temperatures, and the MOR of the anode support tubes with YSZ electrolyte coating at different fabrication processes (green, pre-fired, co-fired, reduced, re-oxidized), were evaluated using a three point bending test. Burst-test strength of the YSZ electrolyte tubes, and dense anode tubes, was determined using a custom P-3100 Instron-Satec test rig with a LTR10948 Ceramic Tube Tester. The rig is capable of two pressure ranges; up to 3000 PSI (20.68 MPa) and intensified up to 15000 PSI (103.42 MPa). Pressurized water was used to fracture the tubes. The pressure rig designed for testing the mechanical strength of ceramic tubes (of varying diameters), including the end caps and the 6:1 intensifier is shown in Fig. 2. Tubes of 80 mm in length were adhered to the two stainless steel end-caps using a two-part epoxy adhesive (5 min Araldite® gel). Data was read from the test equipment and mechanical strength calculated from the breaking pressure values and the dimensions of the tubes. An average of at least 6 values was determined for each tube type. A further end-cap development was undertaken to achieve rapid sample throughput, this incorporated an o-ring seal on

TABLE III Density and porosity of anode and electrolyte materials

Material	Theoretical density (g/cm^3)	Measured density (g/cm^3)	%density	Porosity (%)
Ni	8.88 [10] 100%			
8YSZ	5.94	5.92	Fully dense	0.2% est. from microstructure
NiO	6.67			
50:50 vol% NiO-YSZ	6.31 (calculated)	6.37	100	0.7
∼37 vol% Ni-YSZ	7.48	5.34	71	28.7

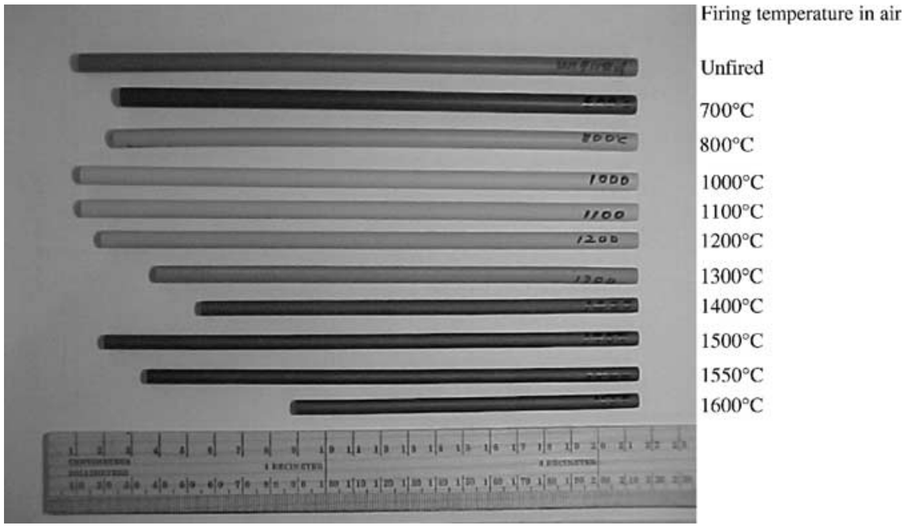

Figure 1 Photograph of NiO-YSZ anode support tubes green and sintered at various temperatures.

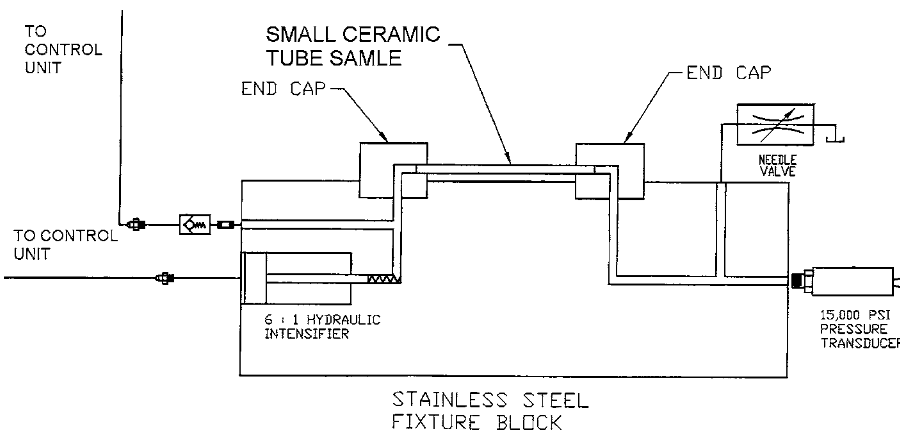

Figure 2 Burst-test stage unit, showing sample, end-caps and pressure intensifier.

the sample tube OD and was compressed using a bolted cylinder clamp. Fig. 3a shows a schematic of this end-cap system. For porous anode tubes the addition of a thin rubber sleeve was utilized on the inside of the tube and wrapped over the sample tube ends to provide a leak tight system (Fig. 3b).

3. Results and discussion

Using the custom Instron-Satec system and electrolyte tubes adhered to the end-caps with epoxy adhesive, the burst test was carried out to determine the strength of the 8YSZ electrolyte tubes. A total of 25 samples were tested and an average strength of 97 MPa was calculated from the burst pressures. Using Weibull analysis it was determined that the strength was 126 MPa with a Weibull modulus of $m = 3$ (see Table IV and Fig. 4). The modulus is relatively low and this can be attributed to the large scatter observed in the results. The scatter in burst strength is likely due to

TABLE IV Burst-strength measurements for uncoated and coated zirconia tubes

Sample tube type	Burst strength (average of 24 samples), standard hoop theory (MPa)	Mean Strength (MPa) and Modulus from Weibell analysis (MPa)
8YSZ (Tosoh), uncalcined, ca. 4 mm Ø, 200 μm wall thickness, 65 mm length	97 ± 28 (fully dense with 0.2% porosity estimated from microstructure)	$\sigma_{0.5} = 126$ $m = 3$

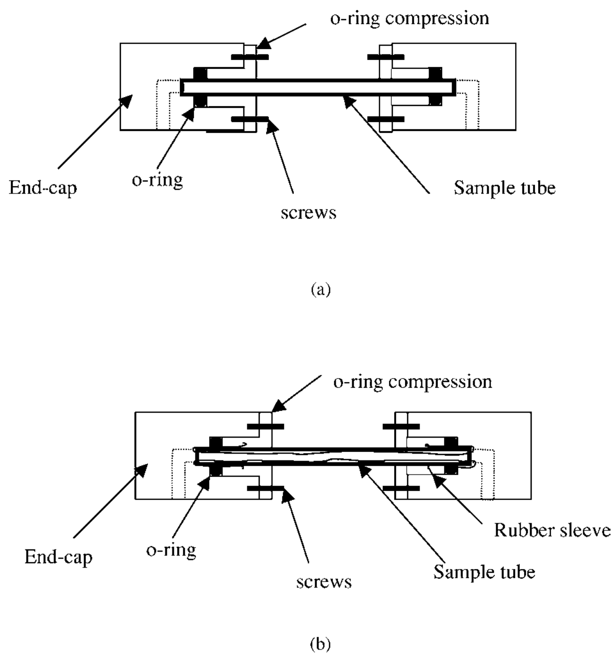

Figure 3 Schematic of the o-ring seal end-cap systems: (a) for dense tubes and (b) for porous tubes.

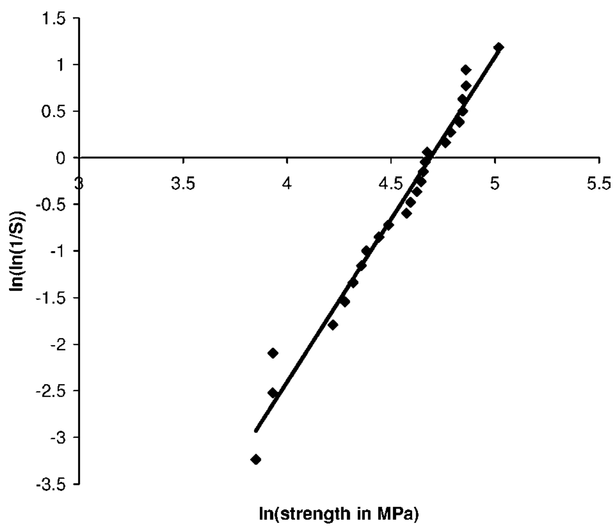

Figure 4 Weibull plot of strengths from burst tested 8YSZ tubes fired at 1475°C.

TABLE V Burst-strength measurements for anode-support tubes

Sample tube type	Burst strength (average of 5 samples), standard hoop theory (MPa)	Porosity (%)	Weibull mean strength (MPa) and modulus
50:50 vol% NiO-8YSZ tube, 4.51 mm ID, 0.51 mm wall thickness, fired at 1475°C	72 ± 23	0.7	$\sigma_{0.5} = 101$ $m = 3$
~37 vol% Ni-8YSZ tube, mm ID, 0.51 mm wall thickness, fired at 1475°C, reduced at 900°C in H_2 4 h	70 ± 16	28.7	$\sigma_{0.5} = 90$ $m = 3$

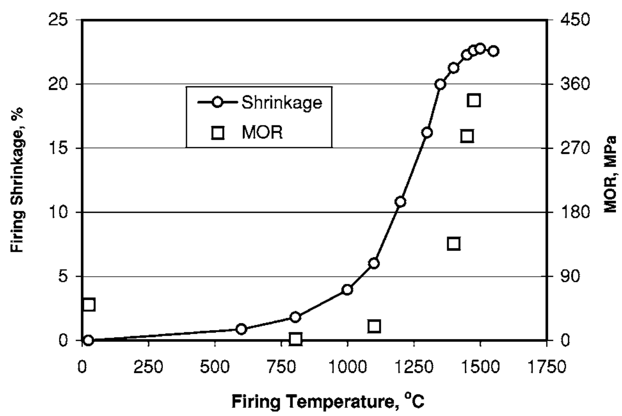

Figure 5 Firing shrinkage and MOR of anode tubes fired at different temperatures.

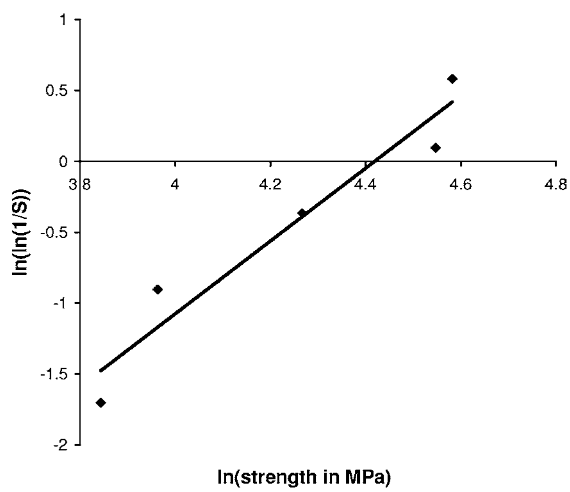

Figure 6 Weibull plot of strengths from burst tested unreduced anode (NiO-YSZ) tubes fired at 1475°C.

the large variation observed in the fabrication procedure. Although a proportion of the electrolyte tubes, and hence cells, are strong enough to withstand handling and operation, a stack typically requires zero tolerance for breakages due to the combustive mixing of fuel and air gases at elevated temperatures. A stronger and hence more reliable cell is required to give stack longevity.

Firing temperatures of anode tubes were determined to be 1475°C from the strength/shrinkage-temperature curve (Fig. 5), considering the porosity requirements. Samples of anode tubes fired at 1475°C and also reduced at 900°C for 4 h in hydrogen, were burst tested to determine their relative strengths. Table V shows the average burst strength for unreduced and reduced anode tubes. It can be seen that the average strength of both sample types is the same within error. Weibull analysis was carried out on the burst strength data to determine the average burst strength and Weibull modulus and the Weibull plots are shown in Figs 6 and 7. It was found that the average burst strength was below that observed for the electrolyte tubes however the modulus was again observed to be 3. The low modulus indicates a large scatter in values. The calculated strength of the as-sintered and reduced anode tubes is within the same order or magnitude as the strengths observed

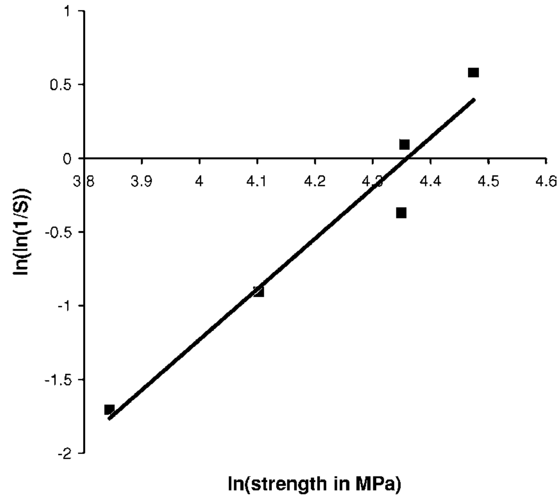

Figure 7 Weibull plot of strengths from burst tested reduced anode (Ni-YSZ) tubes fired at 1475°C.

for planar anode support materials, as described by Mori *et al.* [5], for example, who measured a strength range of 80–120 MPa for 40% Ni-YSZ bars.

Modulus of rupture of the anode tubes at different process stages was examined as shown in Fig. 8. Green tubes are fairly strong for handling. Tubes pre-fired at 1100°C were very fragile and weak. Co-sintering the electrolyte layer with the anode tube caused a 20% decrease in mechanical strength due to the thermal stress. Reduction of NiO to Ni strengthened the material by forming a Ni metal skeleton. Re-oxidizing the reduced anode caused a dramatic loss in strength, and destructive damage to fuel cells as can be seen from Figs 8 and 9. This may be due to the volume change of Ni to NiO, which destroyed the material structure.

4. Conclusions

The mechanical properties of the following SOFC support tubes were investigated: (1) electrolyte-supported tubular SOFC using 8YSZ; (2) anode supported tubular SOFC based on Ni-YSZ cermet, as-sintered and reduced.

An average burst strength of 97 ± 28 MPa was observed for 8YSZ electrolyte tubes and for as-sintered and reduced anode support tubes of 72 ± 23 MPa and 70 ± 16 MPa, respectively. From Weibull analysis a modulus of 3 was found for both the electrolyte and anode tube experimental data. This indicates a large amount of scatter in the measured results. This scatter in the measured burst strengths is likely due to imperfections introduced during the fabrication procedure and needs to be addressed when up-scaling. However, the average burst strength of both the as-sintered and reduced anode tubes is slightly lower than that observed for the electrolyte tubes, the actual breaking pressures are greater due to the greater wall thickness. The strength values for the anode support tubes, both as-sintered and reduced are comparative to values given in the literature for planar anode materials and have proven significantly more reliable in practice. The burst test apparatus provides a rapid assessment of the relative strengths of ceramic tubes giving a guide for pass-fail reference.

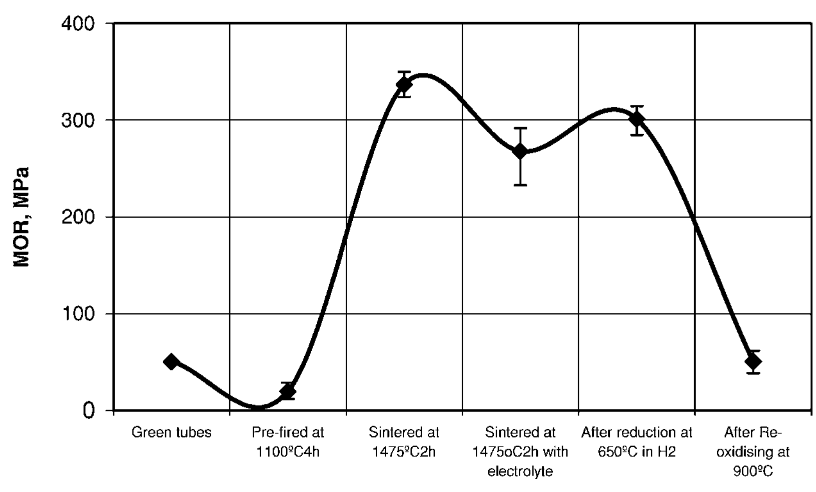

Figure 8 Mechanical properties of anode tubes at different process stages.

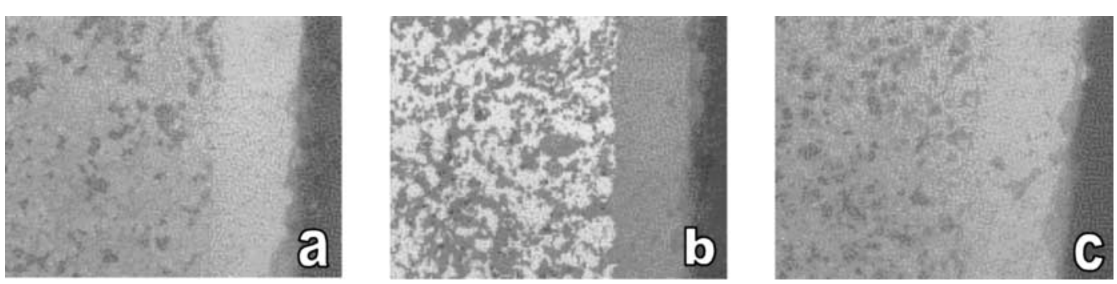

Figure 9 Microstructure of anode support tube at different stages with electrolyte coat. (a) sintered at 1475°C for 2 hours, (b) reduced (a) at 650°C in H_2, (c) re-oxidized (b) at 900°C.

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