Oxygen Transport Ceramic Membranes

Quarterly Report

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Conversion of natural gas to liquid fuels and chemicals is a major goal for the Nation as it enters the 21st Century. Technically robust and economically viable processes are needed to capture the value of the vast reserves of natural gas on Alaska's North Slope, and wean the Nation from dependence on foreign petroleum sources. Technologies that are emerging to fulfill this need are all based syngas as an intermediate. Syngas (a mixture of hydrogen and carbon monoxide) is a fundamental building block from which chemicals and fuels can be derived. Lower cost syngas translates directly into more cost-competitive fuels and chemicals.

The currently practiced commercial technology for making syngas is either steam methane reforming (SMR) or a two-step process involving cryogenic oxygen separation followed by natural gas partial oxidation (POX). These high-energy, capital-intensive processes do not always produce syngas at a cost that makes its derivatives competitive with current petroleum-based fuels and chemicals.

In the mid 80's BP invented a radically new technology concept that will have a major economic and energy efficiency impact on the conversion of natural gas to liquid fuels, hydrogen, and chemicals.[1] This technology, called Electropox, integrates oxygen separation with the oxidation and steam reforming of natural gas into a single process to produce syngas with an economic advantage of 30 to 50 percent over conventional technologies.[2]

The Electropox process uses novel and proprietary solid metal oxide ceramic oxygen transport membranes [OTMs], which selectively conduct both oxide ions and electrons through their lattice structure at elevated temperatures.[3] Under the influence of an oxygen partial pressure gradient,

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[1] Mazanec, T. J.; Cable, T. L.; Frye, J. G., Jr.; US 4,793,904, 27 Dec 1988, assigned to The Standard Oil Company (now BP America), Mazanec, T. J.; Cable, T. L.; US 4,802,958, 7 Feb 1989, assigned to the Standard Oil Co. (now BP America), Cable, T. L.; Mazanec, T. J.; Frye, J. G., Jr.; European Patent Application 0399833, 24 May 1990, published 28 November 1990.

[2] Bredesen, R.; Sogge, J.; "A Technical and Economic Assessment of Membrane Reactors for Hydrogen and Syngas Production" presented at Seminar on the Ecol. Applic. of Innovative Membrane Technology in the Chemical Industry", Cetraro, Calabria, Italy, 1-4 May 1996.

[3] Mazanec, T.J., *Interface*, 1996; Mazanec, T.J., *Solid State Ionics*, 70/71, 1994 11-19; "Electropox: BP's Novel Oxidation Technology", T.J. Mazanec, pp 212-225, in "The Role of Oxygen in Improving Chemical Processes", M. Fetizon and W.J. Thomas, eds, Royal Society of Chemistry, London, 1993; "Electropox: BP's Novel Oxidation Technology", T.J. Mazanec, pp 85-96, in "The Activation of Dioxygen and Homogeneous Catalytic Oxidation", D.H.R. Barton, A. E. Martell, D.T. Sawyer, eds, Plenum Press, New York, 1993; "Electrocatalytic Cells for Chemical Reaction", T.J. Mazanec, T.L. Cable, J.G. Frye, Jr.; Prep Petrol Div ACS, San Fran, 1992 *37*, 135-146; T.J. Mazanec, T.L. Cable, J.G. Frye, Jr.; *Solid State Ionics*, 1992, 53-56, 111-118.

oxygen ions move through the dense, nonporous membrane lattice at high rates with 100 percent selectivity. Transported oxygen reacts with natural gas on the fuel side of the ceramic membrane in the presence of a catalyst to produce syngas.

In 1997 BP entered into an OTM Alliance with Praxair, Amoco, Statoil and Sasol to advance the Electropox technology in an industrially sponsored development program. These five companies have been joined by Phillips Petroleum and now are carrying out a multi-year $40+ million program to develop and commercialize the technology. The program targets materials, manufacturing and engineering development issues and culminates in the operation of semi-works and demonstration scale prototype units.

The Electropox process represents a truly revolutionary technology for conversion of natural gas to synthesis gas not only because it combines the three separate unit operations of oxygen separation, methane oxidation and methane steam reforming into a single step, but also because it employs a chemically active ceramic material in a fundamentally new way. On numerous fronts the commercialization of Electropox demands solutions to problems that have never before been accomplished. Basic problems in materials and catalysts, membrane fabrication, model development, and reactor engineering all need solutions to achieve commercial success.

Six important issues have been selected as needing understanding on a fundamental level at which the applied Alliance program cannot achieve the breadth and depth of understanding needed for rapid advancement. These issues include

1. Oxygen diffusion kinetics (University of Houston)
2. Grain structure and atomic segregation (University of Illinois - Chicago)
3. Phase stability and stress development (University of Missouri - Rolla)
4. Mechanical property evaluation in thermal and chemical stress fields (University of Alaska Fairbanks)
5. Graded ceramic/metal seals (Massachusetts Institute of Technology)

Statement of Work

Task 1   Design, fabricate and evaluate ceramic to metal seals based on graded ceramic powder / metal braze joints.

Task 2   Evaluate the effect of defect configuration on ceramic membrane conductivity and long term chemical and structural stability.

Task 3   Determine materials mechanical properties under conditions of high temperatures and reactive atmospheres.

Task 4   Evaluate phase stability and thermal expansion of candidate perovskite membranes and develop techniques to support these materials on porous metal structures.

Task 5   Assess the microstructure of membrane materials to evaluate the effects of vacancy-impurity association, defect clusters, and vacancy-dopant association on the membrane performance and stability.

Task 6   Measure kinetics of oxygen uptake and transport in ceramic membrane materials under commercially relevant conditions using isotope labeling techniques.

This is the third quarterly report on oxygen Transport Ceramic Membranes. In the following, the report describes the progress made by our university partners in Tasks 1 through 6, experimental apparatus that was designed and built for various tasks of this project, thermodynamic calculations, where applicable and work planned for the future

Task 1 & 2 Development of Ceramic Membrane/Metal Joints

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ABSTRACT

This is the fourth quarterly report on a new study to develop a ceramic membrane/metal joint. The first experiments using the La-Sr-Fe-O ceramic are reported. Some of the analysis performed on the samples obtained are commented upon. A set of experiments to characterize the mechanical strength and thermal fatigue properties of the joints has been designed and begun. Finite element models of joints used to model residual stresses are described.

Preliminary experiments using La-Sr-Fe-O discs.

Several experiments have been performed using ceramic oxygen membrane ($La_6Sr_4FeO_3$) and Haynes 230® discs. The first studies, using "conventional" reactive brazing alloys (with titanium or zirconium additions) showed excessive reactivity between the ceramic membrane and the braze. It is suspected that extensive decomposition of the membrane takes place due to the reaction between the reactive element dissolved in the braze and the oxygen from the ceramic.

Because of the extensive reactivity exhibited by titanium/zirconium-containing alloys, other liquid phase joining techniques were surveyed. Thanks to some preliminary experiments, it has been found that conventional amorphous nickel-based alloys are capable of wetting the ceramic surface. Nickel-based brazing alloys also have the advantage of having relatively low brazing temperatures (1090 C). This brazing temperature is achieved by the additions of boron or silicon to the nickel-based alloy.

Additionally, the fact that boron can be diffused away from the braze, providing that the joint is held at high temperature for long enough time, constitutes an additional advantage since it would be possible (in theory) to braze at one temperature, while operating at a higher one.
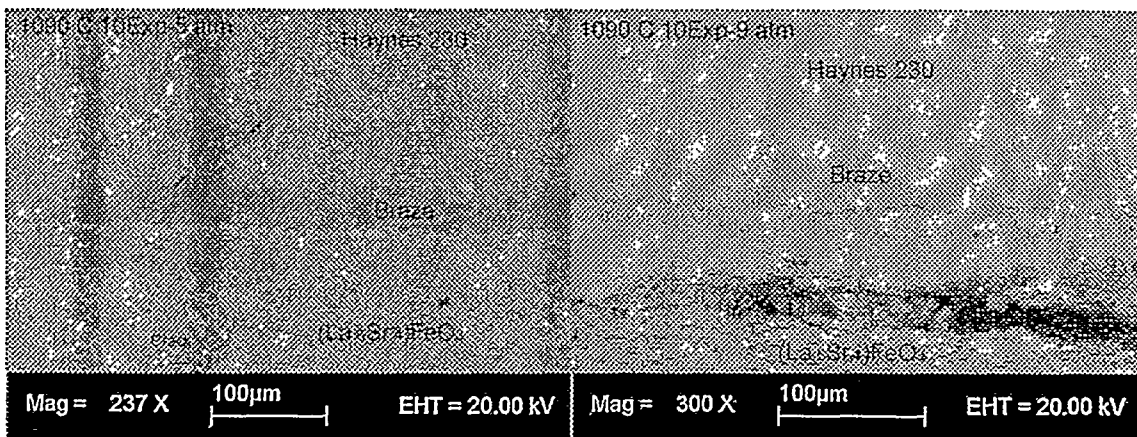

Figure 1 Ceramic membrane/braze/super alloy joint

Despite the good wettability behavior of these brazing alloys two important phenomena have been observed:

- Circumferential cracks, parallel to the ceramic/metal interface, appear to form after the joints are created. Preliminary evidence suggests that this cracking might be reduced if the brazing process takes place under higher oxygen partial pressure environments. In fact, it has been observed that this cracking appears to be minimized when the oxygen partial pressure is above 10^{-5} atm (See Figure 1 and Figure 2). Further research has to be done to verify this preliminary result.
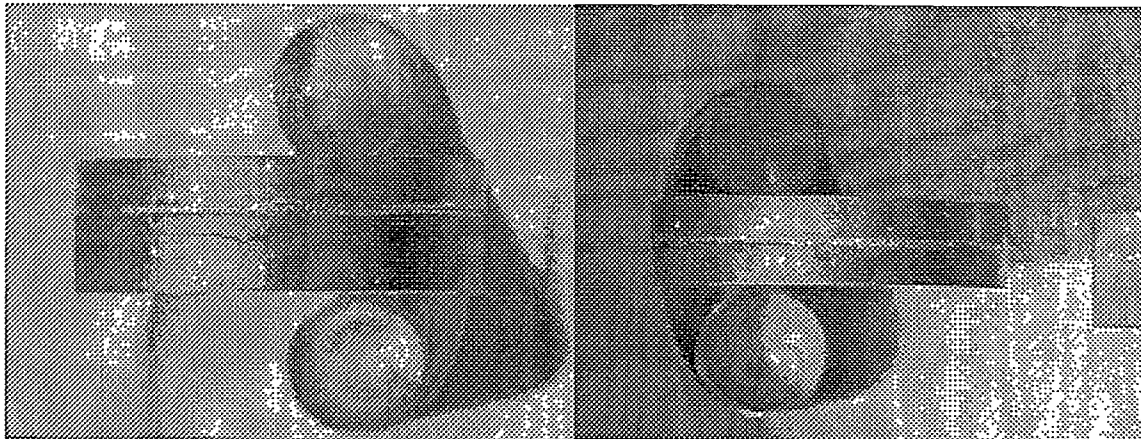

Figure 2 Ceramic membrane/ Haynes 230 joints. Left joint made at 10^{-9} atm. Right joint made at 10^{-5} atm.

- It has become evident that despite the relatively low chemical reactivity of these nickel-based brazing alloys, extensive reactions between the brazing alloy and the ceramic membrane occur when brazing. The following figure shows a typical braze/ceramic interface, with the corresponding chemical compositions obtained by EDS analysis.
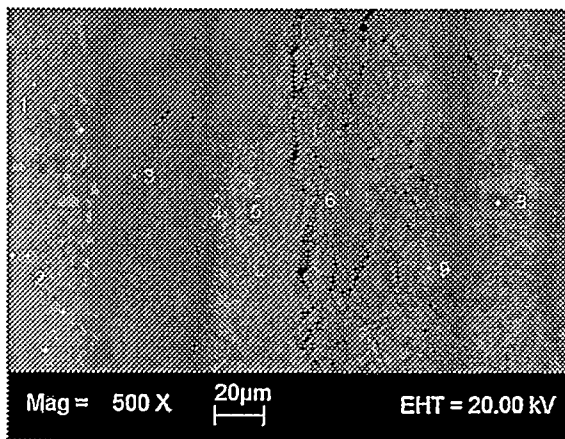
	1	2	3	4	5	6.9	7	8
Ni	56	21	70	0	0	0	0	0
Cr	25	30	9	0	0	0	0	0
W	13	40	0	0	0	0	0	0
Mo	1	0	0	0	0	0	0	0
Ti	0	0	0	0	0	0	0	0
Si	0	0	3	0	0	0	0	0
Fe	2	1	7	1	1	14	15	69
La	0	0	0	23	12	13	15	1
Sr	0	0	82	1	15	8	8	2
O	0	0	0	76	71	65	62	29
Mn	4	4	0	0	0	0	0	0

Mag = 500 X   20μm   EHT = 20.00 kV

Figure 3 Ceramic/braze interface. Compositions obtained using EDS.

The composition analyses of points 4 through 9 in Figure 3 show the extent of the reaction between the ceramic membrane and the brazing alloy. It can be observed that the first zone in contact with the brazing alloy has been depleted of both iron and strontium, while the next layer has only been iron-depleted. The formation of iron-rich "islands" can also be observed, which are not normally observed in the pre-brazing ceramic membrane.
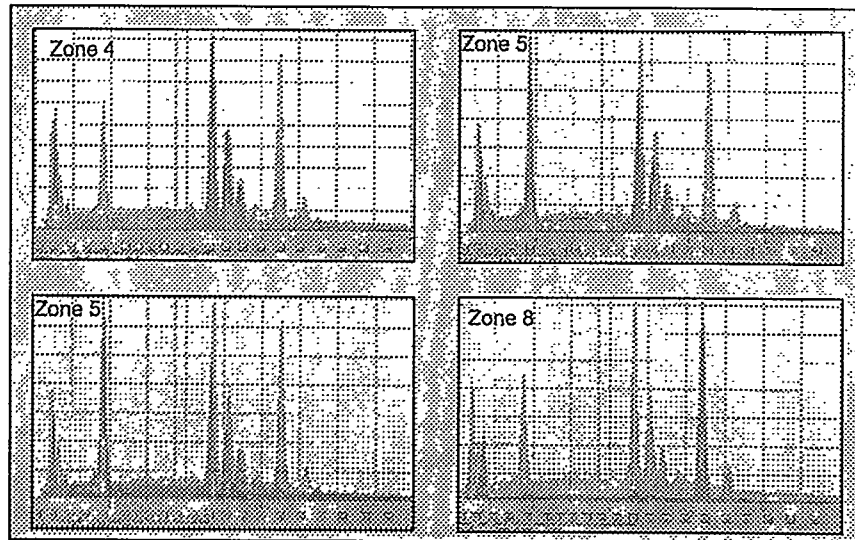

Figure 4 EDS spectra of different zones in previous figure.

The figure above compares the spectrum obtained from a "perovskite" sample before the brazing procedure takes place (green) with the spectrum observed after the braze has reacted with the ceramic surface (red). As can be seen, the composition of the ceramic close to the braze/membrane interface is significantly modified.

It is important to note that the reaction mechanism occurring at the interface has not been elucidated yet and that more research work on this system needs to be done. It is expected that changes in the chemistry of the brazing alloy can reduce the extent of the reaction between the braze and the ceramic.

It is suspected that the excessive reaction observed in the present experiments has a direct relationship with the cracks formed parallel to the ceramic/metal interface. Thus, by studying the reactions at the interface it would be possible to improve the integrity of the ceramic/metal joints.

In the future, a new series of experiments, in which both the chemical composition of the brazing alloy and the atmosphere under which the joining takes place are controlled, will be performed. If possible, samples will be prepared for mechanical shear test experiments.

Properties of the Joints

Testing techniques are being developed to measure and understand the mechanical properties of concentric metal-ceramic membrane joints. Since actual perovskite tubes are currently unavailable, we have chosen to study the properties of alumina tubes brazed around nickel-based alloy rods, using commercially available Ticusil™ brazing alloy. These materials were chosen

because the brazing of alumina with this alloy is well documented in the literature, and because Ni-based alloys with varying thermal expansions and elastic properties are available.

**Table 1: Room Temperature Properties of Materials Used in Experiments**

Material	CTE (μin/in/°C)	E (ksi)	0.2% YS (ksi)
Alumina	8.5	53,070	--
Invar	1	21,460	70.0
Hastelloy B2	10	31,038	57.5
Inconel 600	12	31,100	40.0

We are interested in how the properties of the base metal affect the residual stresses present in the brazed joint. This knowledge will help us design lower-stress joints for the ceramic membrane application.

The testing and analytical methods that are being developed will be applied to the La-Sr-Fe-O/Haynes 230 system when the ceramic (and associated property data) is available.

Measurement of Shear Strength

The geometry of the brazed rod-in-tube samples is shown schematically in Figure 5. The inner diameter of the ceramic tube is 0.257". Two different rod diameters are used: 0.250" and 0.247". The rod and tube are each approximately 0.75" long, with a brazed overlap of approximately 0.30".
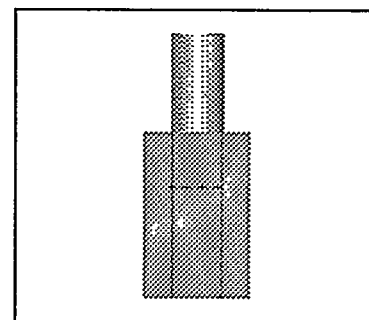
The shear strength of the joints is measured by loading samples in compression using an Instron testing machine. If the braze is weaker than the ceramic tube, the joint will fail by shearing the interface, however if the braze is stronger, the ceramic will fracture in compression.

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Figure 5 Mechanical tests specimens

Preliminary experiments run with Hastelloy B2 and Invar rods brazed to alumina, using a variety of metal rod diameters and cooling rates, led to the design of the current experiment. Brazed joints will be made from three different types of metal rods (Hastelloy B2, Invar, and Inconel 600), each in two diameters (0.250" and 0.247"). Different metals are being used to examine the impact of CTE mismatch on strength, while the different diameters will show if the filler metal thickness affects the strength of the brazed joint. Samples will be made under the following conditions, and their strength will be evaluated under compression loading:

1) Brazed at 850°C for 20min, and cooled at 1.7°/min
2) Brazed at 850°C for 20min, and cooled at 1.7°/min. Subjected to one thermal cycle between 100°C and 700°C, at a rate of 2°/min.
3) Brazed at 850°C for 20min, and cooled at 1.7°/min. Subjected to five thermal cycles between 100°C and 700°C, at a rate of 2°/min.