ECONOMICAL FABRICATION OF MEMBRANE MATERIALS

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INTRODUCTION

The objective of this project is to develop novel approaches for the fabrication of membranes for hydrogen and oxygen separation. In past years this project has focused on the development of high densify infrared processing to rapidly sinter thin support membranes. This year the project has undertaken a new focus. The approach is two-fold: (1) continue the development and use of high density infrared processing as warranted and (2) initiate development of thin ceramic membranes supported on metallic supports. Initial studies are being carried out on novel proton conducting ceramic materials deposited on supported produced by Pall Corporation.

RAPID DENSIFICATION OF CERAMIC MATERIALS

ORNL has investigated the use of both a high density infrared and low density infrared process. The high density process utilizes a unique technology to produce extremely high-power densities of up to 3.5 kW/cm^2 with a single lamp, instead of using an electrically heated resistive element to produce radiant energy; controlled and contained plasma is utilized. The lamp consists of a 3.175-cm-diam quartz tube, which can be 10.16, 20.32, or 38.1 cm long. The lamp is sealed at the ends where the cathode and anode are located. Deionized water mixed with argon or nitrogen gas enters at the cathode side through high-velocity jets impinging at a given angle. Due to the high velocities and pressure, the de-ionized water is impelled to the wall of the quartz tube and spirals down the length of the tube in a uniform 2- to 3-mm-thick film. This water film serves two purposes: (1) to cool the quartz wall and (2) to remove any tungsten particulate that may be expelled from the electrodes. The gas moves in a spiral fashion through the center of the tube, and a capacitive circuit initiates the plasma. The plasma, which has a temperature in excess of 10,000 K, is stable and produces a radiant spectrum from 0.2 to 1.4 microns. The spectrum is primarily in the infrared (0.78 to 1.00 µm), although substantial energy is released in the visible wavelength, similar to the appearance of natural sunlight in energy distribution and color rendition. In contrast, the spectrum at a CO_2 laser with wavelengths near 10.6 microns is absorbed with much lower efficiency. The powder coatings discussed here are highly absorbing because the open areas act like black bodies. The low density light source is a tungsten halogen lamp which require no special cooling or facility for its use.

The samples sintered included both yttrium doped barium cerate (proton conductor for hydrogen separation) and a solid oxide fuel cell membrane composed yttria stabilized zirconia supported on a thick anode (NiO/yttria stabilized zirconia). These samples were prepared by tape casting to produce a porous

support followed by screen printing thick film membranes on its surface. In the case of barium cerate, both the support and membrane were composed of barium cerate.

The high density infrared process demonstrated that samples could easily be sintered to full density. In fact, thin films were fully densified on porous supports without interaction with the support in the case of the fuel cell or densification of the porous support. The sintering process was carried out very rapidly with the round trip cycle time (room temperature to sintering temperature to room temperature) taking no more than 60 minutes. In the case of 1 cm^2 no thermal shock or mechanical failure within the samples was noted. Examples of the samples are shown in Fig. 1.

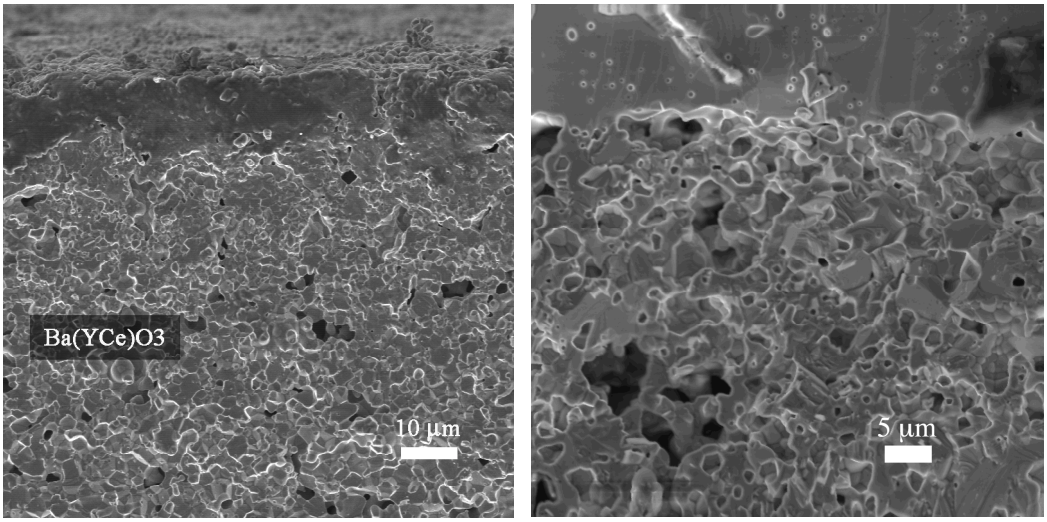

Fig. 1. Examples of barium cerate and a solid oxide fuel cell component sintered using the high density infrared process.

The high density infrared sintering process uses a high voltage power supply to generate the plasma used in sintering. This power supply consumes a great deal of energy during the sintering process that greatly impacts the efficiency and cost effectiveness of the process. In order to improve the economics of the process a low power density tungsten lamp set setup and used to sinter the same set of samples shown in Fig. 1. In order to qualify this process the heat flux of the low density lamp was measured using a heat flux sensor. This analysis determined that the heat flux of the low density lamp could only reach an equivalent heat of 1200°C. This level of heat is too low to sinter the samples shown in Fig. 1. Continued analysis indicated that only the high density lamp produced by Vortek is capable of producing the level of heat to full sintering the samples under investigation.

METALLIC SUPPORTED MEMBRANES STRUCTURES

Metallic supported membranes offer unique opportunity to solve problems with seals and mechanical integrity plaguing all ceramic planar and tubular devices. The use of a metallic support allows seals to be easily made using brazes technology. However, their use is not without the need to technological development. For example, several development issues need to be addressed:

1. Thermal expansion mismatch between the support and electrolyte
2. Creep of the metallic support
3. Potential oxidation depending on use
4. SiO_2 formation under the scale if used for fuel cells
5. Membrane deposition
6. Sintering to avoid oxidation of the metal

ANALYSIS OF POTENTIAL ISSUES

Metallic supports that best match the thermal expansion to materials like cerates are ferritic stainless steels that forms a chromia (Cr_2O_3) scale upon oxidation. These materials are potential candidate supports due to their close, but not exact, thermal expansion match to potential membrane materials. A large number of off-the-shelf ferritic stainless steels are available as the support material; however, their thermal expansions are not closely matched to candidate membrane materials. Figure 2 shows the thermal

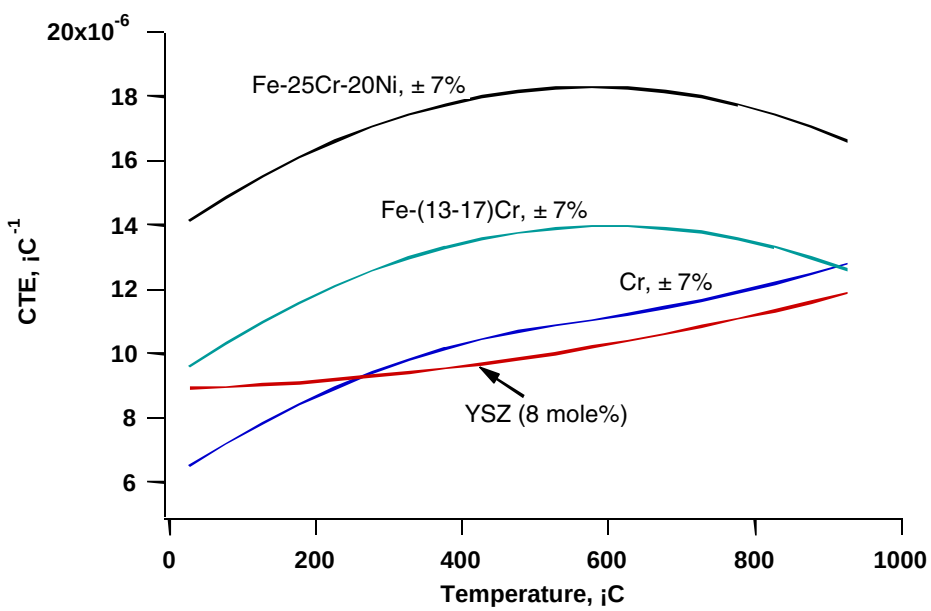

Fig. 2. Schematic overview of CTE data for austenitic Fe-25Cr-20Ni wt%, ferritic Fe-(13-17)Cr, pure Cr, and yttria stabilized zirconia [data from Thermophysical Properties of Matter, Volume 12, Y. S. Touloukian, R. K. Kirby, R. E. Taylor, and P. D. Desai, eds., 1979].

expansion of YSZ compared to several ferritic steels. Chrome concentrations in these alloys typically have to be in excess of 13 wt% to achieve a coherent chromia scale. One chromia-forming alloy of interest would be the Plansee Cr-5Fe-1Y_2O_3 wt% alloy, which was designed to match the thermal expansion characteristics of the YSZ electrolyte. However, because Cr-5Fe-1Y_2O_3 is brittle at room temperature, it is extremely expensive to machine and is currently not economically feasible at this point in time. Near net shaped powder processing is being pursued in order to reduce machining costs of this material.

One of the primary concerns with porous metals used at elevated temperatures is creep. Very little data has been collected on creep of porous materials, however, one fact is certain, it is significantly higher than that of a dense metallic sample. Microstructural engineering through controlled processing can reduce creep.

Two additional concerns with the use of ferritic stainless steels as the support if used for fuel cells are: (1) oxidation during processing of the air electrode and (2) oxidation during operation in the presence of a buffered gas (H_2, CO_2, H_2O). Figure 3 shows the parabolic rate constant for ferritic stainless steels as a function of temperature. At 1200°C the corresponding diffusion coefficient for oxygen diffusion into ferritic stainless steel is in the range 10^{-8} to 10^{-11} cm^2/sec. During sintering of the air electrode, this range of diffusion coefficients indicates that for a 1 hour (3600 seconds) soak in air the chromia scale will range from approximately 1 μm to 60 μm.

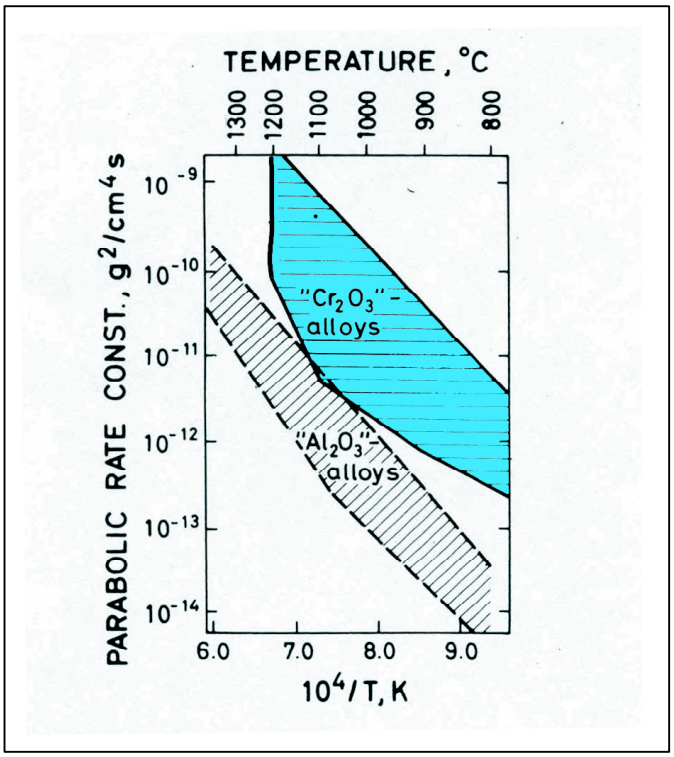

Fig. 3. Scatter bands for literature values of the parabolic rate constants for formation of chromia scales on binary chromium alloys. [P. Kofstad, High Temperature Corrosion, Elsevier Applied Science, New York 1988.]

The stability of chrome oxide was determined using the Ellingham diagram as a function of temperature and environment. The Ellingham diagram clearly indicates that any scale formed during processing will be stable in the operating environment of the fuel cell at all temperatures.

The diagram also indicates that a fuel environment with steam is quite oxidizing, and it would be expected that chromia scale would continue to grow during fuel cell operation at 700°C, albeit at a very

slow rate. Literature [C. T. Fujii and R. A. Meussner, *J. Electrochem. Soc.*, **111** 1215 (1964)] data clearly indicates that Fe-Cr alloys, with up to 15% Cr, oxidize in Ar-H_2O environments. Additional data [K. Przyblski and G. J. Yurek, *Materials Science Forum*, **63** 1–74 (1989)] indicate the growth rate of chromia is independent of oxygen partial pressure at 800 and 900°C from 1 atm to 10^{-22} atm in a H_2-H_2O atmosphere. Lower oxygen partial pressures will reduce the iron content in the scale that may alter the conductivity of the scale.

A final concern with the use of ferritic stainless steels is the residual Si level in the alloy. It is well established that minor additions of Si (0.5–2 wt% range) to Cr_2O_3-forming alloys such as ferritic steels result in near continuous or continuous SiO_2 formation at the alloy/scale interface [B. Ahmad and P. Fox, *Oxid. Met.*, **52**, 113 (1999)]. Although usually beneficial for oxidation resistance, such SiO_2 would significantly degrade the electrical conductivity of the scale, making the alloy unsuitable for use in SOFC applications. It has recently been shown [M. P. Brady, B. A. Pint, D. T. Hoelzer, I. W. Wright, and T. R. Amrstrong, submitted to *Electrochemical and Solid State Letters*] by cross-section transmission electron microscopy (TEM) that a Si impurity level of only 0.05 wt% resulted in the formation of a nearly continuous amorphous SiO_2 layer, up to 0.5 micron thick in some regions, at the alloy scale interface in Y_2O_3 dispersion strengthened Fe-13Cr wt% exposed for 10,000 h at 700°C in air (Fig. 4). This level of Si is well within the impurity range present in commercially available Cr_2O_3 forming ferritic steels. It is likely that many Cr_2O_3 forming alloys evaluated for performance in fuel cell environments contained similar or even higher levels of Si impurities, and that their electrical performance was adversely effected by SiO_2 at the alloy/scale interface. Unless specifically characterized in cross-section by TEM or other high resolution techniques, the presence of the SiO_2 would be missed.

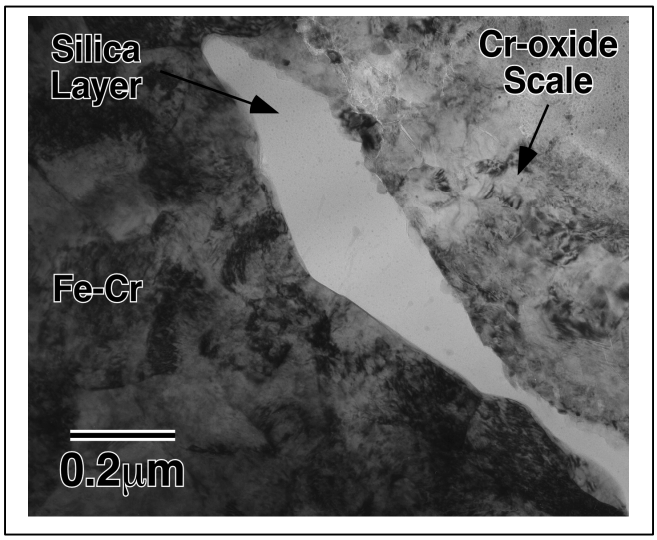

Fig. 4. TEM cross-section micrograph of Y_2O_3 dispersion strengthened Fe-13Cr wt% exposed for 10,000 h at 700°C in air showing SiO_2 formation at the alloy/Cr_2O_3 interface.

CONCLUSIONS

The use of metallic supports for thick film ceramic membranes has the potential to solve several key development issues- robustness and sealing. ORNL is pursuing the development of proton conducting membranes supported on 0.5 mm thick stainless steel supports. The membranes are being deposited using

slurry deposition processes and sintering processes have been developed that prevent oxidation of the support material. Microstructures of the membranes and test data on the flux of hydrogen through the membranes will be determine later this year and reported on later.