LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

LLNL-TR-740369

Process Parameter Evaluation and Optimization for Advanced Material Development Final Report CRADA No. TC-1234-96

L. Hrubesh, T. W. McGann

October 20, 2017

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

DISCLAIMER

Process Parameter Evaluation and Optimization for Advanced Material Development

Final Report
CRADA No. TC-1234-96
Date Technical Work Ended: June 7, 1999

Date: September 5, 2001 Revision: 4

A. Parties

This project was a relationship between Lawrence Livermore National Laboratory (LLNL) and Boeing North American, Inc.

The Regents of the University of California
Lawrence Livermore National Laboratory
7000 East Avenue
Livermore, CA 94550
Larry Hrubesh
Principal Investigator
Telephone: (925) 423-1691
Fax: (925) 423-9242

Boeing North American, Inc. (BNA)
2401 E. Wardlow Road
Mail Code: C078-0533
Long Beach, CA 90807-5309
Timothy W. McGann
Senior Manager, Advanced Materials & Process Technology
Telephone: (562) 593-0780
Fax: (562) 982-7684

B. Project Scope

This project was established as a three-year collaboration to produce and characterize silica aerogels prepared by a Rapid Supercritical Extraction (RSCE) process to meet BNA, Inc. application requirements.

The objectives of this project were to study the parameters necessary to produce optimized aerogel parts with narrowly specified properties and establish the range and limits of the process for producing such aerogels. The project also included development of new aerogel materials useful for high temperature applications.

The results of the project were expected to set the conditions necessary to produce quantities of aerogels having particular specifications such as size, shape, density, and mechanical strength.

BNA, Inc. terminated the project on April 7, 1999, 10-months prior to the anticipated completion date, due to termination of corporate funding for the project. The technical accomplishments achieved are outlined in Paragraph C below.

C. Technical Accomplishments

The project consisted of three phases.

During Phase I, LLNL performed the research and development necessary to establish the parameters, which optimized RSCE aerogels to meet BNA application requirements.

During Phase II, LLNL refined the RSCE process. Sample aerogels produced were characterized at LLNL and at BNA, Inc. LLNL and BNA shared their characterization data with each other.

During Phase III, LLNL synthesized aerogels and applied the RSCE method to dry them.

Samples were delivered to BNA for characterization and testing. BNA characterized properties and performed high temperature application tests.

Process Parameter Study

We completed experimental design experiments with the intent of obtaining a parametric model that allows production of optimized (ie. aerogel properties) aerogels by the RSCE method. A set of 20 screening experiments was performed; these experiments combined 17 process parameter variables, each with extreme values selected to bind the range for the process. For example, one of the parameters is the rate of decompression after supercritical condition is reached; the experimental bounds of 10 psi/min (the lowest rate) and 100 psi/min (the highest rate). The set of screening experiments was developed using RS/Discover software and the same software was used for the statistical analysis and model development. The three measured properties were: (1) optical clarity, (2) strength, (3) thermal conductivity.

The results of the first 20 screening experiments showed that 14 of the 17 parameters had statistical significance to determine the value of a physical property. Nine of the 14 parameters were found to affect either two or all three of the physical properties. Four of the 14 parameters were found to have the most significant effect on increasing the key property while simultaneously decreasing the thermal conductivity. The four most significant parameters are: the rates of heating and decompressing the molds, the maximum temperature reached during heating, and the precursor water ratio in the mixed solution. Not all of the significant parameters have a positive significance (ie. some are significant, but negatively affect a given physical property from the direction of interest.) Therefore, in the process of optimization, we derived a model from these experiments, that optimized all three of the physical properties; but that model gave less than maximum or minimum achievable values for some of the physical properties. However, this experimental design also identified the parameters that can be adjusted to maximize or minimize a given physical property.

Another set of experiments added the necessary data to complete the statistical model. Only 10 more experiments were needed because we accepted a linear model for the parameters. These experiments had the same 17 parameters as in the first 20 experiments, but only nine of the 17 parameters were varied, the other eight were fixed. We completed this set of experiments and finalized the optimization model. With the model, we have defined the process conditions necessary to obtain silica aerogels with optimized values for the three properties of interest, and we have identified the conditions necessary to maximize or minimize each of the selected properties.

Develop Database

All of the results of LLNL measurements for the screening experiments (including BET surface area, density, optical clarity, modulus, and thermal conductivity for representative samples) have been entered into a database. Archival data for the density and modulus of historical samples produced by LLNL for BNA is also included in the database. Digitized photos of representative samples from the screening experiments are also included in the database.

Develop Refractory Aerogel

Silica aerogels sinter rapidly at temperatures exceeding 900°C, limiting their use in high temperature applications. Even if the pre-sintered aerogels were useable at elevated temperature, they would have a relatively high thermal conductivity due to the densification. Aerogels of other metal oxides or alloys of metal oxides could be sufficiently thermally stable to delay the onset of sintering to higher temperatures, thus being useable at elevated temperatures.

We have synthesized samples of pure alumina gels and alumina-silica gels to prepare aerogels for thermal stability measurements. These types of aerogels in granular form are already known to be more stable at 1000°C than silica aerogels. Initial attempts to make large monoliths gave crack-damaged pieces due to reactions with moisture upon removal from the autoclaves. We were able to produce good quality monoliths that were stable against moisture by employing a vapor-phase treatment of the aerogel with chlorotrimethysilane. This treatment stabilizes the aerogels to atmospheric conditions; however, the aerogels revert to the hydrophilic state after heating them during the tests for thermal stability.

The instability to moisture found for the pure alumina aerogels is not as severe for mixtures of alumina and silica aerogels. Such aerogels are quite strong but they tend to sinter at lower temperatures than the pure alumina aerogels. We have prepared monolithic alumina-silica aerogels and we measured several properties of these aerogels, including strength, optical clarity, thermal conductivity, and high temperature stability. We have measured the temperature stability of alumina and alumina-silica aerogels and compared the shrinkage rate with that of the pure silica aerogels. Our data confirm the slower rate of sintering in the alumina-silica aerogel, particularly for 1000°C temperature. Pure alumina aerogel monoliths are stable up to 1100°C.

We also synthesized pure tantala aerogels and made preliminary measurements of the thermal stability of pure tantala aerogels up to 1100°C temperature. The results with aerogels having a density between 0.2 and 0.3 g/cc are similar to results that we obtained for alumina aerogels.

<u>Other</u>

During this CRADA we explored methods to seal the porosity of aerogels at the surfaces.

We explored two ways to seal the surface of the aerogels: metal coating and a silicone-like membrane. Two thousand angstroms thick gold metal deposited on the silica aerogel seals the surface porosity and provides a hydrophobic protective surface.

However, we found that the gold coating has pinholes that allow penetration of other fluids/solvents into the aerogel. In addition, we determined that 2000Å would reflect significantly at all wavelengths; less thickness is necessary to prevent significant reflection. The other coating approach is to make a membrane or film (~3-50 micrometers thick) using methyltriethoxysilane (Owens-Corning trade name: GR650), and bond the film to the surface of the aerogel. The film is non-porous, therefore hydrophobic, and it temperature stable since it is essentially the same material as the aerogel. This material can also be used with other metal oxide aerogels. Further tests for this material and this approach to sealing the aerogels were interrupted by the termination of the project.

D. Expected Economic Impact

The anticipated economic impact was to establish the range and limits of the process for producing aerogels by the RSCE process and to develop new aerogel materials, useful for high temperature applications. The results from this work are useful for more efficient and less expensive production of aerogels, thus providing an economic advantage in the commercialization of these materials.

E. Partner Contribution

BNA provided measurements of the aerogels produced at LLNL, including: thermal conductivity and optical properties of LLNL aerogels.

BNA provided LLNL with the design of a thermal flux meter, and BNA consulted LLNL concerning the construction and use of the instrument.

F. Documents/Reference List

<u>Reports</u>

Seven (7) Progress report memos dated: 4/4/97, 5/15/97, 6/27/97, 7/22/97, 9/5/97, 10/27/97 & 11/8/97.

<u>Patent/Copyright Activity</u>

None

<u>Subject Inventions</u>

None

<u>Background Intellectual Property</u>

<u>LLNL</u>

U.S. Patent No. 5,420,168
Date Issued: 5/30/95
Method of Low Pressure and/or Evaporative Drying of Aerogel
Steven T. Mayer, James L. Kaschmitter, and Richard w. Pekala.

U.S. Patent No. 5,275,796
Method for Producing Metal Oxide Aerogels Having Densities in the Range Less than 0.003 g/cc to 0.02g/cc
Date Issued: 1/4/94
Thomas M. Tillotson, John F. Poco, Lawrence W. Hrubesh, Ian M. Thomas

U.S. Patent No. 5,409,683
Method for Producing Metal Oxide Aerogels
Date Issued: 4/25/95
Thomas M. Tillotson, John F. Poco, Lawrence W. Hrubesh, Ian M. Thomas

U.S. Patent No. 5,686,031
IL 9471A
Method for Rapidly Producing Microporous and Mesoporous Materials
Date Issued: 11/11/97
Paul R. Coronado, Robert W. Hopper, Lawrence W. Hrubesh, John F. Paco

IL-9471B – Patent pending

IL 9226 - Inactivated

G. Acknowledgement

Participant's signature of the final report indicates the following:

1) The Participant has reviewed the final report and concurs with the statements made therein.
2) The Participant agrees that any modifications or changes from the initial proposal were discussed and agreed to during the term of the project.
3) The Participant certifies that all reports either completed or in process are listed and all subject inventions and the associated intellectual property protection measures generated by his/her respective company and attributable to the project have been disclosed and included in Section E or are included on a list attached to this report.
4) The Participant certifies that if tangible personal property was exchanged during the agreement, all has either been returned to the initial custodian or transferred permanently.
5) The Participant certifies that proprietary information has been returned or destroyed by LLNL.

T.W. McGann — 12/15/01

Timothy W. McGann — Date
Senior Manager, Advanced Materials & Process Technology
Boeing North American, Inc.

Lawrence H. Hrubesh — 1/3/02

Lawrence H. Hrubesh — Date
Principal Investigator
Lawrence Livermore National Laboratory

Karena McKinley — 1/15/02

Karena McKinley — Date
IPAC Director
Lawrence Livermore National Laboratory

Attachment I – Final Abstract

Process Parameter Evaluation and Optimization for Advanced Material Development

Final Abstract (Attachment I)
CRADA No. TC-1234-96
Date Technical Work Ended: June 7, 1999

Date: July 31, 2001 Revision: 2

A. Parties

This project was a relationship between Lawrence Livermore National Laboratory (LLNL) and Boeing North American, Inc.

The Regents of the University of California
Lawrence Livermore National Laboratory
7000 East Avenue
Livermore, CA 94550
Larry Hrubesh
Principal Investigator
Telephone: (925) 423-1691
Fax: (925) 423-9242

Boeing North American, Inc. (BNA)
2401 E. Wardlow Road
Mail Code: C078-0533
Long Beach, CA 90807-5309
Timothy W. McGann
Senior Manager, Advanced Materials & Process Technology
Telephone: (562) 593-0780
Fax: (562) 982-7684

B. Project Scope

This project was established as a three-year collaboration to produce and characterize silica aerogels prepared by a Rapid Supercritical Extraction (RSCE) process to meet BNA, Inc. application requirements.

The objectives of this project were to study the parameters necessary to produce optimized aerogel parts with narrowly specified properties and establish the range and limits of the process for producing such aerogels. The project also included development of new aerogel materials useful for high temperature applications.

The results of the project were expected to set the conditions necessary to produce quantities of aerogels having particular specifications such as size, shape, density, and mechanical strength.

BNA, Inc. terminated the project on April 7, 1999, 10-months prior to the anticipated completion date, due to termination of corporate funding for the project.

C. Expected Economic Impact

The anticipated economic impact was to establish the range and limits of the process for producing aerogels by the RSCE process and to develop new aerogel materials, useful for high temperature applications. The results from this work are useful for more efficient and less expensive production of aerogels, thus providing an economic advantage in the commercialization of these materials.

D. Project Dates

February 21, 1997 – June 7, 1999