UAF-ANL-DOE HTM Final Report

Project Information		
DOE Award No.:	DE-FG02-09ER46628	
Name of Institution:	University of Alaska Fairbanks (UAF)	
Project Title:	Novel Dense Membranes for Hydrogen Separation for Energy Applications	
Principal Investigator:	Dr. Sukumar Bandopadhyay (PI)	30% Partial Support
Period Covered:	Sep. 2009 – Aug. 2013	
Lists of Contributing People and Participating National Lab:	1. Dr. Uthamalingam (Balu) Balachandran, Sr. Scientist/Manager, Ceramics Section, Argonne National Laboratory , Argonne, IL	No Financial Support
	2. Dr. Nagendra Nag, Group Manager, Advanced Process Development, Surmet Corporation, Buffalo, NY	No Financial Support
	3. Lily, Yongjun Zhang, Ph.D. Student, UAF	Full Financial Support
A Brief Description of Project Goals and Objectives:	The main objectives of this project are: (1) Characterization of the thermo mechanical properties of the novel dense HTM bulk sample; (2) Development of a correlation among the intrinsic factors (such as grain size and phase distribution), and the extrinsic factors (such as temperature and atmosphere) and the thermo-mechanical properties (such as strengths and stress) to predict the performance of a HTM system (HTM membrane and porous substrate) ; and (3) Evaluation of the stability of the novel HTM membrane and its property correlations after thermal cycling.	
Planned Activity of Next year:	N/A	
Lists of Other Projects:		

Financial Information*
DOE Grant Amount: $419,894.00

Match Amount: $ 44998	**Match Source: University of Alaska Fairbanks**
UAF Grant Spent to Date: $444,705	**Match Spent to Date: $50,936**

*More detailed information at the table attached

A Brief Description of Accomplishments

The commonly used methods for hydrogen separation presently are: pressure swing adsorption (PSA), temperature swing adsorption, electrical swing adsorption and cryogenic processes [1, 2, and 3]. These technologies require either extremely high energy or a long time period, thus making them very expensive while producing a purity of hydrogen great than 99%. Hence, there is a growing need for the development of an environmentally benign, inexpensive technology for separating hydrogen from syngas. Membrane-related hydrogen separation processes are considered attractive alternatives to PSA and other energy-driven processes depending upon purity and scale of production. Advanced membrane technologies [4-8] may finally prove to be the key to successful, economical production of pure hydrogen.

Most research in hydrogen membrane industry is focused on the areas of separation technologies and characterizations of hydrogen fluxes. No significant work has been performed to determine the effect of the intrinsic factors (such as grain size and phase distribution) and extrinsic factors (such as temperature and atmosphere) on the macro-structural and thermo mechanical properties of hydrogen transfer membranes (HTM). It is recognized that none of these membranes will be used without a porous support. Therefore, a good porous support is essential on which a functional membrane can be deposited. A clear understanding of the correlation between the microstructural and the thermo-mechanical properties of a porous substrate is, therefore, required to define the complete HTM system, which consists of a functional HTM membrane and a porous substrate.

A novel dense HTM bulk sample was developed by Argonne National Laboratory (ANL) for high hydrogen permeance (ANL-3e HTM), and was provided to the University of Alaska Fairbanks. One of the key requirements is that the cermet membrane system should not fail during cycling, and the thermal expansion and chemical expansion must be similar. Cermet membranes must also have sufficient mechanical strength to withstand the stress induced due to the changes in temperature and feed gas composition. It is generally accepted that changes in the temperature produce stress in all membranes including the ANL-3e membranes because they consist of two different materials with different coefficients of thermal expansion. Change in feed gas composition also produces stress because the lattice parameter of Pd in the ANL 3-e HTM depends on the hydrogen concentration in the feed gas. It must be understood, however, that cycling is of no interest for property correlation unless it is a system problem. The building up of

stress is considered as one of the major problems. The origin and cause of this stress must be clearly understood. It is also important to examine the role of lattice expansion and chemical expansion, as well as which one is dominant and how it manifests itself.

The main objectives of this project are: (1) Characterize the thermo mechanical properties of the novel dense HTM bulk sample; (2) Develop a correlation among the intrinsic factors (such as grain size and phase distribution), and the extrinsic factors (such as temperature and atmosphere) and thermo-mechanical properties (such as strengths and stress) to predict the performance of a HTM system (functional HTM membrane and porous substrate); and (3) evaluate the stability of the novel HTM membrane and its property correlation after thermal cycling.

In the initial phases of the project, a reference material of alumina and several substrate ceramic material of toughened zirconia polycrystalline were selected to be evaluated for the thermo-mechanical properties, such as elastic properties, flexural strength, Vickers hardness and coefficient of thermal expansion. The thermo-mechanical properties were investigated at room temperature as well as at elevated temperatures. The effects of thermal cycling for temperature ranging from 50ºC to 850ºC on the mechanical properties and on the stability of the reference materials were investigated using a customized thermal cycling equipment. Both the as-received and the thermal-cycled samples were analyzed by X-ray diffraction (XRD) for its phase analysis and surface texture analysis. Scanning electron microscopy (SEM) was employed to understand the mechanism of the microstructural changes and its effects on the mechanical properties.

In the current phase, the hydrogen transport membrane (HTM) cermet bulk sample supplied by Argonne National Laboratory (ANL) was characterized for its physical and mechanical properties at both room temperature and at elevated temperature up to 1000ºC. Micro-structural properties, such as X-ray Diffraction (XRD) phase analysis, thermogravimetry and differential thermal analysis (TG/DTA), texture, microanalysis of chemical composition and residual stress were also evaluated in order to understand the changing mechanism of the microstructure properties and its effects on the mechanical properties of materials. The HTM raw powder was used for its phase analysis, texture, TG/DTA and residual stress in order to compare the change in the properties after being processed to HTM solid sample at high temperature and pressure. A correlation of the microstructural and thermo mechanical properties of the HTM system was established based on the results of the thermo-mechanical and micro-structural properties characterizations for both HTM and the substrate material.

For the ANL's HTM cermet bulk sample, its density is about 11.3 g/cc and average dynamic Young's modulus (E-Value) is approximately 145 GPa with a Poisson's ratio (ν) of 0.34. The Vickers Hardness Numbers ($\overline{HV}$ numbers) values of HTM cermet samples averaged in the range of 2.0 ~ 2.2 GPa, regardless of the loading forces in the range of 100-1000 g. The mean flexural strength (σ_{fs}) for HTM cermet is approximately 356 MPa at room temperature and it decreases to 284 MPa as the temperature is increased to 850ºC. The mean flexural strength values are summarized in Table 1. Loading-displacement curves for the flexural strength (σ_{fs}) tests for HTM cermet are plotted in Figure 1. The HTM cermet samples at room temperature and at 500ºC fractured without any significant plastic deformation, and thus, are considered to be a brittle solid. Whereas, at 850ºC, the HTM cermet samples fractured preceded by extensive plastic deformation, and thus, behaved more like a ductile material, as shown in Figure 1.

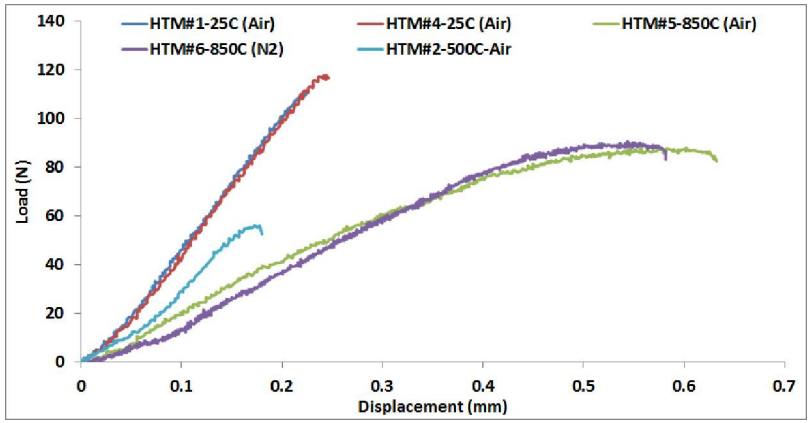


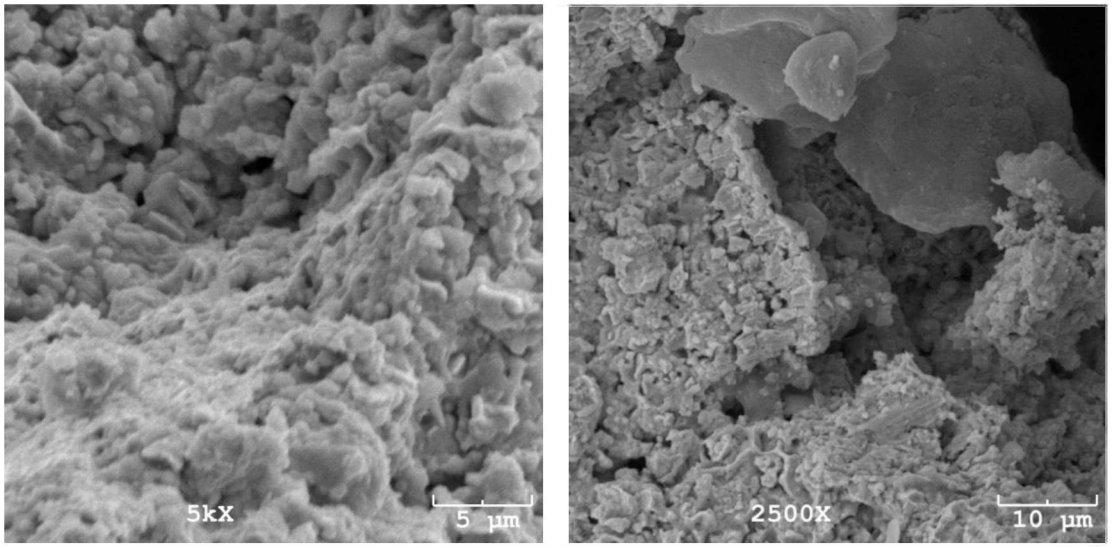
Figure 1 : Load-displacement curves of 4-point bending tests for HTM at three different testing temperatures: 25ºC, 500ºC, and 850ºC

Table 1: Flexural strength for HTM at three different testing temperatures

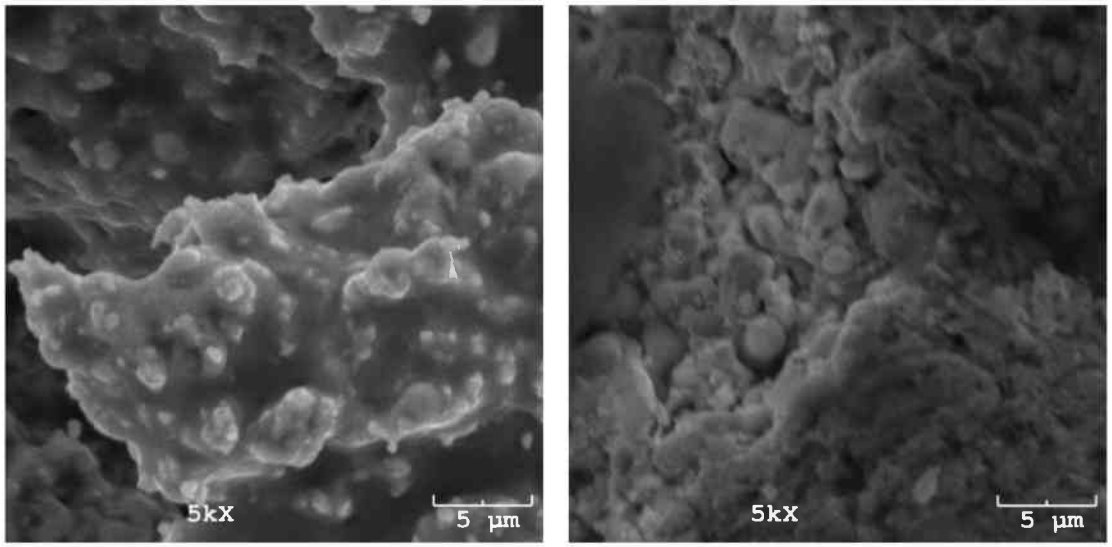
Sample ID	Temperature (ºC)	Atmosphere	σ_{fs} (MPa)	Mean σ_{fs} Value (MPa)
HTM#1	25	Air	342.51	356.56
HTM#4	25		370.61	
HTM#2	500		175.16	175.16
HTM#5	850		284.74	284.50
HTM#6	850	N2	284.25	

SEM observations of HTM fractured halves after its flexural strength test at room temperature of 25ºC indicate that the cracks originate from the inherent pre-existing pores and the micro-cracks, as shown in Figure 2 (a) . When the temperature is increased to 500ºC, the cracks are found to initiate from the ZrO_2 phase, as shown in Figure 2 (b). At the elevated temperature of 850ºC, the cracks develop from the thermal-spalling or shearing in both air and the N_2 environment, as seen from Figure 2 (c) and (d). The HTM

crystalline particles on the HTM sample tested in air at 850°C, as shown in Figure 2 (c), is due to the oxidation of Pd phase to PdO, as verified by both the XRD and the TG/DTA analysis.



(a) 25ºC in air (b) 500ºC in air



(c) 850ºC in air (d) 850ºC in N_2

Figure 2 : Scanning Electron Microscopy (SEM) observation after flexural strength tests for HTM at 25, 500 and 850ºC in both air and N_2

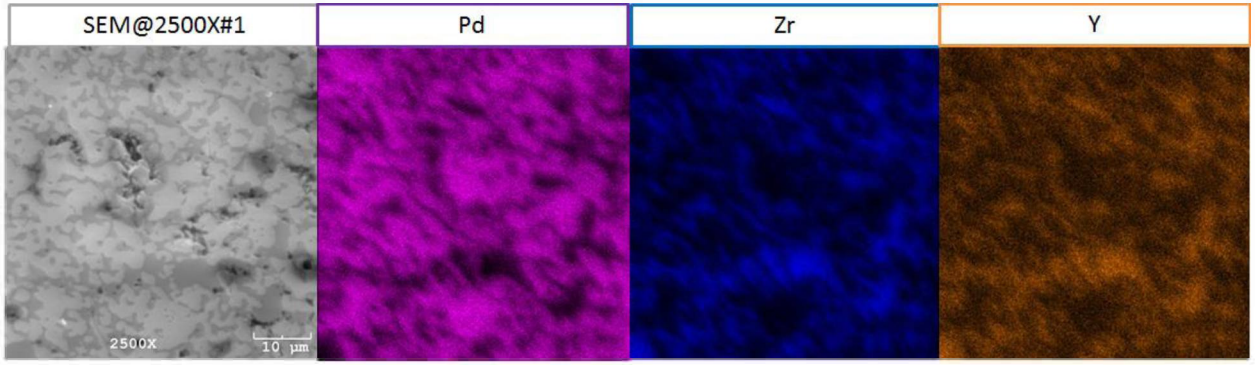
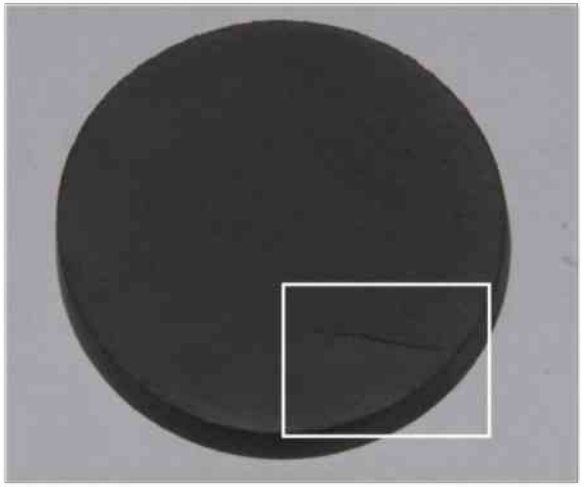
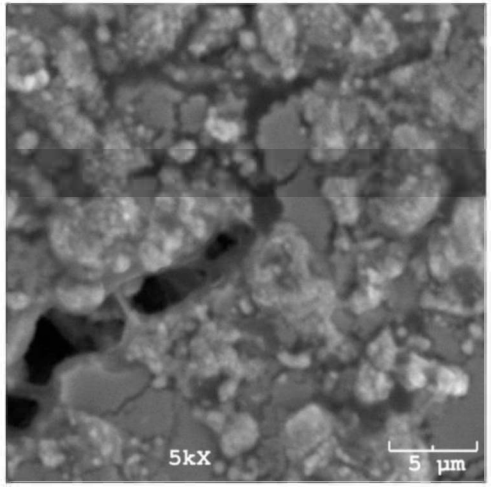


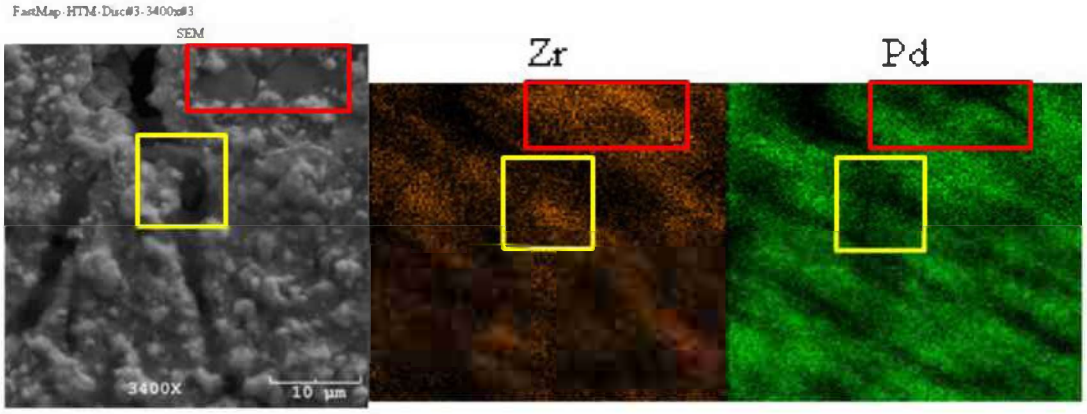
Figure 3: Surface morphology for HTM as-received by SEM with EDS



(a) Visual observation of a Macro crack



(b) SEM Surface Morphology

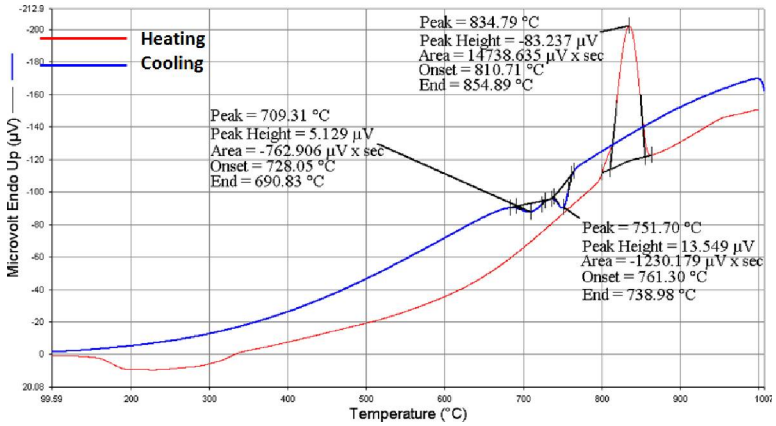


(c) SEM with EDS

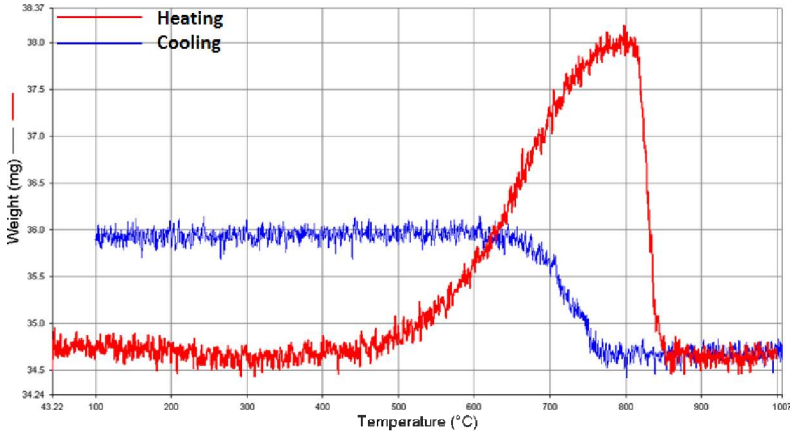
Figure 4: Fractography observation for cracks on HTM surface after 500 thermal cycling treatment between 50-850ºC in Air

As compared to the surface morphology of HTM cermet as-received shown in Figure 3, visually observable cracks appeared on the surface of HTM cermet with continuous thermal cycling after 500 thermal cycles, as shown in Figure 4.

The average Coefficient of Thermal Expansion (CTE), α_{avg}, for the HTM cermet in air is approximately $10x10^{-6}$/K, and closely approximates to that of the HTM cermet in N_2. The differential thermal analysis (DTA) reveals that the exothermic peak centered at 800ºC during the heating process is associated with the oxidation of Pd to PdO. Whereas, the exothermic peaks centered at 650ºC during the cooling process where PdO is dissociated back to Pd and oxygen, as plotted in Figure 5 (a). The associated weight gain and the weight loss for the respective oxidation and the dissociation between Pd and PdO could also be observed from the Thermogravimetry Analysis (TGA), as shown in Figure 5 (b).



(a) Endothermic peak during heating process and exothermic peaks during cooling process



(b) Weight changes during both heating and cooling processes

Figure 5: Thermogravimetry (TG) and differential temperature analysis (DTA) for HTM powder in air

Electron microanalysis, such as the powder diffraction by X-ray Diffraction (XRD) (Figure 6), X-ray florescence (XRF), Scanning Electron Microscope (SEM) with energy dispersive spectrometers (EDS) (Figure 3 and Figure 4) and the electron microprobe equipped with EDS verifies that the HTM cermet sample is approximately a composite of 70–80 wt % of Pd, and 20–30 wt % of YSZ. The XRD powder diffraction results show an increased amount of PdO in HTM cermet after 120 and 500 thermal cycles, as shown in Figure 6, which is consistent with the observation of the TG/DTA results.

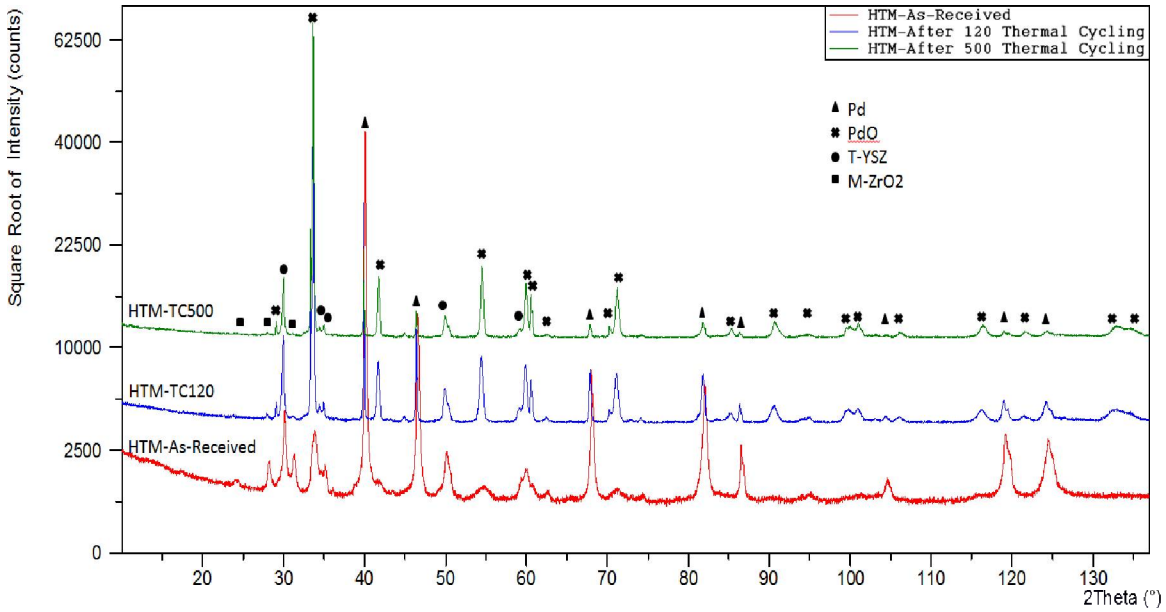


Figure 6: XRD phase analysis for HTM cermet as received and after 120 and 500 thermal cycles in Air

The normal stress and shear stresses from the Mohr's circle (Figure 7) indicate that the residual stress in the HTM cermet sample is mainly as compressive residual stress in the magnitude of -135 to -155 MP, and with very little shear stress (in the magnitude of 10 MPa). The magnitude of change in the normal stress and the shear stress is insignificant in the HTM after 120 thermal cycles, as shown in Figure 7. However, the principle normal stress changes from compressive to tensile residual stress and a significant increase in the shear stress in the HTM after 500 thermal cycles, as shown in Figure 7.

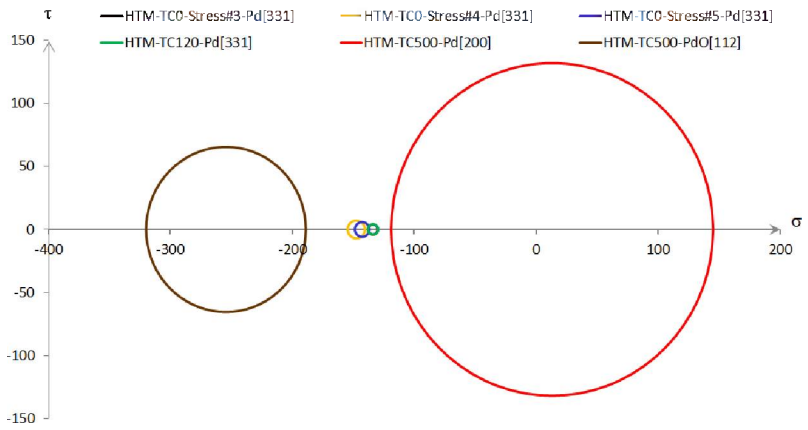


Figure 7: Mohr's circle calculated from the residual stresses for HTM cermet both as received (HTM-TC0), and after 120 (HTM-TC120) and 500 thermal cycles (HTM-TC500) in Air

Based on all results and analysis of the thermo mechanical properties for the HTM cermet bulk samples, several important conclusions can be drawn. The mean σ_{fs} at room temperature is approximately 356 MPa for the HTM cermet. The mean σ_{fs} value decreases to 284 MPa as the temperature increases to 850ºC. The difference in atmosphere, such as air or N_2, had an insignificant effect on the flexural strength values at 850ºC for the HTM cermet.

The HTM cermet samples at room temperature and at 500ºC fractured without any significant plastic deformation. Whereas, at 850ºC, the HTM cermet samples fractured, preceded by an extensive plastic deformation. It seems that the HTM cermet behaves more like an elastic material such as a nonmetal ceramic at the room temperature, and more like a ductile material at increased temperature (850ºC).

The exothermic peak during the TG/DTA tests centered at 600ºC is most likely associated with both the enthalpy change of transformation from the amorphous phase into crystalline zirconia and the oxidation of Pd phase in HTM cermet in air. The

endothermic peak centered at 800ºC is associated with the dissociation of PdO to Pd for the HTM cermet sample in both inert N_2 environment and air. There is a corresponding weight gain as oxidation occurs for palladium (Pd) phase to form palladium oxide (PdO) and there is a weight loss as the unstable PdO is dissociated back to Pd and oxygen.

The normal stress and shear stresses from the Mohr's circle indicate that the residual stress in the HTM cermet sample is mainly as compressive residual stress in the magnitude of -135 to -155 MP, and with very little shear stress (in the magnitude of 10 MPa). The magnitude of change in the normal stress and the shear stress is insignificant in the HTM after 120 thermal cycles. However, the principle normal stress changes from compressive to tensile residual stress and there is a significant increase in the shear stress after 500 thermal cycles. The calculated value based on the equation and the Mohr's circle is found to be consistent with the experimental value for the as-received HTM cermet samples. At some rotation (ϕ) angle, the residual stress was found to be as tensile stress. Most ceramic material is weak in tension, and develops microscopic cracks. With treatment of 120 thermal cycles between 50–850ºC, the HTM- sample exhibited thermally-induced cracks on the surface. Visually observable cracks appeared on the surface of HTM cermet with continuous thermal cycling, after 500 thermal cycles.

The XRD powder diffraction analysis indicated an increased amount of crystalline PdO in HTM cermet after 120 and 500 thermal cycles as compare to the as-received samples. The Pd peaks were found to significantly decrease in peak intensity with thermal cycling. Higher peak intensity for PdO phase was observed with increased number of thermal cycles. A monoclinic zirconia phase was first identified in the as-received HTM sample. However, with thermal cycling treatment of both 120 and 500 thermal cycles, the M-ZrO_2 phase is transformed to the tetragonal YSZ, which is consistent with the thermal analysis results by TG/DTA.

Correlations of the microstructural and thermo-mechanical properties of both selected reference material and ANL-3e HTM cermet bulk sample are affected mainly by porosity and microstructural features, such as grain size and pore size/distribution. The Young's Modulus (E-value), especially, is positively proportional to the flexural strength for materials with similar crystallographic structure. For different crystallographic materials, physical properties such as E and density are independent of mechanical properties, such as flexural strength. Microstructural properties, particularly, grain size and crystallographic structure, and thermodynamic properties

are the main factors affecting the mechanical properties at both room and high temperatures. The oxidation and the plasticity of Pd phase mainly affect the mechanical properties of HTM cermet at high temperature or with thermal cycling treatment. Changes in the residual stress and microstructure affect the mechanical properties of HTM when subjected to high temperature or thermal cycling treatment.

References

1. Stocker, J., M. Whysall, and G. Miller, *30 Years of PSA Technology for Hydrogen Purification.* UOP LLC; 1998, 1998.
2. S., S. and G. T.C., *Purification of hydrogen by Pressure Swing Adsorption.* Sep., Sci. Technol, 2000. **35**: p. 11.
3. Adhikari, S. and S. Fernando, *Hydrogen Membrane Separation Techniques.* Industrial & Engineering Chemistry Research, 2006. **45**(3): p. 7.
4. Balachandran, U, Lee, T.H, and S.E. Dorris, *Hydrogen production by water dissociation using mixed conducting dense ceramic membranes.* International Journal of Hydrogen Energy, 2007. **32**(4).
5. Iwahara, H., *Hydrogen pumps using proton-conducting ceramics and their applications.* Solid State Ionics, 1999. **125**(1-4): p. 8.
6. Dorris.S.E., Lee.T.H., and Balachandran. U., *U.S. Patent, 6,569,226, May 27, 2003.* 2003.
7. Y.S., C., et al., *Performance of alumina, zeolite, palladium, Pd-Ag alloy membranes for hydrogen separation from town gas mixture.* J. Membr. Sci, 2002. **204**: p. 12.
8. Balachandran, U., et al.,, *Dense Membranes for Hydrogen Separation From Mixed Gas Streams.* 23rd Annual International Pittsburgh Coal Conference, Pittsburgh, PA, 2006.

Current Status of the Student Supported:

Yongjun Zhang, Interdiciplinary PhD student in Materials Science and Engineering, University of Alaska Fairbanks, Thesis Title: " Correlations of Microstructural and Thermomechanical Properties of A Novel Hydrogen Transfer Membrane", in preparation, (Anticipated Thesis Defense Date -- December 6, 2013).

List of Publications Resulted from this Project:

Publications from HTM Project (In Preparation)

1) Characterization of Thermo-Mechanical and microstructural Properties for a Novel Hydrogen Transport Membrane (Cermet-HTM).

2) Correlation of Thermo-mechanical Properties and Microstructure for a Novel Hydrogen Transport Membrane (Cermet-HTM).

3) Residual Stress and the Effect of Thermal Cycling on the Residual Stress on Novel Hydrogen Transport Membrane (Cermet-HTM).

4) Correlation and Comparison of the Microstructural Properties by XRD, SEM with EDS, XRF and Microprobe for a Novel Hydrogen Transport Membrane (Cermet-HTM).

5) Effect of Texture on Mechanical and Microstructural Properties for Alumina and a Novel Hydrogen Transport Membrane (Cermet-HTM).

6) Multiphase Transformation of Novel Hydrogen Transport Membrane (Cermet-HTM) During Thermal Treatment by TG/DTA and XRD Analysis

7) Study of Residual Stress and Thermal Properties for Selected Substrates for a Novel Hydrogen Transport (Cermet-HTM).

8) Characterization of Thermo-Mechanical and Microstructural Properties of Selected Substrates for a Novel Hydrogen Transport (Cermet-HTM).

Current and Pending Support: None

USDOE Hydrogen Separation									
August 15, 2009 - August 14, 2013									
334762-68064									
Updated:	9/9/2013								
			Exp to Date		Projected		Encumbered	Balance	
Salary/Benefits	Proposed	Awarded	Hours	Amount	Hours	Amount		Hours	As Awarded
Bandopadhyay, Sukumar (F9)	$77,993.00	$98,439.27	826.00	$98,439.27	0.00	$0.00	$0.00		($0.00)
Zhang, Jing (F9)	$44,656.00	$42,301.55	632.00	$42,301.55	0.00	$0.00	$0.00		$0.00
Grad Student (GN/GT)	$105,225.00	$99,519.18		$93,536.91	0.00	0.00	$0.00		$5,982.27
Zhang, Yongjun (Lily)			70 pp	$86,564.27	0.00	$0.00	$0.00		
Gu, Yanhong			5.6 pp	$6,972.64	0.00	$0.00			
Grad Health Insurance	$4,500.00	$2,855.00		$2,855.00		$0.00	$0.00		$0.00
Salary/Benefits Subtotal	$232,374.00	$243,115.00		$237,132.73		$0.00	$0.00		$5,982.27
Travel	$24,836.00	$2,356.00		$2,355.80		$0.00	$0.00		$0.20
Services	$0.00	$20,272.00		$21,701.31		$0.00	$0.00		($1,429.31)
Supplies	$24,096.00	$30,723.00		$31,723.27		$0.00	$0.00		($1,000.27)
Equipment	$0.00	$0.00		$0.00		$0.00	$0.00		$0.00
Student Aid	$41,719.00	$19,721.00		$19,688.00		$0.00	$0.00		$33.00
F&A - 45.1%	$126,869.00	$133,707.00		$132,104.01		$0.00	$0.00		$1,602.99
Total	$449,894.00	$449,894.00		$444,705.12		$0.00	$0.00		$5,188.88