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**DEVELOPMENT OF HIGH PERFORMANCE REFRACTORY FIBERS
WITH ENHANCED INSULATING PROPERTIES AND LONGER
SERVICE LIFETIMES**

Phase II Final Report

**By
Yifang Cai
J. M. Curtis
D. L. DePoorter
P. C. Martin
D. R. Muñoz**

May 1995

Work Performed Under Contract DE-FC07-89ID12880

**For
U.S. Department of Energy
Office of Industrial Technologies
Washington, D.C.**

**By
Colorado School of Mines
Schuller International**

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**IMPROVED REFRACTORY FIBER AND
INDUSTRIAL BENEFIT DEVELOPMENT**

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**For
U. S. Department of Energy
Idaho Operations Office, Idaho Falls, ID
Sponsored by the Office of the Assistant Secretary
for Energy Efficiency and Renewable Energy
Office of Industrial Technologies
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EXECUTIVE SUMMARY

The overall objective of this research project is the development of improved high performance refractory fibers with enhanced insulating properties and longer service lifetimes. Application of these fibers in the aluminum, glass, cement, and iron and steel industries will significantly decrease energy consumption and increase domestic end-user industrial competitiveness. This project was planned to have three phases.

Phase I was to assess the current technology and use patterns of existing refractory fibers, to establish a data base on currently used refractory fibers, and to develop an estimate of the potentially attainable energy savings as a result of developing enhanced insulating property and service lifetime fibers. The current use patterns of refractory fibers span a wide range of industries and high temperature furnaces within those industries. The majority of high temperature fiber applications are in furnaces operating between 2000 and 2600°F. The fibers used in furnaces operating within this range provide attractive thermal resistance and low thermal storage at reasonable cost. Higher temperature applications require significantly more expensive materials.

A series of heat treatment studies performed in Phase I, reported in DOE/ID/12880-1, has shown that the refractory fibers, as initially manufactured, have attractive thermal conductivities for high temperature applications but the fibers go through rapid devitrification and subsequent crystal growth processes upon high temperature exposure. Exposure of the as-manufactured fibers to furnace temperatures well below the service temperatures of the fibers causes significant thermal conductivity and microstructural changes. These changes result in higher heat losses through the furnace walls and shortened fiber service lifetime because of the increased brittleness of the fibers.

Development of improved fibers, maintaining the favorable characteristics of the existing as-manufactured fibers, could save between one percent (1%) and four percent (4%) of the energy consumed in high temperature furnaces using refractory fibers. The resultant savings is on the order of 0.01 to 0.03 quadrillion Btu/y. These savings were calculated based on models comparing furnaces insulated with existing fibers that degrade and furnaces insulated with fibers that would not degrade. Therefore, Phase II of the study was initiated.

The Mountain Technical Center of Schuller International, Littleton, Colorado and the Metallurgical and Materials Engineering Department and the Engineering Division of the Colorado School of Mines, Golden, Colorado, under United States Department of Energy Cooperative Agreement No. DE-FC07-89ID12880, have continued with Phase II of a three phase study to investigate the development of high performance refractory fibers with enhanced insulating properties and longer service lifetimes. This report presents the results of Phase II of the study, performed from August, 1991, through May, 1995.

Phase II was to develop new refractory fiber compositions, to expand the data base under development, produce new fibers at pilot-scale, evaluate the production methods and produced fibers, and select candidate fiber compositions for subsequent full-scale production and industrial tests.

Based on the results and models developed during Phase I, fiberization of twenty-five compositions based on the Al_2O_3 - SiO_2 - ZrO_2 ternary system with additions in some cases was attempted. Twenty-four compositions were successfully fiberized. Three existing fiber compositions were evaluated. A total of twenty-seven fiber compositions were evaluated during Phase II. All fibers were vitreous as formed. All fibers were subjected to heat treatment and the

shrinkage and relative amounts and identities of crystalline and vitreous phases determined as a function of heat treatment time and temperature.

Four theoretical models were developed during Phase II of the project, a shrinkage model, a devitrification kinetics model, a delta-density (change in density) model, and a fiberization model. The shrinkage model quantifies the mechanism of linear and thickness shrinkage in refractory fiber insulating blankets. The devitrification kinetics model can be used to predict shrinkage in refractory insulating fibers as a function of heating time and temperature and was also used as a basis for selection of fiber compositions in Phase II. The delta-density model further explains the shrinkage of initially vitreous fibers and was also used to select fiber compositions for Phase II. The fiberization model describes the mechanism and quantifies the parameters controlling fibers formed by a melt-spinning process.

The reference fiber for performance against which the fibers manufactured during Phase II were compared was the Alumina-Silica-Zirconia (ASZ) fiber from Phase I. Although some of the fibers formed during Phase II exhibited properties as good as the reference ASZ fiber, no fiber was formed with a significantly improved performance.

This work, although not successful in accomplishing the project goals, does provide significant technical benefits to refractory insulating fiber manufactures and users. Specifically,

- the mechanisms of both linear and thickness shrinkage for vitreous refractory fibers have been determined and quantified,

- the kinetics of devitrification have been quantified and utilized in models to predict shrinkage during service, and

- the mechanism of fiber formation in the melt spinning process has been investigated using a scaled experimental model system.

The science of both the heat effects on vitreous fibers and of the melt spinning process are identified and summarized as a result of this work and presented in the body of this report.

Because a significantly improved refractory insulating fiber was not produced during Phase II of this project, Phase III will not be undertaken.

This project has resulted in several publications with more in preparation. The publications to date include:

Martin, P.C., G.L. DePoorter and D.R. Muñoz. DOE/ID/12880-1: Development of High Performance Refractory Fibers with Enhanced Insulating Properties and Longer Service Lifetimes. Phase I. Enhanced Insulating Properties and Service Lifetime Proof-of-Principle Demonstration. Final Report. Prepared for the USDOE under Cooperative Agreement DE-FC07-89ID12880. 1991.

Cai, Y., Numerical Modeling of Heat Transfer in a Furnace Wall at High Temperature with Convection and Radiation Boundary Conditions. Colorado School of Mines MS Thesis T-3979, 1990.

Lo, P.C.W., Devitrification and Recrystallization Processes in Ceramic Refractory Fibers. Colorado School of Mines MS Thesis T-4004, 1991.

Curtis, J.M., Devitrification and Shrinkage of Alumina-Silica Based Refractory Insulating Fibers. Colorado School of Mines MS Thesis T-4527, 1993.

Cai, Y., Modeling Fiber Formation by the Spinning Process. Colorado School of Mines Ph.D. Thesis T-4618, 1994.

Cai, Y., D.R. Muñoz, G. DePoorter, and P.C. Martin. Modeling Fiber Formation by the Spinning Process. ASME, FED-Vol.206/AMD-Vol.191, Developments in Non-Newtonian Flows, 1994, pp.89-96.

**DEVELOPMENT OF HIGH PERFORMANCE REFRACTORY FIBERS
WITH ENHANCED INSULATING PROPERTIES AND LONGER
SERVICE LIFETIMES**

**PHASE II: IMPROVED REFRACTORY FIBER AND INDUSTRIAL
BENEFIT DEVELOPMENT**

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1. INTRODUCTION

1.1 Project Objectives

The overall objective of this research project (under Cooperative Agreement NO. DE-FC07-89ID12880) is the development of improved high performance refractory fibers with enhanced insulating properties and longer service lifetimes. Included are:

- ⇒ The exploitation of a more complete silica, alumina, and zirconia ternary phase diagram.
- ⇒ The assessment of current technology, including the development of a data base of existing fiber applications in the glass, aluminum, cement, iron, steel, and ceramic industries.
- ⇒ The development of new fibers with the goals of higher service temperatures, lower shrinkage during use, improved long-term thermal properties, increased lifetime projections, and better understood and controlled properties.
- ⇒ The production and testing of new fibers at pilot and full plant scales.
- ⇒ The assessment of the energy and cost savings attainable through the development of improved fibers.
- ⇒ The transfer of research results to industry.

These objectives are to be accomplished in three phases. Titles of each of the phases and corresponding objectives are:

Phase I: Enhanced Insulating Property and Service Lifetime Proof-of-Principle

To assess the current technology and use patterns of existing refractory fibers, to establish a data base on currently used refractory fibers, and to develop an estimate of the potentially attainable energy savings as a result of developing enhanced insulating property and service lifetime fibers.

Phase II: Improved Refractory Fiber and Industrial Benefit Development

To develop new refractory fiber compositions, to expand the data base under development, to produce new fibers at pilot-scale, to evaluate the production methods and produced fibers, and to select candidate fiber compositions for subsequent full-scale production and industrial tests.

Phase III: Pre-Commercialization of Technology

To evaluate full-scale production of improved fibers, to perform full-scale industrial tests, to evaluate the characteristics of improved refractory fibers, to continue assessments of industrial interest in the benefits of improved refractory fibers, to finalize the energy and cost savings analyses, and to transfer the results of this research to industry.

1.2 Phase I Results

The Phase I Final Report, DOE/ID/12880-1: Development of High Performance Refractory Fibers with Enhanced Insulating Properties and Longer Service Lifetimes. Phase I. Enhanced Insulating Properties and Service Lifetime Proof-of-Principle Demonstration., summarizes in detail the results of Phase I of this research. A general summary of the results follows. Details of the technical results are included in Section 2 as an introduction to the logic and rationale for Phase II of this research.

The current use patterns of refractory fibers span a wide range of industries and high temperature furnaces within those industries. The majority of high temperature fiber application are in furnaces operating between 2000°F and 2600°F. The fibers used in furnaces operating within this range provide attractive thermal resistance and low thermal storage at reasonable cost. Higher temperature applications require significantly more expensive materials. The applications and analyses of the observed energy savings through the use of existing refractory fibers have been documented in the open literature and were included in the technology data base in the Phase I Final Report.

A series of heat treatment studies performed in Phase I has shown that the refractory fibers, as initially manufactured, have attractive thermal conductivities for high temperature applications but the fibers go through rapid devitrification and subsequent crystal growth upon high temperature exposure. Exposure of the as-manufactured fibers to furnace temperatures well below the service temperatures of the fibers causes significant thermal conductivity and microstructural changes. These changes result in higher heat losses through the furnace walls and shortened fiber service lifetime because of the increased brittleness of the fibers.

Development of improved fibers, maintaining the favorable characteristics of the existing as-manufactured fibers, could save between one percent (1%) and four percent (4%) of the energy consumed in high temperature furnaces using refractory fibers. This savings is on the order of 0.01 to 0.03 quadrillion Btu/y. These savings were calculated based on models comparing furnaces insulated with existing fibers that degrade and furnaces insulated with fibers that would not degrade. Therefore, Phase II of the study was initiated.

1.3 Summary of Phase II Tasks

The originally proposed Phase II Tasks are summarized below.

Task 1 - Development of New Candidate Fiber Compositions

- Subtask 1.1 Evaluate the results of Phase I devitrification studies with emphasis on identification of potential mechanisms of fiber crystallization development.
- Subtask 1.2 Select candidate fiber compositions with potentially higher initial melting temperatures, lower shrinkage at service temperatures, and reduced devitrification rates.
- Subtask 1.3 Perform initial melting point and devitrification studies, including single hole bushing fiberization to determine fiberization potential.

- Subtask 1.4 Determine handleability of the fibers and investigate preliminary health aspects of the selected fiber compositions by way of preliminary solubility studies.

Task 2 - New Fiber Manufacture - Pilot Scale

- Subtask 2.1 Demonstrate the fiberization potential of candidate refractory fiber compositions determined in Task I on a Pilot Plant-scale.
- Subtask 2.2 Produce test quantities of successfully fiberized fiber compositions.

Task 3 - New Fiber Characterization

- Subtask 3.1 Complete thermal treatments for baseline insulating and microstructural determination.
- Subtask 3.2 Complete thermal properties determination.
- Subtask 3.3 Sample characterization

Task 4 - Energy Saving Determinations

Task 5 - Demonstration of Benefits to Industry

- Subtask 5.1 Discussions with industrial users.
- Subtask 5.2 Calculation of Savings

1.4 Summary of Phase II Results

Phase II experimental results have provided significant technical information:

1. The mechanisms of both linear and thickness shrinkage for vitreous refractory fibers have been determined and quantified.
2. The kinetics of devitrification have been quantified and utilized in models to predict shrinkage during service.
3. The mechanism of fiber formation in the melt spinning process has been investigated using a scaled experimental model system.

Several experimental fibers compositions were selected based on the results mentioned above. Fiberization runs were attempted for these compositions with varying degrees of success. Heat treatments, shrinkage measurements, and x-ray diffraction analysis before and after heating were performed on the fibers obtained.

No fibers were obtained that performed better than existing vitreous refractory insulating fibers. Attempts to fiberize a composition in the Al_2O_3 - SiO_2 system near the mullite composition were unsuccessful.

These initial experimental results at the start of the Phase II tasks lead to the adjustment of the Phase II tasks as described below.

1.5 Realigned Phase II Tasks

The accomplished Phase II Tasks are summarized below.

Task 1 - Development of New Candidate Fiber Compositions

- Subtask 1.1 Evaluate the results of Phase I. devitrification studies with emphasis on identification of potential mechanisms of fiber crystallization development.
- Subtask 1.2 Select candidate fiber compositions with potentially higher initial melting temperatures, lower shrinkage at service temperatures, and reduced devitrification rates.

Task 2 - Mechanism of Fiberization During Melt-Spinning

- Subtask 2.1 Qualitatively and quantitatively model the formation of fibers in the melt-spinning process.
- Subtask 2.2 Use the results of the modeling to predict system parameters for forming new fiber compositions using the melt spinning process.

Task 3 - New Fiber Manufacture - Pilot Scale

- Subtask 3.1 Demonstrate the fiberization potential of candidate refractory fiber compositions determined in Task I on a Pilot Plant-scale.
- Subtask 3.2 Produce test quantities of successfully fiberized fiber compositions.

Task 4 - New Fiber Characterization

- Subtask 4.1 Complete thermal treatments for baseline shrinkage and microstructural determination.
- Subtask 4.2 Sample characterization

Task 5 - Provide Phase II Report

1.6 Logic and Rationale for Phase II Experiments

Phase II investigations were based on the logic diagram shown as Figure 1.1. The experiments were based on the results from four models developed during Phase II:

1. Shrinkage Model
2. Devitrification Kinetics Model
3. Delta- Density Model

4. Fiberization Model

Figure 1.1 is divided horizontally into sections entitled "Old Technology" and "New Technology." Experiments in the former are based on the Shrinkage and Devitrification Kinetics Models while experiments in the latter are possible because of the Fiberization Model with input from the Delta Density, Shrinkage, and Devitrification Kinetics Models. Note that one set of experiments, glass ceramic fibers, is shown as being both Old and New Technology.

The use of the Devitrification Kinetics Model to select fiber compositions is illustrated in Figure 1.2. Similarly, the use of the Fiberization Model to select fiber compositions is illustrated in Figure 1.3.

All of the concepts illustrated in Figures 1.1, 1.2, and 1.3 were utilized to select, fiberize where possible, and evaluate successful new fiber compositions that were hoped to have improved performance characteristics over the existing melt-spun refractory fibers. The goal of this report is to describe the models, list the fiber compositions chosen while including the scientific reasoning for their selection, and summarize the experimental results on fiber formation and fiber properties.

1.7 Organization of Phase II Report

The Phase II results will be presented as follows:

1. Introduction
2. Summary and Further Analysis of Phase I Results
3. Description of Theoretical Models
4. Fiber Compositions Chosen
5. Results of Fiberization Tests
6. Properties of New Fibers Formed

Appendices

In some sections the text will include only a summary of a concept with the detailed description included as an Appendix. Along with the discussions of the work found in the appendices the major conclusions of the work also are presented in the appendices. Following each appendix are the references for that appendix.

Figure 1.1. Logic Diagram for Phase II

Figure 1.2. Role of Devitrification Kinetics Model in Choosing Fiber Compositions

Figure 3. Role of Fiberization Model in Choosing Fiber Compositions

2. SUMMARY AND FURTHER ANALYSIS OF PHASE I RESULTS

This chapter will summarize the Phase I results and describe the further analysis of the Phase I results that provided the basis for the fiber compositions chosen for Phase II.

2.1 Fiber Compositions and Manufactured State

The fiber compositions evaluated in Phase I of the project are summarized in Table 2.1. In this report the fibers will not be referred to by their trade names but by abbreviations or names representing their compositions. Table 2.2 gives both the trade name and the abbreviation to be used in this report.

Table 2.1: Fiber Compositions Evaluated in Phase I

Fiber	Al ₂ O ₃ (wt. %)	SiO ₂ (wt. %)	ZrO ₂ (wt. %)	Cr ₂ O ₃ (wt. %)	Use Temp (°F)
Kaowool 2600	52	48			2300
Kaowool Zr	34	46	20		2400
Cerachrome	42.5	55		2.5	2600
Saffil	96	4			2800
Fibermox	72	27			3000

Table 2.2: Abbreviations for Fibers

Fiber	Abbreviation or Name
Kaowool 2600	AS
Kaowool Zr	ASZ
Cerachrome	ASC
Saffil	Alumina
Fibermox	Mullite

The AS, ASZ, and ASC fibers are vitreous in their manufactured state. The Alumina and Mullite fibers are polycrystalline in their manufactured state.

2.2 Measured Shrinkage After Heat Treatment

The measured shrinkage, from Phase I results, for the fibers at 2600°F are tabulated in Table 2.3.

Table 2.3: Measured Shrinkage at 2600°F

Fiber	Heating Time (hours)	Shrinkage Width (%)	Shrinkage Length (%)	Shrinkage Thickness (%)
AS	4	9.8	8.4	15.5
	24	11.3	8.6	9.5
	168	11.5	10.5	23.1
ASZ	4	4.3	5.4	14.6
	24	7.2	2.9	16.0
	168	4.9	5.6	8.9
ASC	4	5.7	3.7	18.8
	24	5.9	5.8	19.2
	168	13.1	9.6	29.7
Mullite	4	0.8	0.7	0.0
	24	1.0	0.7	0.0
	168	2.0	1.7	0.0
Alumina	4	3.4	2.4	6.3
	24	2.3	2.0	0.0
	168	1.9	2.2	2.4

2.3 Phases Present in Heat-Treated Fibers

The Phase I results and the more detailed study by Lo [Lo, 1991, see Section A1.5 References] show that the heat treatment of the vitreous fibers resulted in devitrification of these fibers. The devitrification products of the vitreous fibers after heating at 2600°F for 168 hours are given in Table 2.4. The equilibrium phases for each of these fibers are also listed. The order of appearance of the crystalline phases in the heat treated fibers was also determined by Lo [Lo, 1991, see Section A1.5 References]. These results are summarized in Tables 2.4 to 2.8. The abbreviations used are defined in Table 2.5.

Table 2.4: The Devitrification Products and Equilibrium Phases of the Vitreous Fibers

Fiber	Observed Devitrification Products	Equilibrium Phases
AS	Mullite Cristobalite	Mullite Cristobalite
ASZ	Mullite Cristobalite t-Zirconia m-Zirconia Zircon	Mullite Cristobalite Zircon
ASC	Mullite Cristobalite	Mullite Cristobalite

Table 2.5: Abbreviation used in Tables Showing Order of Appearance of Phases

Abbreviation	Crystalline Phase
M	Mullite
C	Cristobalite
tZ	t-Zirconia
mZ	m-Zirconia

Table 2.6: Order of Appearance of Crystalline Phases in AS Fiber

Temp. (°F)	Time 15 s	Time 30 s	Time 45 s	Time 60 s	Time 10 min	Time 20 min	Time 30 min
2600	M	M	M	M	M	M	M,C
2400	M	M	M	M	M	M	M
2200	M	M	M	M	M	M	M
2000	nil	M	M	M	M	M	M
1800	nil	nil	nil	nil	M	M	M

Table 2.7: Order of Appearance of Crystalline Phases in ASZ Fiber

Temp. (°F)	Time 15 s	Time 30 s	Time 45 s	Time 60 s	Time 10 min	Time 20 min	Time 30 min
2600	tZ, M	tZ, M	tZ, M	tZ, M	tZ, M, mZ	tZ, M, mZ	tZ, M, mZ,C
2400	tZ, M	tZ, M	tZ, M	tZ, M	tZ, M	tZ, M	tZ, M
2200	tZ, M	tZ, M	tZ, M	tZ, M	tZ, M	tZ, M	tZ, M
2000	nil	nil	nil	nil	tZ, M	tZ, M	tZ, M
1800	nil	nil	nil	nil	nil	tZ	tZ

Table 2.8: Order of Appearance of Crystalline Phases in ASC Fiber

Temp. (°F)	Time 15 s	Time 30 s	Time 45 s	Time 60 s	Time 10 min	Time 20 min	Time 30 min
2600	M	M	M	M	M,C	M,C	M,C
2400	M	M	M	M	M	M,C	M,C
2200	M	M	M	M	M	M	M
2000	M	M	M	M	M	M	M
1800	M	M	M	M	M	M	M

2.4 Changes in Thermal Conductivity After Heat Treatment

Thermal conductivities of the fibers evaluated in Phase I were measured before and after heat treatment. The results of those measurements are summarized in Table 2.9.

Table 2.9: Apparent Thermal Conductivity at 1000°F Mean
Temperature for Fibers Heat Treated at 2600°F

Fiber	Time at 2600°F (h)	Apparent Thermal Conductivity (BTU-in/h-ft ² -°F)
AS	As Received	0.65
	4	0.84
	24	0.88
	168	0.68
ASZ	As Received	0.71
	4	0.83
	24	0.83
	168	0.77
ASC	As Received	0.71
	4	0.78
	24	0.83
	168	0.82
Alumina	As Received	0.71
	4	0.78
	24	0.79
	168	0.78
Mullite	As Received	0.69
	4	0.79
	24	0.77
	168	0.79

2.5 Summary of Phase I Results

A series of heat treatment studies performed during Phase I has shown that the refractory fibers, as initially manufactured, have attractive thermal conductivities for high temperature application but that the fibers go through rapid devitrification and subsequent crystal growth upon high temperature exposure. Exposure of the as-manufactured fibers to furnace temperatures well below the service temperatures of the fibers causes significant thermal conductivity and microstructural changes. These changes result in higher heat losses through the furnace walls and shortened fiber service lifetimes because of the increased brittleness of the fiber.

2.6 Further Analysis of Phase I Results

The initially vitreous fibers, upon heat treatment, undergo significant microstructural changes. These changes include devitrification and significant shrinkage of blankets in all three dimensions. The initially crystalline fibers, upon heat treatment, do not undergo microstructural changes as significant as do the initially vitreous fiber. The shrinkage of blankets was minimal in all three directions for these initially crystalline fibers.

The ASZ fiber showed significantly less shrinkage than either the AS or the ASC fiber. The measured shrinkage of the ASZ fiber was between that of the crystalline fibers and the AS and ASC vitreous fibers. A possible reason for the improved behavior of the ASZ fiber can be obtained by examining Table 2.6, Table 2.7, and Table 2.8 which show the order of appearance of the crystalline phases during the devitrification process. For the AS and ASC fibers the crystalline phases that appear during devitrification are the equilibrium phases that would be expected for the crystallization of a liquid with the same composition as that of the glass. This assumes that the AS fiber is essentially a binary system and that the ASC fiber is essentially a ternary system. For the ASZ fiber the crystalline phases that appear during the devitrification process are not the equilibrium phases. In fact, given the composition of the ASZ fiber in the ternary ASZ system, neither the $t\text{-ZrO}_2$ nor the $m\text{-ZrO}_2$ would be expected to appear under equilibrium conditions.

An examination of the residual glass composition as the ASC fiber devitrifies, [Lo, 1991, see Section A1.5 References], showed that the residual glass composition becomes less refractory as crystallization progresses. Reanalysis of the data in Lo, [Lo, 1991, see Section A1.5 References], by Curtis, [Curtis, 1993, see Section A1.5 References], showed that the residual glass composition, as the ASZ fiber devitrifies, becomes more refractory. The crystallization behavior of the ASZ fiber led to compositions based in this system being the primary focal points in the Phase II investigations.

The initially vitreous fibers examined in Phase I were manufactured by a process similar to melt-spinning. Fibers manufactured by a melt-spinning process must start from a liquid with a viscosity in a very narrow range of values. Nearly pure Al_2O_3 fibers can not be manufactured by the melt-spinning process as currently configured because the viscosity of an Al_2O_3 melt is out of the acceptable range for current melt-spinning operations. Similar problems exist with trying to fiberize melt compositions near that of mullite. Part of the Phase II effort was to understand the fiberization process to determine if lower viscosity melts could be fiberized by a modified melt-spinning process.

2.7 Models Developed in Phase II

Four models were developed during Phase II based on the results and experience from the Phase I effort. These models are:

1. Shrinkage Model
2. Devitrification Kinetics Model
3. Delta-Density Model
4. Fiberization Model

The new fiber compositions chosen in Phase II were based on predictions from the four models. The logic diagrams presented in Chapter 1 show, in general, how these models were used for this purpose. Further descriptions of the models are presented in Chapter 3.

3. DESCRIPTION OF THEORETICAL MODELS

Four theoretical models were developed during Phase II to aid in the selection of new fiber compositions. They are:

1. Shrinkage Model
2. Devitrification Kinetics Model
3. Delta-Density Model
4. Fiberization Model

A brief description of each of the models will be given here. Detailed descriptions of each model are included as appendices.

3.1 SHRINKAGE MODEL

The arrangement of the fibers in a manufactured fiber blanket must be considered when a mechanism for shrinkage is considered. There is a random orientation of the fibers in the plane of the blanket, but significantly less fibers are oriented in the direction normal to the plane of the blanket. Therefore, the shrinkage in the plane of the blanket must be examined separately from the shrinkage in the thickness of the fiber blanket. Different mechanisms control the shrinkage in these two cases. Devitrification of the fibers controls the shrinkage in the plane, linear shrinkage, of the fiber blanket while sintering of the fibers in the blanket controls the thickness shrinkage. Complete details of the derivation of the shrinkage model are included as Appendix 1. A brief summary of the model is given here.

3.1.1 Linear Shrinkage

Linear shrinkage results from devitrification of the initially vitreous fiber. It is shown in Appendix 1 that the linear shrinkage is a simple function of the density of the fiber. The linear shrinkage is given by

$$\text{Linear Shrinkage} = 1 - \frac{\rho_o}{\rho_i} \quad (3.1)$$

where ρ_o = initial density of the fiber
 ρ_i = density of the fiber at some intermediate time.

A comparison of the measured and calculated shrinkage for the vitreous fibers is summarized in Table 3.1.

Table 3.1: Comparison of Calculated and Measured Linear Shrinkage due to Devitrification at 2600°F

Fiber	Heat Treatment (hours)	Measured Linear Shrinkage (%)	Calculated Linear Shrinkage (%)
AS	4	9.1	7.1
	24	10.0	7.6
	168	11.0	8.1
ASZ	4	4.9	3.6
	24	5.1	3.9
	168	5.3	4.2
ASC	4	4.7	7.9
	24	5.9	8.4
	168	11.4	8.7

3.1.2 Thickness Shrinkage

SEM micrographs of heated refractory fiber blankets frequently show joining of the fibers at the contact points. The fiber joining or sintering is caused by the viscous flow of liquids. With increasing temperature, the viscosity of the glass fiber decreases, and a liquid phase may form. The resulting viscous flow of liquid or relatively low-viscosity glass causes the fiber centers to approach each other and increases the contact area between the fibers. When the fiber centers are drawn together, some shrinkage necessarily occurs. As shown in Appendix 1, the thickness shrinkage is caused by viscous flow of fibers oriented predominantly in the X-Y plane with the shrinkage occurring in the Z-direction. Shrinkage in the Z-direction is given by

$$\left(\frac{\Delta S}{S}\right)_z = \frac{1}{2} \left[-\frac{\Delta \rho}{\rho} - 2 \left(\frac{\Delta M}{M} \right)_x \right] \quad (3.2)$$

where ρ = fiber blanket bulk density
 M = linear shrinkage.

Thickness shrinkages calculated from Equation 3.2 and measured thickness shrinkages are compared in Table 3.2.

Table 3.2: Calculated and Measured Thickness Shrinkages due to Viscous Sintering at 2600°F

Fiber	Heat Treatment (hours)	Measured Thickness Shrinkage (%)	Calculated Thickness Shrinkage (%)
AS	4	15.5	12.2
	24	9.5	8.2
	168	23.1	21.4
ASZ	4	14.6	9.6
	24	16.0	10.6
	168	8.9	5.2
ASC	4	18.8	13.1
	24	19.2	14.0
	168	29.7	27.0

3.1.3 Summary

Analysis of the Phase I results shows that the linear shrinkage in initially vitreous refractory insulating fibers is due to devitrification into crystalline phases most of which are more dense than the initial fiber. Thickness shrinkage occurs by viscous sintering of the fibers at the contact points.

3.2 DEVITRIFICATION KINETICS MODEL

The devitrification data obtained by Lo, [Lo, 1991, see Section A1.5 References], was used by Curtis, [Curtis, 1993, see Section A1.5 References], to quantify the kinetics of devitrification of the vitreous fibers studied during Phase I. The kinetic model of Johnson-Mehl-Avrami was applied to the devitrification of the AS and ASC glass fibers during the period of single phase crystallization. The volume fraction crystallized was found as a function of time and temperature. Linear shrinkage in the fibers was calculated as a function of volume fraction crystallized. Complete details of the model are given in Appendix 2.

The analysis is based on the Johnson-Mehl-Avrami equation

$$f_c = 1 - e^{-kt^n} \quad (3.3)$$

where
 f_c = volume fraction crystallized,
 k = rate constant
 t = time
 n = Avrami coefficient.

The rate constant, k , is given by an Arrhenius type equation

$$k = v e^{-\left(\frac{E}{RT}\right)} \quad (3.4)$$

where
 v = frequency factor
 E = Activation Energy
 R = Gas Constant
 T = Absolute Temperature.

Combining Equations 3.3 and 3.4 gives an expression for the volume fraction of the fiber crystallized as a function of time, temperature, and experimentally determined parameters for the fiber devitrification.

$$f_c = 1 - \exp\left(-\left(v \exp\left(-\frac{E}{RT}\right)\right)^n\right) \quad (3.5)$$

The Phase I data has been analyzed for the parameters in Equation 3.5. The results of the analysis are summarized in Table 3.3.

Table 3.3: Kinetic Parameters for the Devitrification of Refractory Insulating Fibers

Fiber	E (kcal/mole)	n (average)	v (1/s)
AS	131	0.257	7.7×10^{13}
ASZ (t-ZrO ₂)	53	0.519	1.1×10^4
ASZ(Mullite)	94	0.192	9.6×10^{10}
ASC	155	0.192	7.9×10^{16}

The utility of the devitrification kinetics model is that it can be used to calculate linear shrinkage as a function of time and temperature for the fibers evaluated in Phase I. As shown in Appendix 2, linear shrinkage is given by

$$\text{Linear Shrinkage} = 1 - \frac{\rho_g}{\rho_g + f_c(\rho_c - \rho_g)} \quad (3.6)$$

where
 ρ_g = initial density of the glassy fiber
 ρ_c = equilibrium crystal density
 f_c = volume fraction crystallized from Equation 3.5.

Calculated results from this model are included in Appendix 2.

3.3 DELTA-DENSITY MODEL

As shown above and in Appendix 1, the linear shrinkage in a melt-spun, vitreous fiber can be directly related to the change in density upon devitrification by the equation

$$\text{Percent Linear Shrinkage} = 100 \left(1 - \frac{\rho_{\text{glass}}}{\rho_{\text{crystal}}} \right) \quad (3.7)$$

where ρ_{glass} = the initial density of the glassy fiber
 ρ_{crystal} = the density of the devitrified (crystallized) fiber.

The crystalline density can be found by knowing the final distribution of crystalline phases and the density of each phase by the rule of mixtures for densities:

$$\frac{1}{\rho_{\text{crystal}}} = \sum_i \left(\frac{w_i}{\rho_i} \right) \quad (3.8)$$

where w_i = weight fraction of the i^{th} crystalline phase
 ρ_i = density of the i^{th} crystalline phase.

As can be seen from Equation 3.7, if the density of the final equilibrium crystal assemblage in a devitrified fiber is equal to the initial density of the vitreous fiber, the fiber will not shrink upon devitrification. By making estimates of the density of liquids in the ASZ system, regions of the phase diagram were chosen where the difference in density, or Delta-Density, between the glass and final crystalline assemblage was a minimum. Details of these calculations are given in Appendix 3 and further discussed in Chapter 4.

3.4 FIBERIZATION MODEL

Commercial vitreous refractory insulating fibers are produced by a spinning fiberization process called melt-spinning. Fiberization occurs when a glass melt is poured onto rapidly rotating disks. Melt threads are thrown from the disks into a collection chamber while they cool and become glassy fibers.

Molten refractory oxide exits the melt furnace as a stream from an orifice and falls onto a rotating disk. A thin film of liquid is formed on the outside surface of the disk. The density of the liquid is greater than that of the surrounding air and the centripetal acceleration is directed toward the dense fluid and disk axis of rotation. A Rayleigh-Taylor, RT, instability between the air and the liquid occurs. The liquid, having a higher density than the air, is driven from the disk surface and is replaced by the air. Small wave-like perturbations form and grow into fibers on the disk surface due to this RT instability. The initial stage of the perturbation takes the form of a short cylinder and moves in an outward radial direction. As the fiber increases in length and decreases in thickness, the viscosity rapidly increases because of the rapid heat transfer to the surroundings. Finally, the fiber is broken free from the liquid on the disk because the tensile force, due to air drag and the centrifugal acceleration acting on the fiber, exceeds the liquid viscous and surface tension forces at the fiber base.

The entire process can be divided into the following three stages:

1. Perturbations form and grow due to Rayleigh-Taylor instability under action of centrifugal acceleration.
2. The fiber is elongated due to the resulting free surface flow and rapidly cooled by convection and radiation heat transfer with the surroundings.
3. The fiber is broken at its base, because the drag forces and inertia exceed the liquid viscous and surface tension forces at the disk.

The melt-spinning process occurs with molten glass at very high temperatures (2000°C) making it difficult to experimentally evaluate fiber parameters such as fiber diameter and melt instability wavelength. Therefore, the principles of dimensional analysis were utilized to design an experimental model of the spinning process. In addition, several candidate liquids were considered to simulate the glassy refractory melt at room temperature. a parameter called the spinnability, the ratio of the dynamic viscosity to surface tension, was used to select the modeling fluid. From both the literature (Ziabicki, 1976, see references after Appendix 4) and through personal communication (Olds, 1992, see references after Appendix 4), it was found that fibers could be melt spun if the spinnability is approximately 6 s/m. If the surface tension is large relative to the viscosity, liquid tends to form into spheres instead of fibers. Therefore, the spinnability is believed to form a lower limit above which liquids can be spun into fibrous shapes. Based on this limit and because of the low toxicity, glycerin was selected as the modeling fluid.

The three stages described above were then observed in the scale model. Controlled variables within the model include the disk diameter, disk rotation speed and fluid temperature (thus the spinnability) and the flow rate imposed on the rotating disk.

Liquid threads of glycerin were observed with the use of a stroboscope, synchronized to stop the disk motion, and a large format camera. The resulting photographs were used to measure the fiber diameter, length and instability wavelength. These length scales were found to correlate with the product of Reynold's and Weber Numbers.

The fiber velocity during the formation process was measured through the use of a Kodak Ektapro Motion Analysis (or high speed) video. These data were combined with the fiber diameter and wavelength instability to yield an estimate for the fraction of fluid incident on the disk that was fiberized. Details of this portion of the research project can be found in Appendix 4.

4. FIBER COMPOSITIONS EVALUATED IN PHASE II

Fiber compositions evaluated in Phase II were chosen based on the results from Phase I and the theoretical models that were developed based on the Phase I results. The six different sets of experimental fiber compositions chosen based on the models are presented below.

4.1 DEVITRIFICATION KINETICS MODEL

The devitrification kinetics model was used to select compositions (1) that would have less tendency to devitrify, (2) in which the devitrification could be controlled, and (3) in which the devitrification would be allowed and was calculated to cause minimal shrinkage.

4.1.1 Prevent Devitrification

Two sets of fiber compositions were selected that might be more resistant to devitrification than the base ASZ composition. In the ASZ system, Phase I results showed that the residual glass became more refractory as the fiber devitrified. A series of nucleating agents was added to the base ASZ composition to induce devitrification, changing the phases precipitating, and driving the residual glass to a more refractory composition. The compositions used are given in Table 4.1.

Table 4.1: Fiber Compositions in ASZ System Used to Induce Crystallization with a Resulting More Refractory Residual Glass

	1022A	1022B	1023A	1023B	1024A	1024B	1024C	1025A
SiO ₂	48.4	48.6	45.8	45.1	47.5	47.9	48.3	46.5
Al ₂ O ₃	32.1	31.7	31.0	30.4	31.9	30.8	29.1	31.4
ZrO ₂	19.1	18.9	19.4	17.6	18.6	17.6	17.0	18.9
La ₂ O ₃	0.0	0.0	0.0	3.63	1.45	3.26	3.50	0.0
TiO ₂	0.1	0.65	3.74	2.73	0.1	0.13	0.10	0.09
Cr ₂ O ₃	0.0	0.0	0.0	0.0	0.0	0.0	1.71	0.0
WO ₃	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.37

	1026A	1026B	1027A	1027B	1027C	1028A	1028B	1028C
SiO ₂	43.2	41.4	48.0	46.2	45.7	49.7	49.5	49.1
Al ₂ O ₃	28.6	27.2	30.5	29.0	28.2	32.5	32.1	32.5
ZrO ₂	17.7	16.0	19.0	18.7	18.3	13.8	14.5	14.4
La ₂ O ₃	0.0	3.21	0.14	0.0	0.0	3.28	2.35	1.83
TiO ₂	0.07	0.12	0.10	0.08	0.60	0.07	0.11	0.07
Cr ₂ O ₃	0.0	0.0	1.93	6.10	7.44	0.68	1.43	2.06
WO ₃	9.61	11.2	0.0	0.0	0.0	0.0	0.0	0.0

A second set of fiber compositions was chosen to explore the fiberization potential of ASZ fibers with a total system composition in a composition triangle on the ternary equilibrium diagram different than the base ASZ fiber; the crystallization of the new composition in a different composition triangle would be controlled by a higher temperature invariant point and thus thought to possibly be more refractory and more resistant to devitrification. The compositions used are given in Table 4.2.

Table 4.2: Fiber Compositions Used in Trying to Reach Higher Temperature Invariant Point in ASZ System

Sample	SiO ₂	Al ₂ O ₃	ZrO ₂	Total
1029A	47.3	32.0	20.5	99.8
1029B	44.2	33.4	22.3	99.9
1029C	41.4	35.1	23.3	99.8
1029D	38.0	36.8	25.1	99.9
1029E	33.3	39.5	27.1	99.9
1029F	29.2	41.4	29.2	99.8

4.1.2 Control Devitrification

Two strategies were used in choosing fiber compositions where the devitrification would be controlled by a heat treatment prior to installation. In one case, the fibers would be pre-shrunk with an annealing stage before installation. Existing experimental fibers were used for this study; their compositions are given in Table 4.3. These are alumina-silicate fibers with either additions of TiO₂ or ZrO₂ and TiO₂.

Table 4.3: Existing AS Fibers with TiO₂ and ZrO₂

Fiber	Al ₂ O ₃	SiO ₂	TiO ₂	ZrO ₂
236	35.92	54.28	9.80	0.0
237	35.67	56.74	7.59	0.0
238	41.53	40.11	16.12	2.24

The second set of fibers were chosen from the results obtained on the fibers whose compositions are given in Table 4.1. Fiber compositions chosen for specific heat treatment to obtain a glass-ceramic fiber are given in Table 4.4.

Table 4.4: Fiber Compositions Chosen for Glass-Ceramic Study

	1022A	1025A	1027A	1027C	1023B
SiO ₂	48.4	46.5	48.0	45.7	45.1
Al ₂ O ₃	32.1	31.4	30.5	28.2	30.4
ZrO ₂	19.1	18.9	19.0	18.3	17.6
La ₂ O ₃	0.0	0.0	0.14	0.0	3.63
TiO ₂	0.1	0.10	0.10	0.60	2.73
Cr ₂ O ₃	0.0	0.0	1.93	7.44	0.0
WO ₃	0.0	2.37	0.0	0.0	0.0

4.1.3 Accept Devitrification

Accepting that vitreous refractory insulating fibers devitrify when initially heated and knowing that the shrinkage results from the density difference between the initial glass and the final crystalline phases, fiber compositions were chosen that were predicted to have minimal density change after devitrification. These compositions were chosen based on the Delta-Density model. Fiber composition chosen are given in Table 4.5. For these compositions the wheel speed on the melt-spinner was varied over the RPM range shown in Table 4.5.

Table 4.5: Fiber Compositions Based on the Delta-Density Model

Sample	SiO ₂	Al ₂ O ₃	ZrO ₂	Total	Spinner RPM
CSM-26	42.5	26.7	30.1	99.3	7000 - 12000
CSM-27	40.7	21.9	37.0	99.6	7000 - 12000

4.2 FIBERIZATION MODEL

The fiberization model was used to predict the required RPM for the wheels in the melt-spinner to fiberize a low viscosity fiber. The fiber composition, near the mullite composition with a small amount of ZrO₂, is given in Table 4.6 along with the range of wheel speeds used.

Table 4.6: "Mullite" Fiber Composition Based on the Spinnability Analysis

SiO ₂	Al ₂ O ₃	ZrO ₂	Spinner RPM
26.0	69.0	5.0	4500-6800

5. RESULTS OF FIBERIZATION TESTS

Several new batch compositions were fiberized during Phase II of this project. This section describes the experimental procedures followed for batch calculations and melter operations and lists the compositions tried along with a description of the results.

5.1 FIBERIZATION OF TEST COMPOSITIONS

Test compositions were trial fiberized in the small electric melter at the Mountain Technical Center. The melts were usually conducted in sets of three, with consecutive desired compositions attained by the addition of transition batches to shift the composition from one to the next to account for the molten material remaining in the melter. The following is a brief description of the procedure used to operate the melter and fiberize the desired compositions.

5.1.1 Calculation of Melter Batches

Calculation of batch compositions, based on the desired melt composition, was accomplished on a spreadsheet incorporating analyses of the raw materials. For example, the batch calculation spreadsheets for melts "x869-CSM-26 Final", "x870-CSM-27 Final" and the transition batch between them, "x870-CSM-27" Transition, are shown on the following pages. The inputs to the spreadsheets, assuming the raw materials were unchanged, were the "desired composition," the "Active Melt Composition" from the previous melt, and the assumed weight of the "skull from the last heat" if any. The outputs of the spreadsheet calculation were the weights of the raw materials batched. If the melt was the first in the series, the "Active melt composition" and the "skull from the last heat" were both input as zero values as shown for "x869-CSM-26 Final." If the melt was the second or third in the series, the final composition was calculated assuming that the composition of the melt had been shifted to the desired composition by the addition of the transition batch and the inputs to the spreadsheet were the same type as in "x870-CSM-27 Final." The transition batch between the melts shifted the composition from the first to the second by "doping" the "skull from the last heat." The inputs to the spreadsheet included the "desired composition" calculated for the second heat, the "Active Melt Composition" from the first heat, and the assumed "skull from the last heat." The outputs from the spreadsheet were the weights for the batch composition to accomplish the transition or "doping" of the melt from the first to the second heat. The raw materials for each batch composition were weighed and dry blended based on one hundred (100) pound units. The first melt in a series required four of the one hundred pound units, the transition batches required one each of the one hundred pound units, and the second and third melts in a series required one each of the one hundred pound units.

x869-CSM-26 Final

Raw Mat'l			SiO2	Al2O3	ZrO2	TiO2	La2O3	Cr2O3	WO3	Total	LOI+water		
Silica			99.25	0.30	0.00	0.03				99.58	0.42	100	
Alumina			0.02	98.80	0.00	0.00				98.82	1.18	100	
Zircon			32.1	0.60	65.70	0.00				98.40	1.6	100	
Titania			0.1	0.05	0.05	99.00				99.20	0.8	100	
La oxide							99.76			99.77	0.23	100	
Chrome Ox								98.50		99.70			
Tungsten Ox									98.50				
Desired Composition			45.00	24.00	31.00	0.00	0.00	0.00	0.00	100.00			
X868 Active Melt Composition													
skull from last heat	0		0	0	0	0.00	0.00	0.00	0.00	0.00			
100lbs batch	99		44.55	23.76	30.69	0.00	0.00	0.00	0.00	99.00			
Total Melt	99		44.55	23.76	30.69	0.00	0.00	0.00	0.00	99.00			
Zircon	46.71	46.64	14.99	00.28									
silica	29.78	29.73	29.56	00.09									
alumina	23.67	23.64	23.39										
titanla	00.00	00.00											
lanthanum	0.00	0.00											
chromium	0.00	0.00											
tungsten ox	0.00	0.00											
	100.17	100.00											

x870-CSM-27 Transition

Raw Mat'l			SiO2	Al2O3	ZrO2	TiO2	La2O3	Cr2O3	WO3	Total	LOI+water	
Silica			99.25	0.30	0.00	0.03				99.58	0.42	100
Alumina			0.02	98.80	0.00	0.00				98.82	1.18	100
Zircon			32.1	0.60	65.70	0.00				98.40	1.6	100
Titania			0.1	0.05	0.05	99.00				99.20	0.8	100
La oxide							99.76			99.77	0.23	100
Chrome Ox								98.50		99.70		
Tungsten Ox									98.50			
Desired Composition			41.00	17.00	42.00	0.00	0.00	0.00	0.00	100.00		
X869 Active Melt Composition			45.00	24.00	31.00							
skull from last heat	105		47.25	25.2	32.55	0.00	0.00	0.00	0.00	105.00		
100lbs batch	99		36.39	9.48	53.13	0.00	0.00	0.00	0.00	99.00		
Total Melt	204		83.64	34.68	85.68	0.00	0.00	0.00	0.00	204.00		
Zircon	80.87	80.51	25.96	00.49								
silica	10.51	10.46	10.43	00.03								
alumina	09.07	09.03		08.96								
titania	00.00	00.00										
lanthanum	0.00	0.00										
chromium	0.00	0.00										
tungsten ox	0.00	0.00										
	100.45	100.00										

x870-CSM-27 Final

<u>Raw Mat'l</u>		SiO2	Al2O3	ZrO2	TiO2	La2O3	Cr2O3	WO3	Total	LOI+water	
Silica		99.25	0.30	0.00	0.03				99.58	0.42	100
Alumina		0.02	98.80	0.00	0.00				98.82	1.18	100
Zircon		32.1	0.60	65.70	0.00				98.40	1.6	100
Titania		0.1	0.05	0.05	99.00				99.20	0.8	100
La oxide						99.76			99.77	0.23	100
Chrome Ox							98.50		99.70		
Tungsten Ox								98.50			
<u>Desired Composition</u>		41.00	17.00	42.00	0.00	0.00	0.00	0.00	100.00		
<u>X869 Active Melt Composition</u>											
skull from last heat	0	0	0	0	0.00	0.00	0.00	0.00	0.00		
100lbs batch	99	40.59	16.83	41.58	0.00	0.00	0.00	0.00	99.00		
Total Melt	99	40.59	16.83	41.58	0.00	0.00	0.00	0.00	99.00		
Zircon	63.29	63.10	20.32	00.38							
silica	20.43	20.37	20.27	00.06							
alumina	16.59	16.54	16.39								
titania	00.00	00.00									
lanthanum	0.00	0.00									
chromium	0.00	0.00									
tungsten ox	0.00	0.00									
	100.30	100.00									

5.1.2 Melter and Melter Operation

The pilot-scale electric melter at the Mountain Technical Center has been used in the past to melt many different materials and has been used to melt varying quantities of materials depending on the size of the melting pot used. The melting pot used for this project was the two-foot diameter, which is the smallest available for pilot scale testing. Other pots available are three-foot, four-foot and five-foot in diameter. The two-foot diameter pot was selected as the size that would allow enough melt for trial fiberization of sufficient fiber quantities for evaluation and easy transition between compositions. The melter is described below.

The base of the melter is a water-cooled, steel floor plate to which the selected melter pot is attached. The melter pot is steel and also jacketed for water-cooling. There is no seal between the floor and the melter pot and there is no insulation, such as insulating fire-brick, in the pot. The raw material of the batch functions as the insulation lining the sides and bottom of the melter. There is sufficient water cooling so that a thin layer of the batch material remains unmelted, thus protecting the steel of the pot and floor from the hot melt.

The batch composition raw materials, previously dry blended, are melted electrically by high current and voltage from three electrodes submerged in the materials. The electrodes used in this study were molybdenum. As the raw materials melt, the molten material conducts current with finite electrical resistance, thus raising the temperature of the materials and melting additional material until the molten pool is large enough for pouring to the fiberizer as described below. After the melt was poured, the transition batch was introduced to the melter, followed by the next melt composition. After the next batch was molten, the heat was poured for fiberization and the process repeated for the third and final melt of the series.

5.1.3 Fiberizer and Fiber Collection

The molten material was fiberized by allowing a stream of the molten material to exit the base of the melter through a molybdenum orifice. The flow through the orifice was controlled by the position of a molybdenum needle in the opening of the orifice. The free-flowing stream of molten material impacted the circumference of two water-cooled eight-inch diameter wheels spaced close together, spinning in opposite directions at speeds of up to 12,000 rpm. The molten stream contacting the spinning wheels is thrown off, forming fibers, if any. The speed of the spinning wheels could be varied to accommodate varying melt characteristics, described elsewhere in this report.

The fibers formed off of the spinning wheels were collected on a moving chain screen by air movement through the chain. The air movement was created by a high volume capacity fan beneath the chain screen. The fiber layer or blanket formed on the moving chain was rolled up and removed from the chain. The collected fibers were then placed in plastic bags and the bags labeled with the melt number.

5.2 COMPOSITIONS TRIED IN THE MELTER

The compositions tried in the melter and a qualitative indication of the fiberization results are given in Table 5.1.

Table 5.1 Compositions Fiberized and Results

Fiber	SiO ₂ (wt %)	Al ₂ O ₃ (wt %)	ZrO ₂ (wt %)	La ₂ O ₃ (wt %)	TiO ₂ (wt %)	Cr ₂ O ₃ (wt %)	WO ₃ (wt %)	Spinnability Compared to 1022A
1022A	48.4	32.1	19.1		0.1			10
1022B	48.6	31.7	18.9		0.65			9-10
1023A	45.5	31.0	19.4		3.74			9-10
1023B	45.1	30.4	17.6	3.6	2.7			9-10
1024A	47.5	31.9	18.6	1.5	0.1			9-10
1024B	47.9	30.8	17.6	3.3	0.1			9-10
1024C	48.3	29.1	17.0	3.5	0.1	1.7		9-10
1025A	46.5	31.4	18.9		0.1		2.4	9-10
1026A	43.2	28.6	17.7		0.1		9.6	9-10
1026B	41.4	27.2	16.0	3.2	0.1		11.2	9-10
1027A	48.0	30.5	19.0	0.15	0.1	1.9		9-10
1027B	46.2	29.0	18.7		0.1	6.1		9-10
1027C	45.7	28.2	18.3		0.6	7.4		9-10
1028A	49.7	32.5	13.8	3.3	0.1	0.7		9-10
1028B	49.5	32.1	14.5	2.4	0.1	1.4		9-10
1028C	49.1	32.5	14.4	1.8	0.1	2.1		9-10
1029A	47.3	32.0	20.5					10
1029B	44.2	33.4	22.3					10
1029C	41.4	35.1	23.3					9
1029D	38.0	36.8	25.1					8
1029E	33.3	39.5	27.1					7
1029F	29.2	41.4	29.2					4
CSM-26	42.5	26.7	30.1					5
CSM-27	40.7	21.9	37.0					5
Mullite	26.0	69.0	5.0					0 @4500-6800 RPM

Notes for Table 5.1:

- (1) No entry in table means that component was not intentionally added
- (2) The base ASZ fiber has a spinnability of 10. As the number decreases, the amount of fiber produced decreases, while the amount of shot produced increases.
- (3) A "zero" in the spinnability column means that no fiber was produced, only shot.

6. PROPERTIES OF NEW FIBERS FORMED

The new fibers formed during Phase II were evaluated by:

1. Heat treating for predetermined times and temperatures.
2. Measuring for shrinkage.
3. Determining phase assemblages by X-Ray diffraction analysis.

Each set of fiber compositions described in Chapter 4 will be discussed individually.

6.1 FIBER COMPOSITIONS CHOSEN TO PREVENT DEVITRIFICATION

Two approaches were tried to prevent devitrification in the ASZ system. The first strategy was to induce crystallization but to make the residual glass composition more refractory to hinder further devitrification. The second strategy was to make a fiber whose composition is in a composition triangle related to a higher temperature invariant point.

6.1.1 Fiber Compositions in the ASZ System Used to Induce Crystallization with a Resulting More Refractory Residual Glass

Small samples of the fibers were heated for 15 min, 4 hr, and 24 hr at 2600°F to observe the course of devitrification. Larger samples were heated for 1 week at 2600°F to further observe the course of devitrification, but also with measurements taken to observe the amount of shrinkage. A complete description of this work is given by Curtis, [Curtis, 1993, see Section A1.5 References]. The compositions of these fibers are given in Table 4.1 in Section 4.1.1.

The results of the X-Ray diffraction analysis of the heat treated fibers is given in Table 6.1. The abbreviations used in Table 6.1 are explained in Table 6.2.

Table 6.1: Qualitative X-Ray Analysis of Experimental Fibers

Fiber	Heating Time	Cristobalite	Mullite	Zircon	m-ZrO ₂	t-ZrO ₂
1022A	15 min	-	m	-	-	vs
	4 hr	ms	mw	-	mw	ms
	24 hr	s	mw	-	w	s
	1 week	s	mw	mw	mw	ms
1022B	15 min	-	ms	-	-	s
	4 hr	s	mw	-	w	s
	24 hr	m	w	w	w	m
	1 week	ms	mw	m	w	m
1023A	15 min	w	mw	-	w	s
	4 hr	ms	mw	-	mw	s
	24 hr	ms	mw	w	mw	ms
	1 week	mw	mw	m	w	w
1023B	15 min	w	mw	w	w	m
	4 hr	mw	mw	m	w	-
	24 hr	w	mw	m	-	w
	1 week	w	mw	m	-	-
1024A	15 min	w	mw	w	w	s
	4 hr	ms	mw	ms	w	mw
	24 hr	m	mw	ms	w	w
	1 week	m	mw	s	w	w
1024B	15 min	mw	w	w	w	ms
	4 hr	m	mw	ms	w	mw
	24 hr	m	mw	ms	w	w
	1 week	mw	w	mw	w	w

Table 6.1(continued): Qualitative X-Ray Analysis of Experimental Fibers

Fiber	Heating Time	Cristobalite	Mullite	Zircon	m-ZrO ₂	t-ZrO ₂
1024C	15 min	m	w	w	w	ms
	4 hr	ms	mw	m	w	m
	24 hr	m	w	m	w	w
	1 week	m	w	m	-	w
1025A	15 min	mw	w	-	w	s
	4 hr	s	mw	m	w	s
	24 hr	s	mw	m	w	m
	1 week	s	mw	m	mw	ms
1026A	15 min	m	mw	mw	w	ms
	4 hr	s	mw	m	w	m
	24 hr	s	mw	ms	w	m
	1 week	s	mw	s	w	w
1026B	15 min	m	mw	ms	w	w
	4 hr	m	w	ms	w	w
	24 hr	m	w	ms	w	w
	1 week	m	w	ms	w	w
1027A	15 min	mw	mw	w	w	s
	4 hr	s	mw	w	w	s
	24 hr	s	mw	m	w	m
	1 week	s	mw	m	w	m
1027B	15 min	ms	mw	-	w	s
	4 hr	m	w	w	w	m
	24 hr	s	mw	mw	w	s
	1 week	s	mw	m	w	ms

Table 6.1 (continued): Qualitative X-Ray Analysis of Experimental Fibers

Fiber	Heating Time	Cristobalite	Mullite	Zircon	m-ZrO ₂	t-ZrO ₂
1027C	15 min	ms	mw	-	w	s
	4 hr	ms	mw	w	w	ms
	24 hr	m	w	mw	w	m
	1 week	m	w	ms	w	w
1028A	15 min	m	mw	w	w	s
	4 hr	m	mw	m	w	w
	24 hr	m	mw	ms	w	w
	1 week	m	mw	m	w	w
1028B	15 min	m	mw	-	w	s
	4 hr	ms	mw	m	w	mw
	24 hr	ms	mw	ms	w	w
	1 week	m	mw	ms	w	-
1028C	15 min	s	mw	-	w	s
	4 hr	s	mw	m	w	m
	24 hr	ms	mw	ms	w	w
	1 week	m-ms	mw	ms	w	w

Table 6.2: Explanation of Intensity Abbreviations in Table 6.1

X-Ray Peak Area	Intensity	Abbreviation
0-50	Very Weak	vw
50-200	Weak	w
200-400	Moderately Weak	mw
400-800	Moderate	m
800-1000	Moderately Strong	ms
1000-1500	Strong	s
1500+	Very Strong	vs

Results of the preliminary shrinkage measurements are summarized in Table 6.3. These were designed as screening measurements to make gross comparisons of shrinkage.

Table 6.3: "First Pass" Shrinkage Measurements One Week at 2600°F

Fiber	Length Shrinkage (%)	Width Shrinkage (%)	Thickness Shrinkage (%)
1022A	6.3	10.8	57.1
1022B	12.5	11.1	60.0
1023A	36.6	42.9	80.6
1023B	34.2	32.3	91.4
1024A	35.0	28.6	81.8
1024B	45.0	40.0	85.5
1024C	58.8	57.1	94.4
1025A	7.7	4.8	64.1
1026A	27.9	24.2	75.0
1026B	34.8	39.4	82.3
1027A	6.7	16.7	55.6
1027B	50.0	43.8	68.8
1027C	39.1	36.0	47.8
1028A	40.7	39.3	79.2
1028B	48.5	48.6	80.0
1028C	53.3	52.6	80.0

Fiber 1022A is the baseline reference ASZ fiber. Based on the results of the "first pass" shrinkage measurements, Fibers 1022B, 1025A and 1027A were selected for further study. These three fibers appeared to perform about as well as the base ASZ fiber (1022A). Additional shrinkage measurements were made on these three fibers. The results are given in Table 6.4.

Table 6.4: Shrinkage Measurement of Potential Low Shrinkage Fibers
Heat Treatment at 2600°F

Fiber	Heat Treatment Time	Average Linear Shrinkage, (%)
1022A	24 hours	4.7
1022A	1 week	3.6
1022B	24 hours	10.0
1022B	1 week	13.9
1025A	24 hours	8.0
1025A	1 week	5.7
1027A	24 hours	8.5
1027A	1 week	8.8

As can be seen from Table 6.3 and Table 6.4, none of the fibers in this series exhibited shrinkage properties as good as the baseline, ASZ 1022A, fiber.

Complete details of these results are included in Appendix 5.

6.1.2 Fiber Compositions to Reach Higher Invariant Point in the ASZ System

Samples of the fibers were heated for 15 min, and 24 hr at 2600°F to observe the course of devitrification. The compositions of these fibers are given in Table 4.2 in Section 4.1.1.

The results of the X-Ray diffraction analysis of the heat treated fibers are given in Table 6.5. The abbreviations used in Table 6.5 are explained in Table 6.2.

Table 6.5: Qualitative X-Ray Analysis of Experimental Fibers to Reach Higher Temperature Invariant Point in the ASZ System

Fiber	Heating Time	Cristobalite	Mullite	Zircon	m-ZrO ₂	t-ZrO ₂
1029A	15 min	w	w	-	-	m
	24 hours	m	w	vw	w	ms
	1 week	m	w	mw	w	mw
1029B	15 min	-	w	-	w	ms
	24 hours	m	w	mw	w	m
	1 week	m	w	m	w	w
1029C	15 min	-	w	-	w	ms
	24 hours	m	w	mw	w	m
	1 week	m	w	m	w	mw
1029D	15 min	-	w	-	w	s
	24 hours	mw	w	mw	w	m
	1 week	mw	w	m	vw	w
1029E	15 min	-	w	-	w	ms
	24 hours	w	w	m	vw	w
	1 week	-	w	ms	-	vw
1029F	15 min	-	w	-	w	ms
	24 hours	vw	w	m	w	mw
	1 week	-	w	ms	vw	w

Results of the shrinkage measurements at 2600°F are given in Table 6.6.

Table 6.6: Shrinkage at 2600°F of Fibers Designed to Reach a Higher Temperature Invariant Point in the ASZ System

Fiber	Heat Treatment Time	Length Shrinkage (%)	Width Shrinkage (%)	Thickness Shrinkage (%)
1029A	1 week	10.0	7.5	50.0
1029B	24 hours	4.5	6.1	44.4
1029B	1 week	3.6	5.6	58.3
1029C	1 week	5.4	11.1	45.0
1029D	24 hours	12.5	5.4	44.4
1029D	1 week	34.3	37.0	92.3
1029E	1 week	17.9	9.7	84.3
1029F	24 hours	17.2	13.3	39.1
1029F	1 week	11.5	0	81.7

Fibers 1029B and 1029C exhibit similar shrinkage to the 1029A base fiber composition. Fiber 1029F, a composition in the composition triangle controlled by the higher temperature invariant point, did not exhibit improved shrinkage or devitrification behavior.

6.2 FIBER COMPOSITIONS CHOSEN TO CONTROL DEVITRIFICATION

Two approaches attempted in trying to make fibers using a controlled devitrification process. One approach used alumino-silicate fibers containing titania (TiO_2) a classic nucleating agent. The other approach was based on the results reported in Section 6.1.1; the best performing fibers were chosen and then subjected to a selective heat treatment process. Complete details of these experiments and results are included in Appendix 5.

6.2.1 Fibers Containing TiO_2

The composition of these fibers is given in Table 4.3 in Section 4.1.2. These fibers were heat treated and then examined for shrinkage and the crystalline phases present determined by X-Ray diffraction. The results obtained are summarized in Table 6.7.

Table 6.7: X-Ray Diffraction Results After Heat Treatment of $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-TiO}_2$ (ZrO_2) Fibers

Fiber Number	Heat Treatment Time	Heat Treatment Temperature (°F)	X-Ray Diffraction Observations
236, 237	As received	As received	Mostly amorphous, some rutile
	15 min	1800	Some amorphous, mullite nucleation
	15 min	2600	Some amorphous, mullite
	4 hr	1800	Mullite nucleation
	4 hr	2600	Some amorphous, mullite, some cristobalite
	4hr	1800	Some amorphous, mullite, very little cristobalite
	4hr	2600	Little amorphous, mullite, cristobalite
	24 hr	2600	Little amorphous, mullite, cristobalite
238	As received	As received	Partly amorphous, some mullite nucleation
	15 min	1800	Some amorphous, mullite nucleation
	15 min	2600	Mullite, some rutile, some ZrTiO_4
	4 hr	1800	Some mullite and rutile
	4 hr	2600	Very little amorphous, mullite, rutile, some ZrTiO_4 , no cristobalite
	4 hr	1800	Mullite, rutile, ZrTiO_4
	4 hr	2600	Mullite, rutile, ZrTiO_4 , no zircon or cristobalite
	24 hr	2600	Mullite, rutile, ZrTiO_4 , no zircon or cristobalite
	1 week	2600	Mullite, rutile, ZrTiO_4 , no zircon or cristobalite

A week long heat treatment was performed at 2600°F to quantify the shrinkage behavior of these titania containing fibers. Fibers 236 and 237 shrank greatly and formed dense solid masses. Fibers 236 and 237 sintered to form chunks so solid that it was difficult to break them by hand. The high degree of sintering exhibited by these fibers and the amount of shrinkage, although not quantified, was great enough to disqualify these fibers for use as a commercial insulation.

Complete details of these results are included in Appendix 5.

6.2.2 Glass-Ceramic Experiments

The composition of these fibers is given in Table 4.4 in Section 4.1.2. These fibers were heat treated and then examined for shrinkage and the crystalline phases present determined by X-Ray diffraction. The reasons for choosing these compositions are given in Table 6.8.

Table 6.8: Reasons for Choosing Potential Glass-Ceramic Fiber Compositions

Fibers Studied	Composition, (wt %)	Reason Chosen
1022A	48 SiO ₂ , 32 Al ₂ O ₃ , 19 ZrO ₂	Baseline Composition
1025A	Baseline with 2.4 WO ₃	Low Shrinkage
1027A	Baseline with 1.9 Cr ₂ O ₃	Low Shrinkage
1027C	Baseline with 0.6 TiO ₂ and 7.4 Cr ₂ O ₃	Combination of classic nucleating agents
1023B	Baseline with 3.6 La ₂ O ₃ and 2.7 TiO ₂	High shrinkage and sintering

Determining possible heating cycles is the first step needed to create a glass-ceramic fiber. Differential thermal analysis (DTA) was used to determine the first temperature of crystallization upon heating. DTA scans were obtained for each fiber on heating from room temperature to 1200 or 1400°C. All of the scans showed a peak in the DTA at approximately 1035°C. Such an exothermic peak should indicate the onset of crystallization. Therefore, heating cycles were devised to investigate the phases present at temperatures above and below this peak and to try to take advantage of prolonged crystallization at a minimum temperature to maximize nucleation and create a glass ceramic. These heating cycles are shown in Figure 6-1.

In addition to the heating cycles designed to investigate devitrification, another series of heating cycles was chosen to investigate the progression of shrinkage. The fiber chosen for this series of tests was fiber 1023B, which had previously exhibited the most shrinkage and sintering and should, therefore, be the most obvious indicator. Diagrams of these heating cycles are shown in Figure 6-2.

Results of the heat treatments to study devitrification are given in Table 6.9 and Table 6.10. Results of the shrinkage experiments are given in Table 6.11 and Table 6.12.

Figure 6-1 Heating Cycles to Investigate Nucleation Crystallization Effects

Figure 6-2 Heating Cycles to Investigate Nucleation Effects on Shrinkage

Table 6.9: Qualitative X-Ray Analysis of Fibers in Glass-Ceramic Studies Heating Cycle Recipe 10

Fiber	Heat Treatment	Cristobalite	Mullite	Zircon	t-ZrO ₂
1022A	10-1	-	-	-	-
	10-2	-	vw	-	mw
	10-3	vw	w	-	s
	15 min @ 1427°C	-	mw	-	s
	10-4	ms	mw	-	vs
	4 hr @ 1427°C	ms	mw	vw	vs
1025A	10-1	-	-	-	-
	10-2	mw	w	-	vs
	10-3	w	w	w	w
	15 min @ 1427°C	w	w	vw	s
	10-4	w	w	w	w
	4 hr @ 1427°C	ms	mw	mw	ms
1027A	10-1	-	-	-	-
	10-2	-	-	-	vs
	10-3	vw	w	vw	w
	15 min @ 1427°C	w	w	vw	ms
	10-4	w	w	vw	mw
	4 hr @ 1427°C	m	w	w	ms
1027C	10-1	-	-	-	mw
	10-2	-	-	-	vs
	10-3	w	w	-	w
	15 min @ 1427°C	m	w	-	ms
	10-4	w	w	vw	w
	4 hr @ 1427°C	m	w	w	ms

Notes to Table 6.9

Heat Treatment	Time-Temperature Relationships
10-1	600 to 900 °C at 20°/min
10-2	10-1 + 900 to 1040°C @ 14°/min, hold 30 min
10-3	10-2 + 1040 to 1400°C @ 24°/min, hold 15 min
10-4	10-3 + hold at 1400°C for 4 hrs

Table 6.10: Qualitative X-Ray Analysis of Fibers in Glass-Ceramic Studies Heating Cycle Recipe 25

Fiber	Heat Treatment	Cristobalite	Mullite	Zircon	t-ZrO ₂
1022A	25-1	-	vw	-	mw
	25-2	m	mw	-	s
	15 min @ 1427°C	-	mw	-	s
	25-3	s	mw	vw	vs
	4 hr @ 1427°C	ms	mw	vw	vs
1023B	25-1	-	-	-	mw
	25-2	w	m	m	m
	15 min @ 1427°C	vw	w	w	s
	25-3	w	s	s	vw
	4 hr @ 1427°C	w	ms	ms	vw

Notes to Table 6.10

Heat Treatment	Time-Temperature Relationships
25-1	830 to 1030°C in 30 min, hold for 1.5 hr
25-2	25-1 + 1030 to 1430°C in 25 min, hold at 1430°C for 15 min
25-3	25-2 + hold at 1430°C for 3.75 hours (4 hours total)

Table 6.11: Effect of Nucleation Cycle on Shrinkage Heating Cycle Modified Recipe 25

Fiber	Heat Treatment	Length/Width Shrinkage (%)	Thickness Shrinkage (%)
1023B	Modified 25-A	46.1	80.5
1023B	Modified 25-B	37.3	88.6

Notes to Table 6.11

Heat Treatment	Time-Temperature Relationships
Mod. 25-A	830 to 1030°C in 0.5 hr, hold 1.5 hr, 1030 to 1430°C in 0.25 hr, hold at 1430°C
Mod.25-B	1430°C for 4 hr

Table 6.12: Effect of Nucleation Cycle on Shrinkage No ID# Heating Cycle

Fiber	Heat Treatment	Length/Width Shrinkage, (%)	Thickness Shrinkage, (%)
1023B	No ID-A	7-11	21-35
1023B	No ID-B	17-25	68

Notes to Table 6.12

Heat Treatment	Time-Temperature Relationships
No ID-A	20 min at 1030°C
No ID-B	No ID-A + 1030°C to 1400°C in 6 hrs

The key results from these experiments are in Table 6.11 and Table 6.12. No significant improvement in the shrinkage behavior of any of the fibers tests from a "glass-ceramic" heat treatment cycle was observed. It should be recalled that the goal of this method was to create a glass-ceramic fiber. The absence of any substantial differences between the "nucleated" and "non-nucleated" samples, or even decrease in advanced crystalline phases in the nucleated samples relative to the non-nucleated samples, and the absence of any dramatic decrease in shrinkage or sintering indicates that insufficient advantage has been achieved by this method.

6.3 ACCEPT DEVITRIFICATION

The compositions given in Table 4.5 were fiberized. Based on the Delta-Density model, these fibers were expected to have low shrinkages compared with the base fiber composition. Preliminary shrinkage experiments showed that no improvement in shrinkage behavior was observed for these compositions.

6.4 FIBERS BASED ON THE FIBERIZATION MODEL

A "Mullite" fiber composition was selected based on the spinnability analysis (Table 4.6). This consisted of estimating the viscosity of the melt and then selecting a spinner RPM that was predicted to be effective in melt-spinning a fiber from a melt with this viscosity. The experiment produced only shot. The melt froze on the wheels.

APPENDIX 1

LINEAR AND THICKNESS SHRINKAGE MODELS

A1.1 SHRINKAGE MODEL

A1.1.1 Introduction

Fibrous insulation has many advantages over structural insulation, mostly due to the relatively large amount of void space. These advantages include improved thermal shock resistance for a given material, low heat capacity and light weight. Unfortunately, a major problem encountered when using the less expensive amorphous fibers is shrinkage. Shrinkage of installed fiber insulation may cause the void space to be decreased, solid contact area may be increased, and cracks or gaps may form in the insulation layer. All of these effects of shrinkage cause an increase in the thermal conduction which is undesirable in an insulation. Understanding the causes of shrinkage in these fibers may provide a means of preventing the shrinkage.

Three commercial alumina-silica refractory insulating fibers were studied based on the following oxide systems: $\text{Al}_2\text{O}_3\text{-SiO}_2$ (AS), $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-ZrO}_2$ (ASZ), and $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-SiO}_2$ (ACS). These fibers are amorphous (glassy) as manufactured. In use, the fibers are heated to temperatures at which devitrification occurs. The following are the compositions of the three fibers studied:

Fiber	Composition, wt %			Rated Continuous Use Temperature
	Al_2O_3	SiO_2	other	
AS	48	52	-	1260°C(2300°F)
ASZ	32	49	19 ZrO_2	1315°C(2400°F)
ACS	40	53	7 Cr_2O_3	1427°C(2600°F)

Devitrification data was available [Lo 1991] for each fiber at several temperatures. The percent glass remaining versus time data was plotted and modeled as a power function of time, $\%G=at^b$, for each material at each temperature [Curtis 1993]. Using the equations of the modeled curves, the percent glass remaining (%G) can be calculated for any heating time (t) at a given temperature. The devitrification model was used to calculate percent glass remaining at 1427°C for 4, 24 and 168 hours for calculation and comparison with the measured shrinkage at those times.

Shrinkage was measured for all three fibers under controlled conditions by Martin [et al. 1991]. The three fibers were received in needled blanket form (nominal 0.128 kg/m³ or 8 lb/ft³ and 0.0254 m or 1 in. thick). The blankets were cut into 0.305 m (12 in.) squares and similar density test pieces were chosen. Each test piece was placed in a preheated, electric furnace with a controlled setpoint of 1427°C (2600°F). Three sample sets were heated in the furnace (one set each at 4 h, 24 h, and 168 h). Average shrinkage was measured from the edges of the test piece. The results of these measurements are presented in Table A1.1.

Table A1.1 Shrinkage Measurements at 1427°C

Sample	As Manufactured				After Heat-Treatment				Percent Shrinkage			
	L1	L2	T	ρ_b	L1	L2	T	ρ_b	L1	L2	Avg	T
AS:												
4 hour	.306	.308	.028	.126	.276	.282	.024	.179	9.8	8.4	9.1	15.5
24 hour	.298	.305	.027	.136	.264	.279	.024	.185	11.3	8.6	9.9	9.5
168 hour	.304	.304	.074	.130	.269	.272	.021	.213	11.5	10.5	11.0	23.1
ASZ												
4 hour	.304	.302	.033	.100	.291	.286	.028	.129	4.3	5.4	4.8	14.6
24 hour	.301	.305	.032	.104	.279	.296	.027	.137	7.2	2.9	5.0	16.0
168 hour	.297	.307	.031	.104	.283	.290	.028	.127	4.9	5.6	5.2	8.9
ACS												
4 hour	.307	.313	.041	.085	.290	.301	.033	.115	5.7	3.7	4.7	18.8
24 hour	.301	.305	.033	.109	.283	.287	.027	.152	5.9	5.8	5.8	19.2
168 hour	.301	.319	.039	.087	.262	.288	.077	.154	13.1	9.6	11.4	29.7

See [Martin et al. 1991] L1 and L2 = linear dimensions (m) in the plane of the fiber blanket.
T = blanket thickness (m), ρ_b = blanket density (Mg/m^3).

The fibers in a typically manufactured insulation blanket are not completely randomly arranged. Generally, there is a random orientation of the fibers in the plane of the blanket, but very few fibers are oriented in the direction of the thickness of the blanket. Therefore, the shrinkage in the plane of the blanket must be examined separately from the shrinkage in the thickness of the fiber blanket. In fact, different mechanisms are likely to affect the shrinkage in these two cases. Linear shrinkage in a fiber is expected to affect the shrinkage in the plane of the blanket while contact sintering of the fibers in the blanket is likely to affect the thickness shrinkage.

A1.1.2 Theory and Calculations

Assumptions and Derivation of Equations for Linear Shrinkage due to Devitrification

A simple equation for calculating linear shrinkage due to devitrification in a single fiber is derived as follows. Assuming negligible change in fiber diameter (relative to fiber length), the linear shrinkage in a single fiber is given by the following:

$$\text{LinearShrinkage} = \frac{\Delta L}{L} = \frac{\Delta V}{V} = \frac{V_o - V_i}{V_o} \quad (1)$$

where V_o = initial (non-crystalline) volume of one fiber
 V_i = intermediate (partially crystallized) volume per fiber.

The intermediate volume can be calculated from the intermediate glass density, ρ_i (calculated or measured):

$$V_i = \frac{\text{mass}}{\rho_i} \quad (2)$$

Assuming constant mass,

$$V_i = \frac{\rho_o V_o}{\rho_i} \quad (3)$$

where ρ_o = initial glass density (measured).

Substituting these definitions into the equation for linear shrinkage gives the following:

$$\text{LinearShrinkage} = \frac{V_o - \frac{\rho_o V_o}{\rho_i}}{V_o} \quad (4)$$

The initial volume then cancels out of the equation leaving the following simple and straightforward equation which relates linear shrinkage, due to devitrification, to density changes in the fibers:

$$\text{LinearShrinkage} = 1 - \frac{\rho_o}{\rho_i} \quad (5)$$

Only the most basic assumptions and definitions have been used here. It is now obvious that shrinkage due to devitrification is caused mainly by the density increase in going from the glass to higher density crystalline phases. If the crystalline phases were less dense than the glass, expansion rather than shrinkage would occur. However, crystal phases are generally more dense than the glass phase of the same composition. This is a useful relationship for predicting the maximum linear shrinkage in a fiber from readily available density information by substituting the fully crystalline fiber density for ρ_i . By combining equation (5) and intermediate material density information calculated from the devitrification model and x-ray phase studies, it is possible to calculate shrinkage at specific times.

The intermediate fiber density, ρ_i , is calculated as follows:

$$\frac{1}{\rho_i} = \frac{w_g}{\rho_g} + w_c \sum \frac{w_n}{\rho_n} \quad (6)$$

where

ρ_i = intermediate density

w_g = weight fraction of fiber remaining glassy at the given time (as determined from the model)

ρ_g = glass density (measured)

w_c = total weight fraction of crystalline material ($1-w_g$),

w_n = weight fraction of crystalline phase n (from XRD phase studies and examination of the appropriate phase diagrams)

ρ_n = density of crystalline phase n (from literature).

A1.1.3 Comparison of Glass and Crystalline Densities

Table A1.2 presents the densities of all applicable phases present in the fibers at various times. The densities of the glasses were determined experimentally using a pycnometer and a procedure based on that set out by Andrews [1928] and Reed [1988]. The results were averaged over five to eight measurements for each fiber. The densities of the crystalline phases were taken from the literature [Reed 1988, Weast 1983, Baldwin 1970]. The crystalline phases are, in general, more dense than the original glass, so shrinkage is predicted to occur based on equation 5.

Table A1.2. Densities of Phases.

AS glass	2.55 g/cm ³
ASZ glass	2.90 g/cm ³
ACS glass	2.90 g/cm ³
Cristobalite, SiO ₂ ⁽²⁾	2.32 g/cm ³
Mullite, 3Al ₂ O ₃ .2SiO ₂ ⁽¹⁾	3.23 g/cm ³
t-zirconia, ZrO ₂ ⁽³⁾	5.75 g/cm ³
m-zirconia, ZrO ₂ ⁽³⁾	5.86 g/cm ³
Zircon, ZrO ₂ .SiO ₂ ⁽¹⁾	4.7 g/cm ³

1. Reed, J.S. 1988. Intro. to Principles of Ceramic Processing. John Wiley & Sons, NY, NY.
2. Weast, CRC Handbook of Chemistry and Physics, 54th ed. 1983.
3. Baldwin, W.J. 1970. High Temperature Oxides, Part II. ed. A.M. Alper. Academic Press, New York. p 118, 122.

A1.1.4 Calculation of Intermediate Density

Intermediate density is the density of the combined material in a fiber at a stage of partial devitrification. The amounts and identity of each phase (crystalline and glassy) must be known. The devitrification model was used to calculate percent glass remaining and percent devitrification at 1427°C for 4, 24, and 168 hours. The densities of the devitrified phases were taken from literature crystal densities (see Table A1.2). The likely crystalline compositions were determined from XRD phase studies [Lo 1991], and examination of the appropriate phase diagrams. The assumed compositions of the crystalline material in each of the fibers is given in Table A1.3. Glass density was assumed to remain constant and the same as the original composition. This assumption is not strictly correct, because as crystallization proceeds, the composition of the glass changes. However, when the error in the glass density due to this assumption is greatest (after extensive devitrification), its effect on the calculated density is the least because the amorphous fraction of fiber is small. The intermediate densities, calculated using equation 6 and the above compositions and densities, are presented in Table A1.4.

Table A1.3. Assumed Crystalline Compositions During Devitrification of Fibers.

Fiber	Phases	(wt %)	(Mg/m ³)
AS	Cristobalite, SiO ₂	40	2.32
	Mullite, 3Al ₂ O ₃ ·2SiO ₂	60	3.23
ASZ	Intermediate phases (est.)		
	Cristobalite, SiO ₂	49	2.32
	Mullite, 3Al ₂ O ₃ ·2SiO ₂	32	3.23
	t-zirconia, ZrO ₂	14	5.75
	m-zirconia, ZrO ₂	1	5.86
	Zircon, ZrO ₂ ·SiO ₂	4	4.7
	Final phases		
	Cristobalite, SiO ₂	27	2.32
	Mullite, 3Al ₂ O ₃ ·2SiO ₂	45	3.23
	Zircon, ZrO ₂ ·SiO ₂	28	4.7
ACS	Cristobalite, SiO ₂	37	2.32
	Solid-solution mullite,	63	3.36
	(3-x)Al ₂ O ₃ ·xCr ₂ O ₃ ·2SiO ₂		

The solid-solution mullite contains approximately 11wt % Cr₂O₃ in this fiber ($x \approx 0.33$). The density was approximated by multiplying the stoichiometric mullite density by a molecular weight ratio, assuming that the Cr substitutes for Al.

Table A1.4. Calculated Intermediate Density of Fiber Material.

Fiber	Intermediate Density, ρ_i		
	4 hour	24 hour	168 hour
AS	2.74	2.76	2.77
ASZ	3.00	3.01	3.02
ACS	2.84	2.85	2.86

A1.1.5 Calculation of Shrinkage Due to Devitrification

Linear shrinkage due to devitrification was calculated from equation 5. The densities used were the initial glass densities listed in Table A1.2 and the intermediate fiber densities listed in Table A1.4.

A1.1.6 Comparison of Calculated and Measured Linear Shrinkage

Percent linear shrinkage due to density changes upon devitrification was calculated for each fiber using equation 5 with the measured glass densities from Table A1.2 and the intermediate fiber densities from Table A1.4. The calculated percent linear shrinkage due to density changes upon devitrification was compared with measured average percent linear shrinkage [Martin et al. 1991]. These results are presented in Table A1.5 along with the heat-treatment times and modeled percent devitrification. A graphical comparison can be found in Figure A1.1.

Table A1.5. Comparison of Calculated Linear Shrinkage Due to Devitrification (Modeled) and Measured Linear Shrinkage at 1427°C.

Fiber	time, hours	% glass remaining	% glass devitrified	density (Mg/m ³)	calculated % shrinkage	avg measured % shrinkage
AS	4	20	80	2.74	7.1	9.1
	24	14	86	2.76	7.6	10.0
	168	9	91	2.77	8.1	11.0
	max.	0	100	2.79	8.9	
ASZ	4	42	58	3.00	3.6	4.9
	24	36	64	3.01	3.9	5.1
	168	31	69	3.02	4.2	5.3
	max.	0	100	3.17	8.7	
ACS	4	14	86	2.84	7.9	4.7
	24	9	91	2.85	8.4	5.9
	168	5	95	2.86	8.7	11.4
	max.	0	100	2.88	9.2	

Note: measured length/width % shrinkage data from Martin et al. 1991, p. 19.

Figure A1.1 Comparison of Measured Linear Shrinkage and Calculated Linear Shrinkage Due to Devitrification

A1.2 SINTERING

SEM micrographs of heated refractory fiber blankets frequently show joining of the fibers at the contact points. The fiber joining or sintering is caused by the viscous flow of liquids. With increasing temperature, the viscosity of the glass fiber decreases, and a liquid phase may be formed. The resulting viscous flow of liquid or (relatively) low-viscosity glass causes the fiber centers to approach each other and increases the contact area between the fibers. When the fiber centers are drawn closer together, some shrinkage necessarily occurs. It is desirable to determine whether this shrinkage accounts for the thickness ("z-direction") shrinkage in these fiber mats. Several fiber mat geometries were assumed and thickness shrinkage of the fiber mat due to viscous sintering was calculated for each of the possible geometries. Previous works have assumed that shrinkage in refractory fiber blankets is due to viscous flow [Jagota and Dawson 1990], devitrification [Lo 1991], and gravitational force [Scowcroft and Padgett 1973]. Devitrification and viscous flow are the only mechanisms considered here. In the calculation of shrinkage due to

viscous flow, the rate ($\dot{N}$) at which fiber centers approach each other is taken to be the component of the macroscopic deformation rate, D_{kl} , along the contact normal direction. The contact normal is the unit vector perpendicular to the tangent plane of the fiber contact point as in Figure A1.2.

Figure A1.2: Contact Point of Two Fibers

Jagota and Mikeska [1990] present the relationship between $\dot{N}$ and D_{kl} for spherical particles.

$$\frac{\dot{N}}{N} = B_k B_l D_{kl} \quad k = x, y, z; \quad l = x, y, z \quad (7)$$

Where B_k and B_l are the direction cosines of line N . For example, the x -direction cosine of line N is $B_x = dx/N$.

However, the shape of a fiber is cylindrical rather than spherical. Therefore, this analysis is based on cylindrical geometry. It was assumed for this analysis, based on the results of the devitrification analysis, that the shrinkage along the length of a fiber due to devitrification, denoted

$\dot{M}$, provides the largest contribution to the total shrinkage in the direction in which the fiber is oriented when furnace conditions are such that both viscous flow and devitrification can occur. It is assumed in this analysis, as previously, that shrinkage due to devitrification is negligible in the direction normal to the fiber. Because of the combination of the devitrification and viscous flow mechanisms, bulk fiber shrinkage is a function of fiber orientation. Three possible fiber mass

orientations were studied and are described below. The $\dot{M}$ values are taken from the previously discussed measurements (see Table A1.1).

The relationship between the one-dimensional shrinkage rate, $\dot{S}$, in a specific direction and the components of the total deformation rate in the direction of contact normal can be modified and simplified by neglecting shear deformation rate.

$$\frac{\dot{S}}{S} = \frac{\dot{M}}{M} + \frac{\dot{N}}{N} = B_k B_l D_{kl} = B_k^2 D_{kk} \quad k = x, y, z \quad (8)$$

According to the conservation of mass principle, the rate of volume shrinkage is equal to the increasing rate of change of the bulk fiber density. This is also approximately equal to the total deformation rate when the volumetric strain rate is small [Boresi and Sidebottom 1985]. Where the bulk densities are measured directly from the fiber blanket.

$$\frac{\dot{\rho}_b}{\rho_b} = -\frac{\dot{V}}{V} \approx -D_{kk} \quad (9)$$

The following analysis was performed by assuming that there are three ideal arrangements for fibers in the bulk fiber blanket:

A1.2.1 Arrangement 1 (Isotropic) In an isotropic arrangement, the fiber cylinder length is assumed to be oriented along x-, y-, and z-directions (see Figure A1.3). The shrinkage rates, both due to devitrification and viscous flow, are the same in all three directions. Since the arrangement is isotropic, the three direction cosines of line N are also same. The relative shrinkage in each direction is therefore given by substituting $B_x^2 = B_y^2 = B_z^2 = 1/3$ into equation (8) and multiplying both sides of equation (8) by a period of time Δt .

$$\frac{\Delta S}{S} = \frac{\Delta M}{M} + \frac{\Delta N}{N} = \frac{D_{kk} \Delta t}{3} \approx \frac{1}{3} \left(-\frac{\Delta \rho}{\rho} \right) \quad (10)$$

Figure A1.3 Isotropic Arrangement of Fiber Cylinders

A1.2.2 Arrangement 2 (Anisotropic) For an anisotropic arrangement, the fiber cylinders, shown in Figure A1.4, are oriented along the x-direction only. This arrangement implies that the shrinkage rate ($\dot{M}$) resulting from devitrification only exists in the x-direction. Therefore, both $(\dot{M})_y$ and $(\dot{M})_z$ are zero.

Figure A1.4: Anisotropic Arrangement of Fiber Cylinders

It is shown in Figure A1.4 that there are no cylinder centers approaching each other in the x-direction. Therefore, no viscous flow effects exist in this direction, and $(\dot{N})_x$ is zero. The total deformation rate is given below.

$$D_{kk} = \left(\frac{\dot{N}}{N} \right)_y + \left(\frac{\dot{N}}{N} \right)_z + \left(\frac{\dot{M}}{M} \right)_x \quad (11)$$

Assuming that $(\dot{N})_y = (\dot{N})_z$, the relative rate at which the fiber centers move toward each other in the z-direction (from equation (11)) is

$$\left(\frac{\dot{N}}{N} \right)_z = \frac{1}{2} \left[D_{kk} - \left(\frac{\dot{M}}{M} \right)_x \right] \approx \frac{1}{2} \left[-\frac{\dot{\rho}_b}{\rho_b} - \left(\frac{\dot{M}}{M} \right)_x \right] \quad (12)$$

Since the devitrification shrinkage in the z-direction is zero, the relative shrinkage in this direction is obtained by multiplying both sides of equation (8) by Δt .

$$\left(\frac{\Delta S}{S}\right)_z = \left(\frac{\Delta N}{N}\right)_z \approx \frac{1}{2} \left[-\frac{\Delta \rho_b}{\rho_b} - \left(\frac{\Delta M}{M}\right)_x \right] \quad (13)$$

Note that $(\Delta M/M)_x$ is negative and $\Delta \rho_b/\rho_b$ is positive.

A1.2.3 Arrangement 3 ("X-Y") This arrangement lies between the extremes of Arrangements 1 and 2. It is a logical idealization of a vacuum formed fibrous mat. The refractory fiber blanket is generally formed by deposition from air flowing through a conveyor belt and some such preferred orientation may be observed in many blankets. In this arrangement, the fiber lengths are oriented along the x- and y-directions and not in the z-direction (see Figure A1.5).

Therefore, the devitrification rate $\dot{M}$ exists in both the x- and y-directions but not in the z-direction while the fiber centers can move in all three directions.

Figure A1.5: X-Y Arrangement of Fiber Cylinders

Combining the effects of devitrification and viscous flow and assuming that $(\dot{N})_x = (\dot{N})_y$, the total deformation rate for the X-Y arrangement is

$$D_{kk} = \left(\frac{\dot{N}}{N} \right)_x + \left(\frac{\dot{N}}{N} \right)_y + \left(\frac{\dot{N}}{N} \right)_z + \left(\frac{\dot{M}}{M} \right)_x + \left(\frac{\dot{M}}{M} \right)_y \quad (14)$$

Since the number of contacts in the z-direction is twice that in the x- or y-direction from Figure A1.5, $(\dot{N})_z$ is equal to the sum of $(\dot{N})_x$ and $(\dot{N})_y$. Therefore, the relative rate at which the fiber centers move in the z-direction is:

$$\left(\frac{\dot{N}}{N} \right)_z = \frac{1}{2} \left[D_{kk} - 2 \left(\frac{\dot{M}}{M} \right)_x \right] \approx \frac{1}{2} \left[-\frac{\dot{\rho}}{\rho} - 2 \left(\frac{\dot{M}}{M} \right)_x \right] \quad (15)$$

Since the devitrification shrinkage in the z-direction is zero, the relative shrinkage in this direction is obtained by multiplying both sides of equation (8) by Δt .

$$\left(\frac{\Delta S}{S} \right)_z = \left(\frac{\Delta N}{N} \right)_z \approx \frac{1}{2} \left[-\frac{\Delta \rho}{\rho} - 2 \left(\frac{\Delta M}{M} \right)_x \right] \quad (16)$$

Note that $(\Delta M/M)_x$ is negative and $\Delta \rho_b/\rho_b$ is positive.

A1.2.4 Results

The results of this analysis for the three fibers (AS, ASZ and ACS fibers) in blanket form are presented in Figures A1.6-8. The relative shrinkage as a function of time is plotted and compared with measurements of the thickness shrinkage of blankets of the three fiber materials that were exposed to a furnace temperature of 1427°C (2600°F). The calculated and the measured data are also listed in Tables A1.6-8.

Figure A1.6 Thickness Shrinkage Comparison Between Calculation and Measurements for AS Fiber at Temperature, $T = 1427^{\circ}\text{C}$ (2600°F)

Figure A1.7 Thickness Shrinkage Comparison Between Calculation and Measurements for ASZ Fiber at Temperature, $T = 1427^{\circ}\text{C}$ (2600°F)

Figure A1.8 Thickness Shrinkage Comparison Between Calculation and Measurements for ACS Fiber at Temperature, $T = 1427^{\circ}\text{C}$ (2600°F)

Table A1.6. Comparison of Calculated and Measured Thickness Shrinkage for the AS Fiber.

Time (hours)	Measured shrinkage (%)	Calculated shrinkage (%)		
		Isotropic	Anisotropic	X-Y arrangement
4	15.5	14.3	16.8	12.2
24	9.5	12.0	13.1	8.2
168	23.1	21.1	26.5	21.4

Table A1.7. Comparison of Calculated and Measured Thickness Shrinkage for the ASZ Fiber.

Time (hours)	Measured shrinkage (%)	Calculated shrinkage (%)		
		Isotropic	Anisotropic	X-Y arrangement
4	14.6	9.6	12.0	9.6
24	16.0	10.6	13.3	10.6
168	8.9	7.2	8.0	5.2

Table A1.8. Comparison of Calculated and Measured Thickness Shrinkage for the ACS Fiber.

Time (hours)	Measured shrinkage (%)	Calculated shrinkage (%)		
		Isotropic	Anisotropic	X-Y arrangement
4	18.8	11.9	15.5	13.2
24	19.2	13.3	17.0	14.0
168	29.7	25.6	32.7	27.0

The actual fiber orientations for the above three materials are, most likely, different from the ideal arrangements. However, the calculated data obtained from the ideal arrangement which best describes the fiber orientation in the blanket should be close to the measured data for real materials if the viscous flow mechanism is the source of shrinkage. The results show that the z-direction shrinkage for the AS fiber in the X-Y orientation compares well with the measurements while the measurements for the ASZ and ACS fibers are best fit with the Anisotropic orientation. As indicated by these results, fiber orientation is important in affecting bulk fiber shrinkage and, therefore, manufacturing characteristics may be important to overall refractory fiber performance.

Also important may be the fiber composition and the effect it has on viscosity and devitrification. Although gravity may also play an important role in fiber shrinkage, no preferred orientation was observed from the SEM photographs obtained in this study to indicate a strong bias of fiber curvature along any one direction, such as along the direction of the gravitational vector.

A1.3 CONCLUSIONS

The calculated linear shrinkage due to devitrification is consistently slightly less than the measured shrinkage for all of the comparison points. Therefore, it can be concluded that the majority of the linear shrinkage in the plane of the fiber blanket in this time-temperature range is due to devitrification. However, this mechanism does not account for the shrinkage in the "thickness" dimension of these fiber blankets since there is little fiber length that lies in that direction. Therefore, examination of other possible mechanisms was necessary to complete the shrinkage model.

Bulk fiber shrinkage in the direction of the thickness of refractory insulating blankets, z-direction, has been analyzed using three models: Isotropic, Anisotropic, and X-Y. Of the bulk fibers for which measurements were obtained, the Anisotropic and X-Y models provided the best fit with experimental data. Based on geometric arguments, these findings indicate that viscous flow provides the most significant mechanism for shrinkage in the thickness direction of fiber blankets.

It is shown from Figure A1.6 that the best fit point between the calculated data and the measurements is the X-Y arrangement curve at time $t=24$ hours. This is verified by SEM-18404 photograph in which fibers are oriented along two directions.

It is shown from Figure A1.7 that the Anisotropic curve is best fit with the measurement curve at time $t=4$ hours. This is verified by SEM-18396 photograph in which most fibers are oriented along one direction.

It is shown from Figure A1.8 that the best fit point between the calculated data and the measurements is the Anisotropic curve at time $t=24$ hours. This is verified by SEM-18408 photograph in which fibers are oriented along one direction [Martin et al 1991].

We conclude that both devitrification and fiber sintering are important mechanisms in the shrinkage of alumina-silicate refractory insulating fibers. In general, devitrification is the predominant mechanism in the horizontal plane of a fiber mat, and fiber sintering is the predominant mechanism in the vertical dimension of a fiber mat. Models based on these mechanisms have been shown to quantitatively predict shrinkage in both the horizontal and vertical dimensions. The combination of both mechanisms is necessary to provide a complete model for shrinkage in amorphous refractory insulating fibers.

A1.4 NOMENCLATURE

x,y-shrinkage nomenclature (in order of appearance):

AS	$\text{Al}_2\text{O}_3\text{-SiO}_2$
ASZ	$\text{Al}_2\text{O}_3\text{-SiO}_2\text{-ZrO}_2$
ACS	$\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-SiO}_2$
V_o	initial (non-crystalline) volume of one fiber
V_i	intermediate (partially crystallized) volume per fiber
ρ_i	intermediate glass density
ρ_o	initial glass density (measured)
ρ_i	intermediate density (partially crystallized)
w_g	weight fraction of fiber remaining glassy
ρ_g	glass density
w_c	total weight fraction of crystalline material ($1-w_g$),
w_n	weight fraction of crystalline phase, n
ρ_n	density of crystalline phase n (from literature).

Z-shrinkage nomenclature (in order of appearance):

N = distance between fiber centers (contact normal)

$\dot{N}$ = rate at which fiber centers approach each other

x, y, z = coordinates referenced to the exterior of the fiber blanket

k represents the normal component of fiber interaction

l represents the shear component of fiber interaction

B_k and B_l are the direction cosines of line L : $B_x = dx/N$, $B_y = dy/N$, $B_z = dz/N$

D_{kl} = macroscopic deformation rate

M = linear shrinkage due to devitrification

$\dot{S}$ = one-dimensional shrinkage rate

ρ_b = bulk or blanket density,

$\dot{\rho}_b$ = rate of change of bulk fiber density

V = volume,

$\dot{V}$ = rate of volume change

Δt = period of time

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APPENDIX 2

KINETICS OF REFRACTORY FIBER GLASS DEVITRIFICATION

A2.0 ABSTRACT

The kinetic model of Johnson-Mehl-Avrami was successfully applied to the devitrification of two alumina-silica based refractory glass fibers during the period of single phase crystallization. The volume fraction crystallized was found as a function of time and temperature. Linear shrinkage in a fiber was calculated as a function of volume fraction crystallized. This allows the practical prediction of performance of a fiber based on linear shrinkage at the actual use temperature.

A2.1 INTRODUCTION TO KINETICS OF DEVITRIFICATION.

The generally accepted equation for the kinetics of glass crystallization is the Johnson-Mehl-Avrami (JMA) equation 1:

$$f_c = 1 - e^{-kt^n} \quad (1)$$

where f_c = volume fraction crystallized
 k = rate constant
 t = time
 n = Avrami coefficient.

Rearranging this equation gives 2,

$$\ln(-\ln(1 - f_c)) = n \ln(k) + n \ln(t) \quad (2)$$

So, a plot of $\ln(-\ln(1-f_c))$ versus $\ln(t)$ gives a slope of n and an intercept of $(n \ln(k))$.

If an Arrhenius temperature dependence is assumed for the rate constant, the following equations apply:

$$k = ve^{\left(\frac{-E}{RT}\right)} \quad (3)$$

Rearrangement of the Arrhenius equation gives:

$$\ln(k) = \ln(v) - \left(\frac{E}{R} \frac{1}{T}\right) \quad (4)$$

So, a plot of $\ln(k)$ versus $1/T$ gives a slope of $-(E/R)$ and an intercept of $\ln(v)$.

Devitrification data [Lo 1991] was available in the form of weight percent residual glass, %G, and the composition of the glass as wt % oxide for three commercial glass fibers heated at listed temperatures and times. From this information, the volume fraction crystallized may be calculated as in equation 5:

$$f_c = \frac{1}{1 + \frac{w_g}{\rho_g w_c \sum \frac{w_i}{\rho_i}}} \quad (5)$$

where
 w_g = wt fraction glass = %G/100
 w_c = wt fraction crystal = 1- w_g
 ρ_c = density of the crystal = $1/\sum(w_i/\rho_i)$
 where w_i = wt fraction of each crystal phase
 ρ_i = density of each crystal phase present.
 $\rho_{t,T}$ = density at time (t) and temperature (T) = $[w_g/\rho_g + (w_c)\sum(w_i/\rho_i)]^{-1}$
 f_c = volume fraction crystallized = $w_c(\rho_i/\rho_c)$

Using equation 5, and the devitrification data for the three commercial refractory fibers [Lo 1991], the volume fraction crystallized, f_c , at a given time (15-1800s) and temperature (1366°K to 1700°K) was calculated (see Table A2.1). The volume fraction crystallized at each time was plotted in the form of equation 2 and n and k were calculated from the slope and intercept for each temperature. The rate constant and temperature data was plotted in the form of equation 3, and the activation energy and frequency factor were calculated from the slope and intercept. Figure A2.1 and Figure A2.2 illustrate this for the ACS fiber. This procedure is the same as that outlined by Speyer [1994. p.66].

These equations are also applied to non-isothermal analyses such as differential thermal analysis (DTA). In a DTA study, the temperature may be increased at a constant rate and the temperature of the sample, relative to a reference, is measured. Crystallization is observed as an exothermic peak. Some assumptions are necessary for this application to be valid. The major assumption is that nucleation is completed at some lower temperature than that at which crystal growth occurs. Bansal et al. [1983] derive the following equation (6) for the analysis of this data:

$$\ln(T_p^{2/a}) = \ln\left(\frac{E}{R}\right) - \ln(v) + \left(\frac{E}{R}\right)T_p \quad (6)$$

where
 T_p = crystallization temperature (exothermic peak)
 a = crystallization rate
 R = ideal gas constant
 E = activation energy
 v = kinetic frequency factor

Thus, a plot of $\ln(T_p^{2/a})$ vs. $1/T$ should give a line with a slope of (E/R) and an intercept of $\ln(E/R) - \ln(v)$.

Table A2.1: Volume Fraction, f_c , Crystallized at Temperature, T ($^{\circ}\text{K}$)

Fiber	Time, t (s)	f_c , 1700 $^{\circ}\text{K}$	f_c , 1589 $^{\circ}\text{K}$	f_c , 1477 $^{\circ}\text{K}$	f_c , 1366 $^{\circ}\text{K}$
AS	15	0.19		0.14	
	30	0.25		0.16	0.03
	45	0.22		0.21	0.05
	60	0.33		0.28	0.08
	600	0.59	0.37	0.31	0.24
	1200	0.66	0.44	0.31	0.24
	1800	0.66	0.45	0.29	0.24
ACS	15	0.32	0.28	0.15	0.06
	30	0.32	0.26	0.19	0.10
	45	0.32	0.28	0.19	0.14
	60	0.34	0.28	0.22	0.14
	600	0.53	0.41	0.29	0.16
	1200	0.63	0.46	0.26	0.16
	1800	0.75	0.47	0.30	0.16
ASZ	15	0.31	0.27	0.06	
	30	0.30	0.34	0.12	
	45	0.34	0.32	0.23	
	60	0.35	0.34	0.21	
	600			0.31	0.09
	1200			0.27	0.13
	1800			0.32	0.09
ASZ t-ZrO ₂	15	0.15	0.13	0.01	0.01
	30	0.18	0.16	0.04	0.04
	45	0.22	0.16	0.11	0.10
	60	0.30	0.22	0.09	0.09
	600			0.30	0.11
	1200			0.32	0.13
	1800			0.30	0.15
ASZ Mullite	15	0.63	0.55	0.13	
	30	0.59	0.67	0.27	
	45	0.67	0.63	0.47	
	60	0.67	0.67	0.43	
	600			0.60	0.14
	1200			0.51	0.27
	1800			0.63	0.18

Figure A2.1 Plot for Finding Kinetic Parameters n and k from a Series of Isothermal Heat Treatments for the ACS Fiber

Figure A2.2 Plot for Finding Kinetic Parameters E and v from a Series of Isothermal Heat Treatments for the ACS Fiber

A2.2 KINETIC CALCULATIONS AND RESULTING PARAMETERS

A2.2.1 Isothermal Analysis

The devitrification data [Lo 1991] for the three commercially available refractory glass fibers was plotted as described in the above procedure. The reaction rate constant, k , and the Avrami coefficient, n , (related to the mechanism of crystallization) are found from the first plot using equation 2. The resulting kinetic parameters (n and k) may be found in Table A2.2.

The activation energy for crystallization, E , and the pre-exponential in the Arrhenius equation (the frequency factor), v , are found from the slope and intercept of the second plot (Figure A2.2) as in equation 3. The resulting kinetic parameters (E and v) may be found in Table A2.3.

Table A2-2: Kinetic Parameters, n and k , From First Plot of a Series of Isothermal Data for Three Commercial Fibers

Fiber	Temp, ($^{\circ}$ K)	n	k , (1/s)
AS	1700	0.37	9.2×10^{-4}
	1589	0.24	7.0×10^{-5}
	1477	0.17	2.6×10^{-6}
ASZ t-ZrO ₂	1700	0.56	2.2×10^{-3}
	1589	0.39	3.8×10^{-4}
	1477	0.61	2.0×10^{-4}
ASZ Mullite	1700	0.09	4.5×10^{-2}
	1589	0.20	3.2×10^{-2}
	1477	0.29	7.3×10^{-4}
ACS	1700	0.27	9.5×10^{-4}
	1589	0.17	3.3×10^{-5}
	1477	0.14	4.9×10^{-7}
	1366	0.15	1.4×10^{-8}

Table A2-3: Kinetic Parameters From the Second Plot of a Series of Isothermal Data for Three Commercial Fibers

Fiber	E , (kJ/mole)	E , (kcal/mole)	v , (1/s)
AS	550	131	7.7×10^{13}
ASZ, t-ZrO ₂	221	53	1.1×10^4
ASZ, Mullite	393	94	9.6×10^{10}
ACS	651	155	7.9×10^{16}

A2.2.2 Non-isothermal Analysis

DTA runs were completed for the AS fiber at four different heating rates. Information relating to the exothermic peaks observed is listed in Table A2.4. Since there is some scatter in the data, it would have been useful to have obtained more data, but time constraints prevented this. One of the concerns with this analysis is in the differences in the peak shapes observed. The peak shape may indicate that different mechanisms are active and dominating for the same fiber on different runs, possibly due to inhomogeneities in the glass or contamination of the fiber surface with dust or oil from handling prior to placement in the sample crucible. One interpretation of peak shape is that sharp peaks indicate bulk crystallization and broad peaks indicate surface crystallization [Ray & Day, 1990 p.440]. The data given in Table A2.4 for the non-isothermal kinetic study of these fibers using the DTA was plotted using the form of equation 4 for the three choices of crystallization temperature. The resulting kinetic parameters (E and v) may be found in Table A2.5.

Table A2.4: DTA of the AS Fiber

Rate (°C/min)	Height (μ V)	FWHM (°C)	Start (°C)	Cryst. Pt. (°C)	Max Pt. (°C)
30	23.44	4.31	989	1012	1012
30	24.56	6.46	991	1011	1011
50	33.95	6.03	1003	1022	1022
50	12.19	11.25	992	1018	1018
70	28.35	9.48	1004	1026	1026
70	19.85	9.00	1005	1024	1024
90	25.49	13.15	1008	1029	1029

Table A2.5: Kinetic Parameters from Non-Isothermal Analysis for AS Fiber

Temperature	E , (kJ/mole)	E , (kcal/mole)	v , (1/s)
Start	197	47	6.2
Crystallization	305	73	14.8
Maximum	254	61	9.6

A2.3 DISCUSSION OF KINETIC PARAMETERS

A2.3.1 Isothermal Analysis

If the devitrification process follows the model described here (JMA and Arrhenius equations), this analysis should give valuable information about the mechanism of crystallization (time dependence of nucleation and growth) and the temperature dependence of the rate of crystallization.

The mechanism of crystallization can be determined from the value of the Avrami coefficient [Speyer 1994 p.67, Bansal et al. 1983, Henderson 1979, Rogers 1970]. In the literature, n is usually taken to be between one and four, with one representing surface nucleation and four representing homogeneous nucleation with spherical growth [Speyer 1994]. A complete description of the theory of the interpretation of the Avrami coefficient as it applies to devitrification was not found in the literature and it is difficult to say what a value of approximately 0.2 (as was seen in this analysis in Table A2.2) would mean. The smallest coefficient given in the literature is 0.5 for instantaneous nucleation with diffusion controlled growth in one dimension [Rogers 1970]. However, Sestak [1971] derives an equation with several mechanism coefficients to describe a process. It may be that some of the assumptions, such as complete nucleation prior to crystal growth which is assumed for the non-isothermal analyses, do not apply to devitrification in these fibers and a more complex equation is needed.

The above analysis appears to indicate that the activation energy (Table A2.3) for crystallization is least for the ASZ fiber and greatest for the ACS fiber. However, this does not agree with the experimentally observed behavior as evidenced by the data given as weight percent crystallized as a function of time being least for the ASZ fiber. There are multiple factors in this. One difference is that the weight percent crystallized was defined differently for the ASZ fiber since more than one phase crystallized simultaneously. Additionally, the crystallization of the ASZ fiber does not proceed directly to the equilibrium phases, so, although the long term crystallization of tetragonal zirconia can be calculated, this has no actual validity since the tetragonal zirconia will be transformed to monoclinic zirconia and then zircon during the course of devitrification of the ASZ fiber. The theory cannot take into account the subsequent nucleation and growth of these multiple and competing phases. Therefore, only the kinetic parameters calculated for the AS and ACS fibers should be used for comparison.

An initial error analysis based on the equations reveals that there is only a small uncertainty in the value of the activation energy (about 5%), while the value of the frequency factor is far less certain (on the order of 100% uncertainty). It should be noted that this error analysis did not take into account any uncertainty in n and also that the uncertainties of E and v were calculated independent of each other.

A2.3.2 Non-Isothermal Analysis

The non-isothermal analysis was intended to give an independent source for the above kinetic information for comparison. Unfortunately, there was a great deal of scatter in the limited data obtained. The scatter could be due to inherent inhomogeneities in the fibers affecting the nucleation process. Also, it is uncertain whether the mechanism involved in the fiber crystallization was controlled (constrained to one mechanism) during the tests. Contamination of the fibers could have resulted in a dominance of surface nucleation over bulk nucleation on some occasions. This may have produced additional scatter in the data.

Perhaps more importantly, the uncertainty regarding the nucleation process may invalidate the application of this technique. Since the application of the JMA equation to the non-isothermal analysis involves some rather restrictive conditions for the nucleation process, this analysis is less useful than the isothermal analysis.

A2.4 CALCULATION OF VOLUME FRACTION CRYSTALLIZED AS A FUNCTION OF TIME AND TEMPERATURE USING MODELED KINETIC PARAMETERS

The kinetic parameters calculated from the isothermal data using the JMA and Arrhenius equations (equations 2 and 4) for the AS and ACS fibers were used to create 3-dimensional surface plots of fraction crystallized as a function of time and temperature. Equations 2 and 4 were combined to give equation 7.

$$f_c = 1 - \exp \left(- \left(t v \exp \left(- \frac{E}{RT} \right) \right)^n \right) \quad (7)$$

These plots are Figure A2.3 and Figure A2.4. The contour plots accompanying the 3-dimensional surface plots show volume fraction crystallized for varying temperature and time. These contour plots are very useful since they allow a user to easily determine a practical use temperature for each fiber. For example, if the user wanted to keep the volume fraction crystallized below 0.6, the ACS fiber could be used at temperatures less than 1350°K; however, the AS fiber could only be used at temperatures less than 1300°K. Unfortunately, it can also be seen from these plots that it is impossible to completely prevent devitrification in these fibers at the temperatures of interest.

The volume fraction crystallized at 1700°K was calculated using the isothermally derived kinetic parameters for the AS and ACS fibers using equation 4 and a series of times ranging from 1800 seconds (for experimental comparison) to 2 years (a reasonable use period). The same equation was rearranged to calculate the activation energy that would be needed to prevent the majority of crystallization (volume fraction <0.1) at the same temperature and times. For the AS fiber the activation energy, *E*, must be greater than 830 kJ/mol, and for the ACS fiber it must be greater than 970 kJ/mol to keep the volume crystallized less than 10 percent. These are very large activation energies since activation energies for devitrification of conventional network forming glasses are reported to be between 100 and 300 kJ/mol [Negran and Glass 1979]. The same equation was also rearranged to calculate the temperature below which crystallization would be less than 10 percent. For the AS fiber, this is 1130°C, and for the ACS fiber it is 1140°C.

A2.5 CALCULATION OF LINEAR SHRINKAGE AS A FUNCTION OF VOLUME FRACTION CRYSTALLIZED

While the volume fraction crystallized does provide a useful measure of fiber performance, another measure that is more accepted in industry is based on the percent shrinkage in a fiber blanket. It has been shown elsewhere, [Curtis 1993], that the length or width shrinkage in a typical fiber blanket is derived from the linear shrinkage in the length of a fiber. Furthermore, this linear shrinkage is caused by the change in material density upon devitrification as given by the following equation:

Figure A2.3 Volume Fraction Crystallized Calculated from Kinetic Parameters Derived from Isothermal Data for the AS Fiber

Figure A2.4 Volume Fraction Crystallized Calculated from Kinetic Parameters Derived from Isothermal Data for the ACS Fiber

$$\text{Linear Shrinkage} = 1 - \frac{\rho_g}{\rho_{t,T}} \quad (8)$$

where ρ_g = initial density of the glassy fiber)
 $\rho_{t,T}$ = density after heating at time, t, and temperature, T.

The maximum linear shrinkage possible due to devitrification can be found when $\rho_{t,T}$ equals the final or equilibrium crystal density, ρ_c . The crystalline density can be found by knowing the final distribution of crystalline phases and the density of each phase by the rule of mixtures for densities (the additive rule for specific volume):

$$\frac{1}{\rho_c} = \sum \left(\frac{w_i}{\rho_i} \right) \quad (9)$$

where w_i = weight fraction of crystalline phase in the material
 ρ_i = the density of each crystalline phase (from literature).

The final distribution of crystalline phases in the material may be found from the appropriate phase diagram. Therefore, to predict the shrinkage due to devitrification for a new fiber composition, only the composition and the glass density need to be known. The density of the glass can be measured using the pycnometer method, [Reed 1988 p.106, Andrews 1928 p.33-36], but if the fiber has not been manufactured yet, it is necessary to be able to predict the density of the melt-spun glass.

The most frequently used method of predicting glass density from the composition was developed by Huggins and Sun, [1943, Morey 1954 p.224]. They tabulate sets of specific volume factors for many oxides over different composition ranges relative to Si content. Unfortunately, when these specific volume factors were used to calculate the densities of the commercial AS, ASZ and ACS fibers, the calculated density was consistently lower than the measured (pycnometer) density. This may indicate some difference in the glass structure of the melt-spun glass or a difference in the composition range studied. Therefore, specific volume factors were derived for the melt-spun glass fibers using the measured densities as follows: [Scholes 1975 p.385]

A2.5.1 Derivation of Specific Volume Factors for Glass Density in Melt Spun Fibers

The following equation applies for the density of glass (ρ_g) based on composition:

$$\frac{1}{\rho_g} = Sw_{Sg} + Aw_{Ag} + Zw_{Zg} + Cw_{Cg} \quad (10)$$

where w = weight fraction of oxide component in the glass phase
 $S = \text{SiO}_2$, $A = \text{Al}_2\text{O}_3$, $Z = \text{ZrO}_2$, and $C = \text{Cr}_2\text{O}_3$

and S , A , Z and C are empirical constants (specific volume factors) for each of the components in the glass.

Density was measured for the three commercially available fibers using a pycnometer, and the density of vitreous silica is commonly available in the literature. This data is shown in Table A2.6. Substituting the data from Table A2.6 into equation 8 and solving for the variables, empirical specific volume factors can be derived for these glass fibers. The empirical specific volume factors for SiO_2 , Al_2O_3 , ZrO_2 and Cr_2O_3 (S , A , Z , and C respectively) can be found in Table A2.7. These empirical specific volume factors can be used to calculate density of the glass in a melt spun fiber over a wide range of compositions. Of course, use of these factors will result in densities which are most accurate for compositions near to those of the measured fibers.

Table A2-6: Composition and Density of Commercial Melt-Spun Fibers and Vitreous Silica (literature)

Fiber	Al_2O_3 (wt %)	SiO_2 (wt %)	ZrO_2 (wt %)	Cr_2O_3 (wt %)	Density (Mg/m ³)
vit. SiO_2	0	100	0	0	2.20
AS	48	52	0	0	2.55
ASZ	32	49	19	0	2.90
ACS	40	53	0	7	2.61

Table A2-7: Empirical Specific Volume Factors for Calculating the Density of Melt-Spun Fibers From the Composition in Weight Percent

Component	Symbol	Factor
SiO_2	S	0.4545
Al_2O_3	A	0.3278
ZrO_2	Z	0.0937
Cr_2O_3	C	0.1585

Aside: As a measure of the power of the various oxides to increase the density of vitreous silica, the hypothetical oxide glass density was calculated. The hypothetical glass density is simply the inverse of the empirical specific volume factor. The higher the hypothetical glass density, the more power the oxide has to increase the glass density of the mixture. The hypothetical oxide glass densities are as follows: $\rho\text{-Al}_2\text{O}_3 = 3.05$, $\rho\text{-ZrO}_2 = 10.67$, and $\rho\text{-Cr}_2\text{O}_3 = 6.31 \text{ Mg/m}^3$. This shows that the addition of alumina does not greatly increase the glass density, while the addition of zirconia or chromic oxide does greatly increase the glass density relative to vitreous silica.

The ability to predict the maximum amount of linear shrinkage in a fiber, composed of any combination of silica with alumina, zirconia and/or chromic oxide due to devitrification based solely upon the composition of the fiber, as described above is very important since it provides for the design of a fiber with minimum shrinkage within the compositional constraints of manufacture. However, it does not say anything about the use temperature of the fiber if devitrification is not allowable. For that, the kinetic theory must be applied.

At some time and temperature at which devitrification in a fiber is only partially complete, the following equations apply. For a fiber containing only alumina and silica,

$$\frac{I}{\rho} = S w_{Sg} + A w_{Ag} \quad (11)$$

where

$$S = 0.455 \text{ and } A = 0.328.$$

$$w_{Sg} w_g + w_{Sc} w_c = w_S$$

$$w_{Ag} w_g + w_{Ac} w_c = w_A \quad (12)$$

$$w_S + w_A = 1$$

where

- w_{Sg} = weight fraction of silica in the glass phase
- w_{Ag} = weight fraction of alumina in the glass phase
- w_{Sc} = weight fraction of silica in the crystal phase
- w_{Ac} = weight fraction of alumina in the crystal phase
- w_g = weight fraction of glass phase in the fiber
- w_c = weight fraction of crystalline phase in the fiber
- w_S = weight fraction of silica in the fiber
- w_A = weight fraction of alumina in the fiber

Rearrangement of equation 12 gives

$$w_{Sg} = \frac{w_S - w_{Sc} w_c}{w_g} \quad (13a)$$

$$w_{Ag} = \frac{w_A - w_{Ac} w_c}{w_g} \quad (13b)$$

The density of the glass can be found by substituting the equations for weight fraction of each component in the glass (equation 13 into equation 11). This is simply a convenient re-statement of equation 8 using quantities that may more easily be known. The density of a glass containing components other than alumina and silica can be calculated by including the specific volume factors of the additional components into the equations. Specific volume factors for Cr_2O_3 and ZrO_2 in melt-spun glass fibers have been described above.

For any glass fiber that is partially devitrified,

$$w_s + w_c = 1 \quad (14)$$

A2.5.2 Calculation of Intermediate Density as a Function of Volume Fraction Crystallized

To find linear shrinkage in a fiber as a function of time and temperature, it is necessary to find $\rho_{t,T}$. The volume fraction crystallized, f_c , is known as a function of time and temperature, so if $\rho_{t,T}$ can be found as a function of f_c , the result will be a model for linear shrinkage as a function of time and temperature.

$$\frac{I}{\rho_{t,T}} = \frac{w_c}{\rho_c} + \frac{w_g}{\rho_g} \quad (15)$$

$$\frac{w_g}{\rho_g} = \frac{I - (I - w_g)}{\rho_g} = \frac{I}{\rho_g} - \frac{w_c}{\rho_g} \quad (16)$$

The basic definition of volume fraction crystallized, f_c , is

$$f_c = \frac{V_c}{V_{total}} \quad (17)$$

so

$$f_c = \frac{V_c}{V_{total}} = \frac{\frac{m_c}{\rho_c}}{\frac{m_{total}}{\rho_{total}}} = \left(\frac{m_c}{m_{total}} \right) \left(\frac{\rho_{total}}{\rho_c} \right) = w_c \frac{\rho_{t,T}}{\rho_c} \quad (18)$$

Using this expression for f_c gives:

$$\frac{I}{\rho_{t,T}} = \frac{f_c}{\rho_{t,T}} + \frac{I}{\rho_g} - \frac{\rho_c f_c}{\rho_g \rho_{t,T}} \quad (19)$$

Factoring ($\rho_g \rho_{t,T}$) out in the denominator gives :

$$\rho_g = f_c \rho_g + \rho_{t,T} - f_c \rho_c \quad (20)$$

Rearrangement of this gives $\rho_{t,T}$ as a function of f_c :

$$\rho_{t,T} = \rho_g + f_c (\rho_c - \rho_g) \quad (21)$$

Substituting this into the equation for linear shrinkage gives the linear shrinkage as a function of volume fraction crystallized, f_c . Volume fraction crystallized has been modeled as a function of time and temperature.

$$\text{Linear Shrinkage} = 1 - \frac{\rho_g}{\rho_g + f_c (\rho_c - \rho_g)} \quad (22)$$

A2.5.3 Calculation of Linear Shrinkage as a Function of Time and Temperature

Using the above relationships for linear shrinkage as a function of density, density as a function of volume fraction crystallized, and volume fraction crystallized modeled as a function of time and temperature using the JMA and Arrhenius kinetic theory, linear shrinkage in a fiber can be calculated as a function of time and temperature. Equation 22 was used to calculate this relationship. The major difficulty that exists in this calculation is the treatment of the crystal phase(s). The kinetic model is good only for a single phase crystallizing. The kinetic model has been successfully used to describe the crystallization of the AS and ACS fibers when only one phase (mullite) is crystallizing. However, at longer times, a second phase crystallizes in the AS and ACS fibers. This lowers the final crystal density because the initial crystalline phase, mullite, has a density of 3.23 Mg/m^3 while the second crystalline phase, cristobalite, has a density of 2.3 Mg/m^3 . Therefore, several plots are presented here for each fiber. The first set of plots, Figure A2.5 and Figure A2.8 are of linear shrinkage as a function of time and temperature over the time and temperature range of the kinetic model. The second set of plots, Figure A2.6 and Figure A2.9, are the same function over a longer time span. This shows what the shrinkage would be at long times if mullite were the only phase crystallizing. The third set of plots, Figure A2.7 and Figure A2.10, show the long term shrinkage more accurately because the density of the crystal phase is taken to be the density of the final equilibrium crystalline composition. However, the third set of plots are not as accurate for the short times. To get a completely accurate plot over the entire time span of interest, the crystalline and glass-phase compositions in these fibers would need to be modeled in the time and temperature range of interest. This would most likely require an experimental basis. The parameters used in the calculation of these plots are presented in Table A2.8.

Figure A2.5 AS Fiber at $t = 0-1800$ sec, $T = 1093^{\circ}\text{C}$ to 1427°C (2000°F to 2600°F) Glass Density = 2.54 Mg/m^3 and Crystal Density = 3.23 Mg/m^3 (mullite)

Figure A2.6 AS Fiber at $t = 0-730$ days, $T = 1093^{\circ}\text{C}$ to 1427°C (2000°F to 2600°F)
 Glass Density = 2.54 Mg/m^3 and Crystal Density = 3.23 Mg/m^3 (mullite)

Figure A2.7 AS Fiber at $t = 0-730$ days, $T = 1093^{\circ}\text{C}$ to 1427°C (2000°F to 2600°F)
 Glass Density = 2.54 Mg/m^3 and Crystal Density = 3.23 Mg/m^3 (equilibrium crystal composition)

Figure A2.8 ACS Fiber at $t = 0-1800$ sec, $T = 1093^{\circ}\text{C}$ to 1427°C (2000°F to 2600°F)
 Glass Density = 2.61 Mg/m^3 and Crystal Density = 3.3 Mg/m^3 (mulitte ss)

Figure A2.9 ACS Fiber at $t = 0-730$ days, $T = 1093^{\circ}\text{C}$ to 1427°C (2000°F to 2600°F)
 Glass Density = 2.61 Mg/m^3 and Crystal Density = 3.3 Mg/m^3 (mullite ss)

Figure A2.10 ACS Fiber at $t = 0-730$ days, $T = 1093^{\circ}\text{C}$ to 1427°C (2000°F to 2600°F)
 Glass Density = 2.61 Mg/m^3 and Crystal Density = 3.3 Mg/m^3 (equilibrium crystal composition)

Table A2.8: Parameters Used in the Calculation of Linear Shrinkage as a Function of Time and Temperature

Fiber	ν , (1/s)	ν , (1/day)	E (kJ/mole)	E/R (°K)	n	Glass Density (Mg/m ³)	Initial Crystal Density (Mg/m ³)	Final Crystal Density (Mg/m ³)
AS	7.7×10^{13}	6.7×10^{18}	550	6.6×10^4	0.257	2.54	3.23	2.79
ACS	7.9×10^{16}	6.8×10^{21}	651	7.8×10^4	0.192	2.61	3.35	2.87

A2.6 CONCLUSION

The devitrification kinetics of alumina-silica based refractory insulating fibers can be modeled using the JMA theory and practical information regarding potential use conditions can be extracted. Linear shrinkage or volume fraction crystallized can be determined at any time and temperature and as a result, a practical maximum use temperature can be predicted. However, the model is only good during the period of single phase crystallization which occurs at short times. Therefore, some adjustments have been made to the linear shrinkage model to account for the densities of the actual phases crystallizing.

A2.7 NOMENCLATURE.

A	empirical specific volume factor for Al_2O_3 in glass
a	crystallization rate
ACS	alumina - chromic oxide - silica
AS	alumina - silica
ASZ	alumina - silica - zirconia
C	empirical specific volume factor for Cr_2O_3 in glass
E	activation energy
f_c	volume fraction crystallized
k	rate constant
n	Avrami coefficient
S	empirical specific volume factor for SiO_2 in glass
t	time
t- ZrO_2	tetragonal zirconia
T	absolute temperature, °K, (unless specified as °C)
T_p	crystallization temperature (exothermic peak)
R	ideal gas constant
V	volume
w	weight fraction
w_c	weight fraction crystal
w_g	weight fraction glass
w_i	weight fraction of each crystal phase in total crystal material
Z	empirical specific volume factor for ZrO_2 in glass
ρ	density
ρ_c	density of the total crystalline material
$\rho_{t,T}$	intermediate density
ρ_i	density of each crystal phase present
v	kinetic frequency factor

Subscripts:

S	silica, SiO_2
A	alumina, Al_2O_3
g	glass
c	crystal
t	time
T	temperature

for example,

$\rho_{t,T}$	density after heating at time, t, and temperature, T
w_{Sg}	weight fraction of silica in the glass phase
w_g	weight fraction of glass phase in the fiber

A2.8 REFERENCES

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APPENDIX 3

DELTA-DENSITY MODEL

A3.1 INTRODUCTION

As has been shown, the linear shrinkage in a melt-spun fiber can be directly related to the density increase upon devitrification by

$$\text{Per Cent Linear Shrinkage} = 100 \left(1 - \frac{\rho_{\text{glass}}}{\rho_{\text{crystal}}} \right) \quad (1)$$

where

ρ_{glass} = the density of the glassy fiber

ρ_{crystal} = the density of the devitrified (crystallized) fiber

The crystalline density can be calculated from the final distribution of crystalline phases and the density of each phase by the rule of mixtures for densities (the additive rule for specific volume):

$$\frac{1}{\rho_{\text{crystal}}} = \sum \left(\frac{w_i}{\rho_i} \right) \quad (2)$$

where

w_i = weight fraction of crystalline phase i in the material

ρ_i = the density of each crystalline phase (from literature)

The final distribution of crystalline phases in the material may be found from the appropriate phase diagram. Therefore, to predict the shrinkage due to devitrification for a new fiber composition, only the composition and the glass density need to be known. The density of the glass can be measured using the pycnometer method, [Reed 1988 p.106, Andrews 1928 p.33-36], but if the fiber has not been manufactured, it is necessary to be able to predict the density of the melt-spun glass.

The most frequently used method of predicting glass density from the composition was developed by Huggins and Sun [1943, Morey 1954 p.224]. They tabulate sets of specific volume factors for many oxides over different composition ranges relative to Si content. Unfortunately, when these specific volume factors were used to calculate the densities of the commercial AS, ASZ and ACS fibers, the calculated density was consistently lower than the measured (pycnometer) density. This may indicate some difference in the glass structure of the melt-spun glass or a difference in the composition range studied. Therefore, specific volume factors were derived for the melt-spun glass fibers using the measured densities as follows [Scholes 1975 p.385].

A3.2 DERIVATION OF SPECIFIC VOLUME FACTORS FOR GLASS DENSITY IN MELT-SPUN FIBERS.

The following equation applies for the density of glass based on composition. This is the additive rule for specific volume.

$$\frac{1}{\rho_{\text{glass}}} = Sw_s + Aw_A + Zw_z + Cw_c \quad (3)$$

where

$$\begin{aligned} w_s &= \text{wt \% SiO}_2 \\ w_A &= \text{wt \% Al}_2\text{O}_3 \\ w_z &= \text{wt \% ZrO}_2 \\ w_c &= \text{wt \% Cr}_2\text{O}_3 \end{aligned}$$

S, A, Z and C are empirical constants (specific volume factors).

The densities for the three commercially available fibers were measured, and the density of vitreous silica is commonly available in the literature. This data is presented in Table A3.1.

Table 3.1: Composition and Density of Commercial Melt-Spun Fibers and Vitreous Silica

Fiber	wt %, Al ₂ O ₃	wt %, SiO ₂	wt %, ZrO ₂	wt %, Cr ₂ O ₃	Density, (Mg/m ³)
vit.SiO ₂	0	1	0	0	2.20
AS	0.48	0.52	0	0	2.55
ASZ	0.32	0.49	0.19	0	2.90
ACS	0.40	0.53	0	0.07	2.61

Substituting the data from Table A3.1 into equation 3 and solving for the variables, empirical specific volume factors can be derived for these glass fibers. The empirical specific volume factors for SiO₂, Al₂O₃, ZrO₂ and Cr₂O₃ (S, A, Z, and C respectively) are shown in Table A3.2. These empirical specific volume factors (A, Z, and C) can be used to calculate density of the glass in a melt spun fiber over a wide range of compositions. Of course use of these factors will result in densities which are most accurate for compositions near those of the measured fibers.

Table A3.2: Empirical Specific Volume Factors for
Calculating the Density of Melt-Spun Fibers
From the Composition in Weight Per Cent

Component	Symbol	Factor
SiO ₂	S	0.4545
Al ₂ O ₃	A	0.3278
ZrO ₂	Z	0.0937
Cr ₂ O ₃	C	0.1585

As a measure of the power of the various oxides to increase the density of vitreous silica, the hypothetical oxide glass density was calculated. The hypothetical glass density is simply the inverse of the empirical specific volume factor. The higher the hypothetical glass density, the more power the oxide has to increase the glass density of the mixture. The hypothetical oxide glass densities are as follows: ρ -Al₂O₃ = 3.05, ρ -ZrO₂ = 10.67, and ρ -Cr₂O₃ = 6.31 Mg/m³. This shows that the addition of alumina does not greatly increase the glass density, while the addition of zirconia or chromia does greatly increase the glass density relative to vitreous silica.

A3.3 CALCULATION OF DENSITIES AND LINEAR SHRINKAGE

The use of the specific volume factors for calculating glass density allows the prediction of linear shrinkage in a fiber, composed of any combination of silica with alumina, zirconia and/or chromia, due to devitrification based solely upon the composition of the fiber. To this end, a matrix of compositions in the Al₂O₃-SiO₂-ZrO₂ system was chosen consisting of intervals of composition of 5 wt % of each oxide for compositions less than 50 wt % ZrO₂. The empirical specific volume factors were used to calculate the glass density. See Table A3.3 and Figure A3.1. The equilibrium crystalline compositions were calculated for each point in the matrix and the literature densities of the crystal phases were used to calculate the equilibrium crystalline density. See Table A3.4 and Figure A3.2. The linear shrinkage due to devitrification was calculated for each point in the matrix using equation 1 and these calculated glass and crystal densities. See Table A3.5 and Figure A3.3.

Table A3.3: Calculated Glass Density in ASZ Fibers Using Empirical Specific Volume Factors.
Glass Density in Mg/M³ for Weight Fraction Zirconia

wt.fr. silica	Glass Density (Mg/m ³) for Weight Fraction Zirconia					
	0	0.1	0.2	0.3	0.4	0.5
0	3.05	3.29	3.56	3.88	4.27	4.74
0.1	2.94	3.15	3.41	3.70	4.05	4.48
0.2	2.83	3.03	3.26	3.53	3.85	4.24
0.3	2.73	2.92	3.13	3.38	3.67	4.02
0.4	2.64	2.82	3.02	3.24	3.51	3.83
0.5	2.56	2.72	2.90	3.12	3.36	3.65
0.6	2.48	2.63	2.80	3.00	3.22	
0.7	2.40	2.54	2.71	2.89		
0.8	2.33	2.46	2.62			
0.9	2.26	2.39				

Table A3.4: Calculated Crystalline Density in ASZ Fibers Using Literature Densities of Individual Phases.

wt.fr. silica	Crystalline Density (Mg/m ³) for Weight Fraction Zirconia					
	0	0.1	0.2	0.3	0.4	0.5
0	3.98	4.11	4.24	4.38	4.54	4.70
0.1	3.66	3.79	3.90	4.02	4.15	4.29
0.2	3.39	3.52	3.62	3.72	3.93	4.16
0.3	3.18	3.37	3.55	3.75	3.96	4.20
0.4	3.02	3.19	3.35	3.53	3.74	3.97
0.5	2.88	3.02	3.17	3.34	3.52	3.73
0.6	2.75	2.87	3.01	3.16	3.32	
0.7	2.63	2.74	2.86	3.00		
0.8	2.51	2.62	2.73			
0.9	2.41	2.51				

Table A3.5: Calculated Linear Shrinkage in ASZ Fibers

wt.fr. silica	Total Shrinkage (%) for Weight Fraction Zirconia					
	0	0.1	0.2	0.3	0.4	0.5
0	23.4	20.0	16.1	11.5	5.9	-0.9
0.1	19.8	16.7	12.7	8.0	2.4	-4.3
0.2	16.5	13.8	9.7	5.0	1.9	-1.8
0.3	14.0	13.2	11.7	9.8	7.3	4.2
0.4	12.5	11.6	10.0	8.2	6.1	3.7
0.5	11.1	10.0	8.4	6.6	4.4	2.1
0.6	9.8	8.6	6.9	5.1	3.0	
0.7	8.6	7.2	5.5	3.7		
0.8	7.3	5.9	4.2			
0.9	6.2	4.7

Figure A3.1 Calculated Glass Density, (Mg/m³), as a Function of Silica Content for Constant Amounts of Zirconia. The Alumina Content is Calculated by Difference

Figure A3.2 Calculated Equilibrium Crystalline Density, (Mg/m^3), as a Function of Silica Content for Constant Amounts of Zirconia in possible ASZ Fibers. The Alumina Content is Calculated by Difference

Figure A3.3 Calculated Linear Shrinkage, (%), as a Function of Silica Content for Constant Amounts of Zirconia in possible ASZ Fibers. The Alumina Content is Calculated by Difference

A3.4 DISCUSSION AND CONCLUSIONS

The ability to predict the maximum amount of linear shrinkage in a fiber, composed of any combination of silica with alumina, zirconia and/or chromia, due to devitrification based solely upon the composition of the fiber, as described above, is very important since it provides for the design of a fiber with minimum shrinkage within the compositional constraints of manufacture.

Since the presence of zirconia increases the glass density to such a great extent, it may be possible to find an optimum composition to minimize shrinkage by minimizing the difference between the glass density and the crystalline density. The need to minimize the difference in densities had previously been recognized, but it was thought that it would be necessary to minimize the density of the crystalline phase. Little thought had been given to minimizing the difference by also increasing the density of the glass. Cristobalite is the only crystalline phase that has a density near to that of the glass. Unfortunately, the presence of cristobalite is undesirable in a refractory fiber because it undergoes reversible phase transitions upon heating and cooling which are undesirable due to structurally destructive volume changes. ZrO_2 also undergoes reversible phase transformations on heating and cooling. Use of this analysis may make it possible to use a composition which contains little SiO_2 or ZrO_2 in the devitrified fiber.

To determine such a composition, the data calculated from the matrix of shrinkages (Tables A3.3-A3.5 and Figures A3.1 - A3.3) were used to develop a ternary contour plot (Figure A3.4) on the Al_2O_3 - SiO_2 - ZrO_2 phase diagram. The actual matrix points are shown divided into approximate shrinkage ranges. Figure A3.4 suggests that a zero shrinkage fiber may be achieved for a series of compositions bordering 50 wt % ZrO_2 in the ternary alumina-silica-zirconia system. An ideal fiber might contain only a small amount of silica or zirconia and thus would be found near the intersection of the zero-shrinkage contour and the mullite-zircon alkemade line. However, some additional manufacturing problems must be overcome due to the low viscosity of the melt before such a composition could be fiberized. Use of the fiberization model may make this possible.

Figure A3.4 Ternary Contour Plot of Linear Shrinkage Due to Devitrification Calculated from the Composition

A3.5 REFERENCES.

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APPENDIX 4

MODELING FIBER FORMATION BY THE SPINNING PROCESS

A4.1 INTRODUCTION

Commercial refractory insulating fibers are cost effectively produced by a spinning fiberization process. Fiberization occurs when a ceramic melt is poured onto rapidly rotating disks [Westerlund and Hoikka, 1989]. Melt threads are thrown from the disks into a collection chamber while they cool and become glassy fibers. Key features of the fiberization process can be broken into three stages as illustrated in Figure A4.1.

The molten refractory exits the melt furnace as a stream from an orifice and falls onto a rotating disk. A thin film of liquid is formed along the outside surface of the disk. Since the density of the liquid is greater than that of the surrounding air and the centripetal acceleration is directed toward the dense fluid and disk axis of rotation, a Rayleigh-Taylor (RT) instability between the air and liquid develops. The liquid, having a higher density than the air, is driven from the disk surface and is replaced by the air. Small wave-like perturbations form and grow into fibers on the disk surface due to this RT instability. The initial stage of the perturbation takes the form of a short cylinder and moves in the outward radial direction. As the fiber increases in length and shrinks in thickness, the viscosity increases rapidly because of the rapid heat transfer to the surroundings. Finally, the fiber is broken free from the liquid on the disk because the tensile force, due to air drag and the centrifugal acceleration acting on the fiber, exceeds the liquid viscous and surface tension forces at the fiber base.

The entire process can be divided into the following three stages:

Stage 1. Perturbations form and grow due to Rayleigh-Taylor instability under action of centrifugal acceleration.

Stage 2. Fiber is elongated due to the resulting free surface flow and rapidly cooled by convection and radiation heat transfer with the surroundings.

Stage 3. Fiber is broken at its base, because the drag forces and inertia exceed the liquid viscous and surface tension forces at the disk.

Although the refractory melt can generally be considered a Newtonian fluid, the viscosity of the melt changes by several orders of magnitude in a fraction of a second as the fiber cools and solidifies into a glass. The fiber behavior in the glassy state is that of a Bingham plastic (non-Newtonian fluid) as it yields when the fiber breaks free from the disk.

Figure A4.1: Fiber Formation Process

A4.2 PREVIOUS WORK

Westerlund and Hoikka [1989] first introduced a model for the investigation of a breaking mechanism during the formation of mineral fibers with a spinning machine under steady-state conditions. They calculated the temperature, position, and internal tension of a single fiber during the formation process according to the effects of the inertial and aerodynamic forces by assuming that the fiber length, diameter and the fiber speed are constant. They also indicated that the dynamic viscosity increases when a fiber grows due to rapid solidification of the material melt.

Eisenklam [1964] analyzed ligament formation from spinning disks and cups and gave an expression of a growth rate factor due to the Rayleigh-Taylor instability in the direction of inertial force at the interface of an assumed inviscid fluid and air. Expressions are presented and experimentally confirmed for the conditions of drop formation emanating from spinning cups [Fraser et al., 1963]. Photographs were shown identifying three mechanisms of drop formation from rotating cups: (a) direct drop formation at low flow rate, (b) break-down of threads into small spheres at medium flow rate, and (c) sheet disintegration into spheres at high flow rate. The mechanism (b) is similar to the fiber formation process, in which threads form long jets. The jets are stretched and finally break down into strings of drops as they extend into the surroundings.

Hinze and Milborn [1950] derived a semi-empirical relationship between the number of ligaments and dimensionless groups that represent the state of ligament formation from stability considerations of a liquid torus that forms on the outer periphery of the spinning cup. The number of ligaments (Z) was given by

$$Z = 0.215 \left[\frac{\rho \omega^2 D^3}{\sigma} \right]^{5/12} \left[\frac{\rho \sigma D}{\mu^2} \right]^{1/6} \quad (1)$$

Eisenklam [1964] points out that this equation was verified experimentally for small disks ($D=2.5$ cm, but not as large as 10 cm) and liquids whose dynamic viscosity varied widely but whose surface tension and density were practically invariant with respect to temperature. Experiments performed by Hinze and Milborn [1950] also showed that the number of ligaments is independent of the volumetric flow rate, Q . They further analyzed various stages of the development of one single ligament and predicted that the shape of the ligaments was roughly an involute.

Ziabicki [1976] explained the nature and mechanisms of physical phenomena accompanying a continuous polymer fiber formation process. These fibers are formed by the extrusion of the molten fluid through a spinneret, a rounded orifice in a melt container. He also provided critical conditions of fiber formation such as the critical spinnability number. The spinnability of a fluid is the ratio of its dynamic viscosity and surface tension, (μ/σ) . The lower the ratio μ/σ , the more probable the fiber will be broken into drops and the shorter the critical fiber length will be. The critical fiber length is the maximum length for which the liquid can be stretched by the spinning process. Typical values of the spinnability ratio for some materials using various spinning procedures are given in Ziabicki's book [1976].

Chen and Frazier [1992] introduced the rapid solidification processing of titanium aluminides by the melt-spinning method. The process is similar to the refractory fiber spinning process except that the melt is supplied and controlled by a tilt crucible. A personal computer, PC-based, data acquisition system was developed to measure process variables such as the temperature of the melt, the crucible tilt speed and the wheel spinning speed. A charge coupled device, CCD, camera was

used to monitor the melt flow and the ribbon formation mechanisms. The results showed that ribbon formation was dominated by surface tension during the initial stage and by viscous drag in the later stage. The resulting ribbons were acicular or needle-like in appearance.

Although the industrial spinning processes were initiated as early as the 1940's, there is no theoretically sound understanding of this unique operation [Westerlund and Hoikka, 1989]. A partial reason for this is the difficulty associated with measuring and observing fibers during formation at high operating temperatures (1500-2000°C) and rugged manufacturing conditions. Other difficulties relate to small fiber size (1-10 μm in diameter) and rapidly occurring phenomena (disk speeds up to 15,000 rpm) requiring high-speed film photographic techniques. Up to now, the studies in this field have been of general technological nature [Subochev et al., 1989]. However, the way in which a single fiber is generated, elongated and broken up is not entirely understood. Careful experiments were needed to provide a better understanding of the mechanism of fiber formation, thereby resulting in improved process control. Therefore, an experimental device was built to model refractory fiberization by the spinning process.

The purpose of this work is to study the phenomena occurring in the fiber spinning process, i.e. to understand mechanisms of glassy fiber formation, growth, and break-up. Also, the authors have developed empirical relationships between the fiber parameters (including fiber diameter, d , fiber length, L , and instability wavelength, λ , and the controllable parameters and fluid transport properties, including rotation speed, n , disk diameter, D , dynamic viscosity, μ , flow rate, Q , of the liquid melt and surface tension, σ , between liquid and air, to improve control of the fiberizing process. In addition, an improved understanding of the spinning process is valuable to the material scientist. For instance, it may be possible to make low dynamic viscosity fibers using the spinning method. Usually, low viscosity fibers are manufactured as polycrystalline materials using a more expensive sol gel process [Olds, 1992]. Also, because the cilia within the human lung cannot naturally discharge particles that are smaller than 10 μm [Silverman et al., 1971], small diameter fibers in service that fracture and become airborne may represent a potential health problem for maintenance workers. However, small diameter fibers, $<3\mu\text{m}$, result in improved thermal insulation characteristics [Pelanne et al., 1981]. Therefore, manufacturers of refractory fibers are particularly keen on controlling the fiber diameter in the industrial spinning process.

A4.3 EXPERIMENTAL SET UP AND DESIGN

The experimental set up consists of a spinning machine for thread formation, and the stroboscope-camera and high-speed video systems for recording the phenomena. Design of the apparatus is based on dynamic similarity analysis.

A4.3.1 Dynamic Similarity Analysis

Since the actual fiber spinning process occurs too fast to be traced with all but the most expensive motion photographic techniques, the operation temperature is very high, and the fiber thread is too small to be readily observed, it is necessary to select a proper substitute liquid to model the refractory fiber liquid melts. As previously discussed, the spinnability of the liquids was found to be an important criteria for predicting the maximum length for which liquid can be stretched by spinning process [Ziabicki, 1976]. Therefore, the substitute liquid should have approximately the same spinnability as that of the fiber liquid melts to satisfy the length requirements of fiber products.

Properties of refractory fibers, based on the constituents Al_2O_3 and SiO_2 , were studied according to data given by Bansal and Doremus [1986]. The density and surface tension of molten ceramic material, from which refractory fibers are derived are not strong functions of temperature, but are strong functions of fiber composition. However, the dynamic viscosity of these compositions is a very strong function of both material composition and temperature. A typical spinnability number

for the Al_2O_3 - SiO_2 refractory melt is [Olds, 1992]
$$\mu/\sigma = \frac{1.5(Ns/m^2)}{0.3(m/N)} = 5 \text{ s/m}.$$

Several substitute liquid models were considered in the experiment. The dynamic viscosity, surface tension, and spinnability of the candidate liquids are listed in Table A4.1. Note that the ratio, 4.6 s/m, of the viscosity to the surface tension of glycerin at 40°C is close to that suggested, 5 s/m, for fiber melts. Therefore, glycerin was further investigated as the substitute liquid in the experiment.

Other properties of glycerin are similar to those of the refractory fibers according to data found in the literature [Liley et al., 1988]. The density and surface tension of glycerin over the temperature range 20°C to 60°C are almost constant [Weast, 1976]. The viscosity is a function of both the glycerin to water ratio and temperature.

Dynamic similarity analysis was then performed to determine the design criteria for the experiment. It was found that fiberization is related to the Reynolds and Weber numbers based on the Buckingham Pi theorem [Kundu, 1990].

Table A4.1. Spinnability of Candidate Liquids

Liquid	T, (°C)	μ , (N-s/m ²)	σ , (N/m)	μ/σ , (s/m)
Carnauba wax	95.0	0.029	0.032	0.9
SAE 30 oil	15.6	0.038	0.036	10.6
Ethyl alcohol	20.0	0.001	0.023	0.1
Glycerin	20.0	1.41	0.064	22.3
	25.0	0.95	0.063	15.1
	30.0	0.63	0.063	10.0
	40.0	0.28	0.062	4.6
	60.0	0.08	0.061	1.3
	80.0	0.03	0.059	0.5
Machine oil (heavy)	20.0	0.45	0.037	12.0
	40.0	0.11	0.037	3.0
	60.0	0.04	0.035	1.1
	80.0	0.02	0.034	0.5

The model disk diameter at different rotation speeds is calculated for glycerin at temperatures ranging from 20°C to 60°C by matching the Reynolds and Weber numbers with those of the industrial refractory fiberization process. The model disk diameter, based on matching the Reynolds number is

$$D_m = D_f \sqrt{\frac{\omega_f \rho_f \mu_m}{\omega_m \rho_m \mu_f}} \quad (2)$$

and based on matching the Weber number, the model disk diameter is

$$D_m = D_f \left[\frac{\omega_f}{\omega_m} \right]^{\frac{2}{3}} \left[\frac{\rho_f \sigma_m}{\rho_m \sigma_f} \right]^{\frac{1}{3}} \quad (3)$$

Model disk diameters were calculated from the above formula and parameters for a refractory fiber were based on $\text{Al}_2\text{O}_3\text{-SiO}_2$ spinning conditions developed at Schuller International Inc. The physical parameters in the industrial prototype process are $\rho_f = 2900 \text{ (kg/m}^3\text{)}$, $\mu_f = 2.37 \text{ (N-s/m)}$, $\sigma_f = 0.416 \text{ (N/m)}$, $n_f = 12700 \text{ rpm}$, $D_f = 0.203 \text{ m}$.

Corresponding to above actual fiberization parameters, the maximum diameter and maximum rotation speed of model disk were selected as $D_m = 0.5 \text{ m}$ and $n_m = 2500 \text{ rpm}$, respectively and used to find the model characteristics through the dynamic similarity analysis. Based on these critical parameters the experimental device, shown in Figure A4.2, was designed and constructed.

Figure A4.2 Experimental Apparatus

A4.3.2 Spinning Machine Design

The disc, (6), is driven by a variable speed [0 to 2500 revolutions per minute (rpm)] DC motor, (4). Disk speed is measured by tachometer, (7), with a signal generated by a magnetic pickup adjacent to a 30 tooth gear. The calibrated relationship between the disk rotation speed and the DC output voltage of the tachometer is linear.

Three different disks are available for testing. The disks are made of acrylic tube with wall thickness, $t = 6.8$ mm and outer diameters 0.254 m, 0.381 m, and 0.457 m. The outer disk circumference is covered with an adhesive backed, rough grit sandpaper. The sandpaper provides a roughened surface allowing improved wetting between the liquid and the disk than existed when the liquid contacted only the acrylic. Glycerin flows onto the disk circumference through a nozzle, (9). The liquid is supplied by means of a pumping system, (2), which includes an AC motor, a positive displacement gear pump and tubing, and is returned to a temperature controlled container, (3). The flow rate of liquid is measured by flow meter, (10), and controlled by a ball valve, (11). The temperature of the liquid is measured and controlled by a thermistor, (8), and a relay control system. A cover, (5), made of acrylic plate, is provided to contain the liquid spray.

A4.3.3 Stroboscope-Camera System

A Toyo-View 45C large format (102 mm x 127 mm) camera was used to record the fiberization process because of its high resolution. The magnification of the camera can be changed from 2 to 5 by an adjustable bellows. A digital stroboscope with flashing range 100 flashes per minute to 30,000 flashes per minute was used as a light source for the camera. The diameters and length of threads and wavelength of the instability were recorded in the photographs which were later analyzed with the aid of an optical magnifier, 7X, containing a graduated scale.

High shutter speed, 1/2000 to 1/8000 second, photographs were taken with the 35 mm camera using a 300 W quartz-halogen lamp and high-speed film (ISO 1000). The resulting images provided insight into the nature of fiber motion relative to the inertial reference frame. However, this optical system did not have the resolution to allow measurement of fiber diameters (30-100 μ m). The large format camera and strobe light using ISO 800, 400 and 320 Polaroid films has greater resolution and proved to be an effective tool at visualizing the fiber formation, relative to the disk, and allowing the acquisition of quantitative measurements of fiber diameter, length and instability wavelength. This technique was used for disk speeds up to 1560 rpm with the 0.457 m disk.

A4.3.4 High-Speed Video System

A KODAK EKTAPRO 1000 Motion Analyzer was used to record the entire process of fiber formation. It was used to observe the instability initiation and growth, and measure fiber growth velocity. The motion analyzer consists of a imager, a keypad, a processor, a monitor and specialized high-speed tapes.

A4.4 RESULTS AND DISCUSSION

Thread parameters such as fiber diameter, fiber length, and instability wavelength were measured from the recorded pictures. Effects of the controllable parameters on the thread parameters were qualitatively analyzed and the relationship between each thread parameter and the controllable parameters was quantitatively established, which were described in detailed by Cai [1994].

A4.4.1 Observed Phenomenon from Experimental Models

Figure A4.3 and Figure A4.4 are typical high resolution images for low and medium disk speeds, respectively. Note that the thread growth direction deviates from the radial direction of the disk. In fact, the fiber is directed slightly away from the disk rotation direction. This is due to drag resistance from the air. The drag force on the fiber combines with the centrifugal acceleration to provide a means by which the fiber is severed from its base after it grows to its maximum length.

It is at this final stage of the fiber formation model that the researcher must be cautious in accepting the applicability of this particular experiment to the industrial process. To recap what was done, glycerin was utilized because it has appropriate fluid transport properties at a particular temperature. However, as the refractory fiber is thrown from the spinning wheel during the actual industrial fiberization process, a substantial amount of heat is transferred to the surroundings, allowing the fiber to cool from 2000°C to nearly room temperature in a fraction of a second. The refractory properties, primarily the viscosity, will change very rapidly, in fact, so rapidly that the resulting material is a glass when the same process occurring, more slowly (in quasi equilibrium), would yield a crystal.

A4.4.2 Measurements of the Fiber Parameters

The thread parameters, thread diameter, d , thread length, L , and wavelength, λ , of the instability (the distance between two nearest threads), were scaled on the images, such as Figures A4.3 and A4.4, using the disk wall thickness, t , as reference length (the acrylic edge of the disk is approximately 6.8 mm thick), and measured by an optical magnifier with a deviation of ± 0.05 mm. The experimentally determined real thread parameter, F , such as d , L , λ , is calculated by

$$F = \frac{F_m}{M} = F_m \frac{t_r}{t_m} \quad (4)$$

where F_m is the measured thread parameter on a picture, M is the magnification of that picture taken at the specific controllable parameters, it is a ratio of the measured disk wall thickness (t_m) on the photograph to the real disk thickness (t_r). Table A4.2, Table A4.3, Table A4.4, and Table A4.5 show the thread parameters for different disk diameters, rotation speeds and temperatures.

Figure A4.3 High Resolution Image
($n = 90$ rpm, $T = 41^{\circ}\text{C}$, $D = 0.381$ m, $Q = 2.56 \times 10^{-5} \text{ m}^3$, $M = 1.9$)

Figure A4.4 High Resolution Image
($n = 670$ rpm, $T = 25^{\circ}\text{C}$, $D = 0.381$ m, $Q = 1.26 \times 10^{-5} \text{ m}^3$, $M = 3.8$)

Table A4.2. Thread Diameter for 95 wt % Glycerin and 5 wt % Water System

	T, °C	μ , (N-s/m ²)	Calculated thread diameter (μ m) (Disk rotation speed, rpm)					
			(260)	(400)	(670)	(920)	(1200)	(1560)
Disk diameter 0.457 m	25	0.336	100	84	64	50	34	27
	40	0.108	88	75	54	45	31	23
	50	0.051	84	67	48	41	26	20
	60	0.024	80	63	42	35	25	20
Disk diameter 0.381 m	25	0.336	136	99	75	56	46	38
	40	0.108	127	81	65	42	39	32
	50	0.051	113	75	55	36	30	27
	60	0.024	104	67	47	32	26	22

Table A4.3. Thread Length for 95 wt % Glycerin and 5 wt % Water System

	T, °C	μ , (N-s/m ²)	Calculated thread length (mm) (Disk rotation speed, rpm)					
			(260)	(400)	(670)	(920)	(1200)	(1560)
Disk diameter 0.457 m	25	0.336	11.2	9.4	8.2	6.2	5.2	3.6
	40	0.108	10.8	8.0	6.1	4.5	3.6	2.8
	50	0.051	9.6	7.2	5.0	4.0	3.2	2.4
	60	0.024	8.7	6.5	4.8	3.5	2.9	2.2
Disk diameter 0.381 m	25	0.336	17.0	11.1	8.6	6.7	5.7	4.4
	40	0.108	11.1	8.1	6.2	5.0	4.3	3.8
	50	0.051	11.0	7.5	5.5	4.1	3.5	2.5
	60	0.024	9.4	6.7	5.5	3.8	3.2	2.4

Table A4.4. Instability Wavelength for 95 wt% Glycerin and 5 wt% Water System

	T, °C	μ , (N-s/m ²)	Calculated instability wavelength (mm) (Disk rotation speed, rpm)			
			(260)	(400)	(670)	(920)
Disk diameter 0.457 m	25	0.336	3.17	2.17	1.38	0.59
	40	0.108	2.94	1.96	1.32	0.59
	50	0.051	2.30	1.76	1.13	0.56
Disk diameter 0.381 m	25	0.336	4.41	2.45	1.78	0.90
	40	0.108	2.86	1.61	1.09	0.85
	50	0.051	2.72	1.39	0.88	0.65

Table A4.5. Calculation of Thread Growth Rates

Time, τ_i (s)	Picture N_i	Length, L_i , (mm)	ΔN	$\Delta\tau = \Delta N/1000$	ΔL , (mm)	$V = \Delta L/\Delta\tau$ (mm/s)
$\tau_o=0$	122	13.1				
$\tau_1=0.01$	132	19.6	10	0.01	6.5	650
$\tau_2=0.02$	142	27.8	10	0.01	8.2	820
$\tau_3=0.03$	152	38.4	10	0.01	10.6	1060
$\tau_4=0.03$	154	40.7	2	0.002	2.3	1150

The uncertainty of the F value was determined from the uncertainty of its dependent variables, Φ_i (the measurements of disk diameter, disk wall thickness, the wall thickness on the pictures, etc.). The method of estimating the propagation of measurement uncertainty presented by Holman and Gajda [1989] is used to estimate uncertainties in this study. The uncertainty for the experimental results is estimated on the basis of the uncertainties in the primary measurements. The relationship was applied to the experimentally determined function of fiber or controllable parameters, F, so that the uncertainty in that function, W_f , could be determined while using estimates of the uncertainties of each fiber and controllable parameter:

$$W_f = \sqrt{\sum_{i=1}^n \left(\frac{\partial F}{\partial \Phi_i} W_{\Phi_i} \right)^2} \quad (5)$$

The uncertainty calculations were performed for two points, and marked as error bars in Figure A4.6 through Figure A4.8. The calculations show that the uncertainty range for measurements of thread parameters was about ten percent. The fiber growth rates were determined from the high-speed video system as illustrated in Figure A4.5 for only the low disk speeds (90-150 rpm).

Figure A4.5. Thread Growth Velocity Versus Time (data from the motion analyzer recording tape)

RELATIONSHIP BETWEEN THREAD DIAMETER AND REYNOLDS NUMBER * WEBER NUMBER

Figure A4.6. Dimensionless Thread Diameter Versus the Product of Reynold's Number and Weber Number.

Figure A4.7. Dimensionless Thread Length Versus the Product of Reynold's Number and Weber Number.

RELATIONSHIP BETWEEN WAVELENGTH AND REYNOLDS NUMBER * WEBER NUMBER

Figure A4.8. Dimensionless Instability Wavelength Versus the Product of Reynold's Number and Weber Number.

A4.4.3 Effects of the Controllable Parameters on the Thread Parameters

Pictures were taken at different rotation speeds, disk diameters, camera magnifications, M , and liquid dynamic viscosities to systematically study the effects of varying these parameters. To study the effect of disk rotation speed on thread parameters, the disk rotation speed was varied from 90 rpm to 1560 rpm while maintaining all other properties the same. It was observed that the thread diameter and length and instability wavelength, all of the thread parameters, decreased as the disk rotation speed increased. The effect of disk diameter on thread parameters was also studied. The various disk diameters were 0.381 m and 0.457 m. The same thread parameters noted above decreased with increased disk diameter. This was expected because the speed of the disk increased at its circumference by either increasing the disk angular velocity or by increasing the disk diameter. The effects of disk curvature, in the range of disk diameters studied, were thought to be negligible. Glycerin viscosity was also varied by changing the glycerin temperature. The glycerin viscosity varied from 0.336 (N-s/m²) to 0.024 (N-s/m²) corresponding to the temperature varying from 25°C to 60°C, respectively. The thread parameters were found to decrease as liquid viscosity decreased.

A4.4.5 Quantitative Relationship Between the Thread Parameters and the Controllable Parameters

According to the dynamic similarity analysis, the fiberization process is related to the Reynold's, (Re), and Weber, (We), Numbers, which are separate combinations of the fluid properties and controllable parameters. The thread parameters, when plotted against the product of the Reynold's Number and the Weber Number, (Re*We), resulted in acceptable correlations. Plotted in logarithmic form, Figures A4.6 - A4.8 provide relationships between dimensionless fiber diameter, fiber length, and instability wavelength, respectively, as functions of the Reynold's Number*Weber Number product. The linear correlation coefficients, r^2 , were also calculated.

Since Re*We is a combination of the controllable parameters, the relationships between thread parameters and the controllable parameters were quantitatively established using a least square curve fitting routine and are expressed by equations 6-8.

$$\frac{d}{D} = 0.061(Re * We)^{-0.24} = 0.051 \left[\frac{\rho^2 n^3 d^5}{\sigma \mu} \right]^{-0.24} \quad (6)$$

$$\frac{\lambda}{D} = 7.34(Re * We)^{-0.31} = 61.38 \left[\frac{\rho^2 n^3 d^5}{\sigma \mu} \right]^{-0.31} \quad (7)$$

$$\frac{L}{D} = 5.199(Re * We)^{-0.23} = 43.48 \left[\frac{\rho^2 n^3 d^5}{\sigma \mu} \right]^{-0.23} \quad (8)$$

The established relationships between the fiber and the controllable parameters were considered as the mathematical models for the fiberization process. They are of practical value to the fiber manufacturing industry. The relationship between the fiber diameter and the product of Reynold's and Weber Numbers is especially important for improving the fiber performance, because the fiber diameter is a key parameter for thermal insulating performance [Pelanne, 1981]. Equation (6) can be used to control the fiber diameter by adjusting the controllable parameters. For example, to reduce the fiber diameter of a given material, either the disk rotation speed or disk diameter would be increased.

Using the correlations for fiber diameter, length growth rate, and wavelength of instability, an effective mass flow rate was estimated. It was found that approximately 20 percent of the liquid incident on the disk was formed into fibers, the remainder was deflected to the sidewall of the apparatus. It was difficult to see variations in the fraction of fiber production among the experimental runs. Further study is necessary to determine whether this fraction depends on the parameters varied during the experiments.

A4.4.6 Physical Meaning of Mathematical Models

From the experimental results shown in Figures A4.6 through A4.8, it is seen that the fiber diameter, d , and fiber length, L , are almost proportional to wavelength, λ . Wavelength is equal to

$$\lambda = \frac{2\pi}{K} \quad (9)$$

where K is the wave number of the wave-like perturbations. Eisenklam [1964] gives an expression for K on a rotating disk as:

$$K = \sqrt{\left(\frac{\rho}{C\sigma}\right)\left(\frac{\omega^2 D}{2}\right)} \quad (10)$$

where C is a constant, which is proportional to the liquid viscosity.

The wave number, K , increased with increased liquid density, ρ ; disk angular acceleration, $\omega^2 D/2$, and diameter, and decreased with the increased liquid dynamic viscosity, μ and surface tension σ . Since d , L , and λ are inversely proportional to K , they decreased with the increased density, acceleration $\omega^2 D/2$, and disk diameter, D , and increased with increased viscosity, μ , and surface tension, σ . Therefore, the experimental results presented here are consistent with previously determined analytical conclusions.

The growth rate of the RT instability depends on the wave number, K , and can be expressed as $\delta = (aK)^{1/2}$ for a fluid with a constant acceleration, a , [Kull, 1991]. A larger K results in an increased growth rate of the RT instability and a larger number of smaller diameter fibers. Therefore, the centrifugal acceleration is the driving acceleration of fiber formation, while the viscous and the surface tension forces provide a resistance to fiber formation.

A4.5 CONCLUSION

Fiber formation by a spinning process has been modeled by experimental simulation. As a result of this study, the mechanisms of this process are better understood. The effects of the controllable parameters on the fiber parameters were qualitatively studied. Relationships between the fiber parameters and the controllable parameters have been quantitatively established. The results can be used to improve the fiber formation process by appropriate adjustment of the controllable parameters.

A4.6 NOMENCLATURE

a	liquid acceleration
d	fiber or thread diameter
D	diameter of disk
F	experimental determined function
K	instability wave number
L	length of fibers
M	magnification
n	rotation speed of disk
Q	volumetric flow rate of liquid melts
R	radius of disk
Re	Reynolds number
We	Weber number
t	thickness of the disk rim
T	temperature
V	velocity of fiber growth
Z	number of fibers
∂	growth rate of Rayleigh-Taylor instability
ϕ_i	measured parameters
λ	instability wavelength
μ	dynamic viscosity
ρ	liquid density
σ	surface tension between liquid and air
ω	disk angular velocity

SUBSCRIPTS

f	fiber
m	liquid model, or measured variables from pictures
r	real variables
o	initial variables

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APPENDIX 5

EXPERIMENTAL

A5.0. INTRODUCTION

The results of the kinetic study indicate two possible methods of dealing with devitrification. One possibility is to accept that devitrification occurs, but that the devitrification might be controlled and harnessed to make a glass-ceramic fiber from melt-spun fibers. The goal would be to produce polycrystalline fiber similar to those produced by the sol-gel method, but with less expense. Another possibility is that the non-equilibrium behavior of the ASZ fiber which did not fit the kinetic model might be used to advantage in creating a fiber with a more refractory glass phase.

A5.1. MODIFIED ASZ FIBERS

A5.1.1 Analysis of AS, ACS and ASZ Fibers and Choice of Modified Composition

Devitrification of three alumina-silica based refractory glass fibers (AS, ASZ, and ACS) had been examined [Lo 1991] as discussed previously. The third component in two of these fibers (ASZ and ACS) was ZrO_2 or Cr_2O_3 respectively. Shrinkage was also measured for these same fibers [Martin et al. 1991]. Both the ASZ and ACS fibers showed less shrinkage relative to the AS fiber when heated at $1427^\circ C$ for 4 and 24 hours. However, after one week, the ASZ fiber exhibited significantly less shrinkage than either the binary AS fiber or the ACS fiber. The significant difference between the two ternary fibers was that the devitrification of the ACS fiber appeared to follow an equilibrium path (the glass composition followed that expected for an equilibrium liquid during crystallization), whereas the ASZ did not [Lo 1991]. In the ASZ fiber, more glass phase was retained and, furthermore, the glass phase was more refractory. In fact, examination of the effect of the mass absorption coefficient on x-ray analysis revealed that the glass phase was becoming even more refractory than previously thought. The compositional data was obtained [Lo 1991] by assuming that the ratio of the measured x-ray peak intensity, after some period of heat-treatment, to the pure or maximum intensity equaled the weight fraction of that phase in the fiber. The composition and weight fraction of the glass were found by difference [Lo 1991].

Employing the mass absorption coefficient takes into account the effect of the presence of other phases on the measured intensity of x-ray peaks. In determining the extent of the mass absorption effect on the glass composition, the following equation was used [Cullity 1958, p.390 eqn.14-9]:

$$\frac{I_x}{I_{x \text{ pure}}} = \frac{w_x \left(\frac{\mu}{\rho} \right)_x}{w_x \left[\left(\frac{\mu}{\rho} \right)_x - \left(\frac{\mu}{\rho} \right)_{\text{glass}} \right] + \left(\frac{\mu}{\rho} \right)_{\text{glass}}} \quad (1)$$

where

- I_x = the measured intensity of x-ray peak due to phase x in a two-phase mixture of phase x and glass
- $I_{x \text{ pure}}$ = the intensity of the x-ray peak due to phase x when pure
- w_x = weight fraction of component x
- $(\mu/\rho)_x$ = mass absorption coefficient of x

The mass absorption coefficient of the glass was found by assuming that the glass composition was the same as the initial composition of the fiber and employing a linear combination of the mass absorption coefficients of those components. The mass absorption of each of the oxide components is listed in Table A5.1.

Table A5-1: Mass Absorption Coefficients (μ/ρ) for Cu K α Radiation for Several Oxides for use in the Calculations of X-Ray Intensity in a Mixture

Compound	Mol. Wt., (g/mole)	μ/ρ , (cm ³ /g)
SiO ₂	60.08	34.95
Al ₂ O ₃	101.96	31.75
ZrO ₂	123.22	109.16
mullite (3Al ₂ O ₃ ·2SiO ₂)	426.05	32.65
zircon (SiO ₂ ·ZrO ₂)	183.30	84.84

If the mass absorption coefficient of phase x is greatly different from the mass absorption coefficient of the matrix, then ($I_x/I_{x \text{ pure}}$) does not equal the weight fraction as is generally assumed, and the weight fraction will be over or under-estimated when looking only at the x-ray peak intensity. As a result of the difference between μ/ρ for zirconia and zircon and the other components in the ASZ fiber, the weight fraction will be over-estimated when it is assumed to be equal to the intensity ratio. The effect will be greatest for zirconia. The weight fraction of mullite and cristobalite will be slightly under-estimated. To find the actual weight fraction of a phase, x, in a fiber (a mixture of phases) from an observed intensity, the following equation was used:

$$w_x = \frac{\left(\frac{I_x}{I_{\text{pure}}}\right)\left(\frac{\mu}{\rho}\right)_{\text{fiber}}}{\left(\frac{\mu}{\rho}\right)_x - \left(\frac{I_x}{I_{\text{pure}}}\right)\left[\left(\frac{\mu}{\rho}\right)_x - \left(\frac{\mu}{\rho}\right)_{\text{fiber}}\right]} \quad (2)$$

where $I_x/I_{x \text{ pure}}$ = observed intensity originally reported as weight fraction of phase x previously assumed to be $I_x/I_{x \text{ pure}}$ [Lo 1991]

This equation is just a rearrangement of the previous equation to solve for the actual weight fraction (w_x) of a phase in the fiber. $(\mu/\rho)_{\text{fiber}}$ was calculated from the starting fiber composition.

Using this equation, the original glass compositions were recalculated. Crystalline zirconia was over-estimated in the original work, and so as more devitrification of zirconia occurs, the error in the glass composition increases. This can be seen in Figures A5.1 through A5.4 which show both the previously recorded glass composition and the adjusted glass composition. The complete phase diagram is also provided in Figure A5.5 for context and reference.

Figure A5.2 Portion of the ASZ Phase Diagram Showing the Originally Calculated Glass, 1204°C (2200°F)

Figure A5.5 $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-ZrO}_2$ Ternary Phase Diagram

There are definite advantages to creating an amorphous fiber that does not completely devitrify in use. The presence of a retained glass phase reduces shrinkage, due to lower density of the glass phase, and helps retain fiber flexibility, due to the inherent flexibility of the glass over that of crystalline phases. However, the glass phase is usually less refractory than the crystalline phases. As devitrification progresses, the glass composition may tend to follow the corresponding phase boundary trough composition as if it were an equilibrium liquid phase, thus becoming less refractory. A fiber that retained more glassy phase during use and that, furthermore, retained a glassy phase that became more refractory with extended use, would be desirable. Based on the non-equilibrium devitrification behavior and low shrinkage exhibited by the ASZ fiber, it was thought that adding small amounts of nucleating agents to the base ASZ composition might actually improve the performance by encouraging the non-equilibrium behavior. It was hoped that the nucleating agents would cause phases to crystallize preferentially that caused the composition of the glassy phase to shift to regions of the phase diagram with higher liquidus temperatures. In the ASZ system, this would translate to the crystallization of more mullite and less zircon.

Of course, because nucleating agents were chosen as additives, if the approach of direct use after production did not produce the desired phases preferentially, the same fibers could be used to investigate another possible approach. The same fibers could be used to create, by further processing, a glass ceramic in which crystallization is complete, or nearly complete, before the fiber is put into use as a refractory insulator.

The nucleating agents were chosen by starting with a list of traditional nucleation agents for refractories, [Beall 1971 p.81], and eliminating those which were considered to be too expensive or which had a low melting point. Although HfO_2 is expensive, it was further considered because of its high melting point and similarity to zirconia, but it was finally decided not to use it because its expense would prohibit any commercial production. Additionally, La_2O_3 was added to the list.

A5.1.2 Manufacture of Modified ASZ Fibers

The fibers were manufactured by the melt-spinning process at Schuller. Each fiber identification number ending in "A" was a fresh batch. Each fiber identification number ending in "B" or "C" was made by adding new material to the remainder of the previous melt. Quantitative EDS analysis was attempted, but gave inaccurate results on these fibers, probably due to geometric effects (sample roughness due to fibrous form), [Goldstein et al. 1981 p.338]. Therefore, the compositions of the resulting fibers were chemically analyzed at Schuller. For reference, those results are presented in Table A5.2.

Table A5.2: Oxide Compositions of Refractory Fibers (Chemical Analysis Performed at Schuller)

	1022A	1022B	1023A	1023B	1024A	1024B	1024C	1025A
SiO ₂	48.4	48.6	45.8	45.1	47.5	47.9	48.3	46.5
Al ₂ O ₃	32.1	31.7	31.0	30.4	31.9	30.8	29.1	31.4
ZrO ₂	19.1	18.9	19.4	17.6	18.6	17.6	17.0	18.9
La ₂ O ₃	0.0	0.0	0.0	3.6	1.5	3.3	3.5	0.0
TiO ₂	0.1	0.7	3.7	2.7	0.1	0.1	0.10	0.1
Cr ₂ O ₃	0.0	0.0	0.0	0.0	0.0	0.0	1.71	0.0
WO ₃	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.4

	1026A	1026B	1027A	1027B	1027C	1028A	1028B	1028C
SiO ₂	43.2	41.4	48.0	46.2	45.7	49.7	49.5	49.1
Al ₂ O ₃	28.6	27.2	30.5	29.0	28.2	32.5	32.1	32.5
ZrO ₂	17.7	16.0	19.0	18.7	18.3	13.8	14.5	14.4
La ₂ O ₃	0.0	3.2	0.1	0.0	0.0	3.3	2.4	1.8
TiO ₂	0.1	0.1	0.1	0.1	0.6	0.1	0.1	0.1
Cr ₂ O ₃	0.0	0.0	1.9	6.1	7.4	0.7	1.4	2.1
WO ₃	9.6	11.2	0.0	0.0	0.0	0.0	0.0	0.0

A5.1.3 Experimental Methods Specific to Modified ASZ Fibers.

Small (1-2g) samples of the fibers were heated for 15 min, 4 hr, and 24 hr at 1427°C to observe the course of devitrification. Larger samples were heated for 1 week at 1427°C to further observe the course of devitrification, but also with measurements taken to observe the amount of shrinkage. Qualitative x-ray analysis of these heat-treated samples is shown in Table A5.3 and Table A5.3A.

Table A5.3: Qualitative X-Ray Analysis of Experimental Fibers

Fiber	Heating Time	Cristobalite	Mullite	Zircon	m-ZrO ₂	t-ZrO ₂
1022A	15 min	-	m	-	-	vs
	4 hr	ms	mw	-	mw	ms
	24 hr	s	mw	-	w	s
	1 week	s	mw	mw	mw	ms
1022B	15 min	-	ms	-	-	s
	4 hr	s	mw	-	w	s
	24 hr	m	w	w	w	m
	1 week	ms	mw	m	w	m
1023A	15 min	w	mw	-	w	s
	4 hr	ms	mw	-	mw	s
	24 hr	ms	mw	w	mw	ms
	1 week	mw	mw	m	w	w
1023B	15 min	w	mw	w	w	m
	4 hr	mw	mw	m	w	-
	24 hr	w	mw	m	-	w
	1 week	w	mw	m	-	-
1024A	15 min	w	mw	w	w	s
	4 hr	ms	mw	ms	w	mw
	24 hr	m	mw	ms	w	w
	1 week	m	mw	s	w	w
1024B	15 min	mw	w	w	w	ms
	4 hr	m	mw	ms	w	mw
	24 hr	m	mw	ms	w	w
	1 week	mw	w	mw	w	w

Table A5.3 (continued): Qualitative X-Ray Analysis of Experimental Fibers

Fiber	Heating Time	Cristobalite	Mullite	Zircon	m-ZrO ₂	t-ZrO ₂
1024C	15 min	m	w	w	w	ms
	4 hr	ms	mw	m	w	m
	24 hr	m	w	m	w	w
	1 week	m	w	m	-	w
1025A	15 min	mw	w	-	w	s
	4 hr	s	mw	m	w	s
	24 hr	s	mw	m	w	m
	1 week	s	mw	m	mw	ms
1026A	15 min	m	mw	mw	w	ms
	4 hr	s	mw	m	w	m
	24 hr	s	mw	ms	w	m
	1 week	s	mw	s	w	w
1026B	15 min	m	mw	ms	w	w
	4 hr	m	w	ms	w	w
	24 hr	m	w	ms	w	w
	1 week	m	w	ms	w	w
1027A	15 min	mw	mw	w	w	s
	4 hr	s	mw	w	w	s
	24 hr	s	mw	m	w	m
	1 week	s	mw	m	w	m
1027B	15 min	ms	mw	-	w	s
	4 hr	m	w	w	w	m
	24 hr	s	mw	mw	w	s
	1 week	s	mw	m	w	ms

Table A5.3 (continued): Qualitative X-Ray Analysis of Experimental Fibers

Fiber	Heating Time	Cristobalite	Mullite	Zircon	m-ZrO ₂	t-ZrO ₂
1027C	15 min	ms	mw	-	w	s
	4 hr	ms	mw	w	w	ms
	24 hr	m	w	mw	w	m
	1 week	m	w	ms	w	w
1028A	15 min	m	mw	w	w	s
	4 hr	m	mw	m	w	w
	24 hr	m	mw	ms	w	w
	1 week	m	mw	m	w	w
1028B	15 min	m	mw	-	w	s
	4 hr	ms	mw	m	w	mw
	24 hr	ms	mw	ms	w	w
	1 week	m	mw	ms	w	-
1028C	15 min	s	mw	-	w	s
	4 hr	s	mw	m	w	m
	24 hr	ms	mw	ms	w	w
	1 week	m-ms	mw	ms	w	w

Table A5.3A: Explanation of Intensity Abbreviations in Table A5.3

X-Ray Peak Area	Intensity	Abbreviation
0-50	Very Weak	vw
50-200	Weak	w
200-400	Moderately Weak	mw
400-800	Moderate	m
800-1000	Moderately Strong	ms
1000-1500	Strong	s
1500+	Very Strong	vs

The shrinkage measurements are referred to here as "first-pass" shrinkage measurements since they were intended to be applied to all of the fibers as a first-pass measurement of shrinkage for gross comparisons. The "first-pass" shrinkage results are included in Table A5.4.

Table A5.4: "First-Pass" Shrinkage, One Week Heat-Treatment at 1427°C

Fiber	Shrinkage, %		
	Length	Width	Thickness
1022A	6.3	10.8	57.1
1022B	12.5	11.1	60.0
1023A	36.6	42.9	80.6
1023B	34.2	32.3	91.4
1024A	35.0	28.6	81.8
1024B	45.0	40.0	85.5
1024C	58.8	57.1	94.4
1025A	7.7	4.8	64.1
1026A	27.9	24.2	75.0
1026B	34.8	39.4	82.3
1027A	6.7	16.7	55.6
1027B	50.0	43.8	68.8
1027C	39.1	36.0	47.8
1028A	40.7	39.3	79.2
1028B	48.5	48.6	80.0
1028C	53.3	52.6	80.0

The complete method for these "first-pass" shrinkage measurements is as follows. During manufacture, fiber mats are rolled into manageable bundles as they leave the collection belt. Sections were cut out of the roll with "L" being the "length-wise" direction as on the collection belt, and "W" being the direction of the "width". If the roll seemed to naturally break up into layers, presumably corresponding to layers from the collection belt, these were chosen as the height of the sample, "H", otherwise, an arbitrary thickness was selected. Measurements were made with an ordinary ruler marked to 1/16 inches. However, physical variations in the sample size account for a greater error than the measuring device, especially for the post heat-treatment measurements.

Note: although the mass of the sample was recorded prior to heat-treatment, it was not possible to use this information to determine possible mass changes in the samples because, invariably, pieces

of fiber break off when the samples are removed from the porous zirconia support plate after heat-treatment.

In addition to the "first-pass" shrinkage measurements, additional fiber blanket shrinkage measurements were performed on those fibers that were deemed to have low shrinkage from the "first-pass" tests. These measurements were intended to be more accurate. The procedure follows. Needled fiber blankets of the low shrinkage fibers (1022A, 1022B, 1025A and 1027A) were cut into approximately 3.5" squares. These squares were measured and weighed and placed on refractory board. Fragments of heating elements (moly-disilicide) were placed on top of the fiber mats slightly in from the edge of the fiber piece and the distance from edge to edge of the fragments was measured. This measurement was used after heat-treatment to reduce error due to uneven shrinkage and warping of the edges of the fiber mat. The refractory board with the fiber mats was placed in and withdrawn from the furnace while the furnace was at 1427°C. Shortly after the refractory board was removed from the furnace, the fiber mats were removed from the refractory board to cool. The results of these additional heat-treatments are included in Table A5.5 and Table A5.6

Table A5.5: Shrinkage at 1427°C for 24 Hours Heat-Treatment of Low-Shrinkage Fiber

Fiber	Average Shrinkage, (%)
1022A	4.7
1022B	10.7
1025A	8.1
1027A	8.5

Table A5.6: Shrinkage at 1427°C for One Week Heat-Treatment of Low-Shrinkage Fiber

Fiber	Average Shrinkage, (%)
1022A	3.6
1022B	12.5
1025A	5.7
1027A	8.8

A5.1.4 Discussion and Results of Study of Modified ASZ Fibers

The entire series of modified refractory fibers was studied with x-ray diffraction to observe the course of crystallization. Quantitative analysis was attempted using the matrix flushing technique with corundum as an internal standard, [Chung 1974]. However, anomalous concentrations of mullite were observed with this technique (roughly twice that possible using the batch fiber composition and stoichiometric composition of mullite). This was consistent in all of the fiber samples investigated with the internal standard and has been observed by others, [Ganz 1982 p.139]. Because of the presence of the glass phase, it was risky to guess at the relative amounts of crystalline phases present. Therefore, the intensities of the peaks were classified as to strength (from weak to strong) and tabulated. This analysis shows that the relative amounts of phases present and the rapidity of crystallization at 1427°C has been affected by the additions. The purpose, however, was to affect the course of crystallization such that more mullite and less zircon crystallized so as to increase the refractory nature of the retained glass phase. This does not appear to have been achieved. The intensity of the mullite peak in the modified fibers is comparable to or less than that observed in the baseline composition (1022A). Furthermore, in all of the modified fibers, zircon appears at shorter heat-treatment times, and the intensity of the zircon peak is greater than that of the baseline composition.

Additionally, the results of the shrinkage studies (Tables A5.4 - A5.6) show that shrinkage is greater in all of the modified fibers than in the baseline composition (fiber 1022A). Industry standards specify less than 3 percent shrinkage and the baseline composition is the only fiber that comes close to achieving that small amount of shrinkage. The shrinkage of several of the fibers appeared to be nearly as small as that of the baseline in the first pass shrinkage tests, Table A5.4, but more accurate shrinkage tests, Table A5.5 and Table A5.6, showed the shrinkage of the modified fibers to be greater than that of the baseline.

A5.2 GLASS-CERAMIC FIBERS

A5.2.1 Alumina-Silica Based Refractory Fibers Containing TiO_2

A5.2.1.1 Choice of TiO_2 -AS Fiber Composition

The addition of TiO_2 and, to a lesser extent, ZrO_2 is expected to promote crystal nucleation in aluminosilicate glasses, [McMillan 1979, p.74-76]. Glass fibers shrink upon devitrification, becoming significantly less effective for insulation purposes. It may be beneficial to create a fiber which is already crystalline when produced, and therefore shrinks less in use. Therefore, it is of interest to study the devitrification of aluminosilicate fibers containing TiO_2 and/or ZrO_2 . Rapid and complete crystallization would, in this case, be a desirable property.

To ensure that the composition would be able to be fiberized with existing processing methods, and also to retain a basis of comparison, compositions based on the AS fiber were chosen. The following fiber compositions were proposed:

SiO_2 , wt %	Al_2O_3 , wt %	TiO_2 , wt %
49	46	5
47	43	10

However, it was learned [Olds 1992] that fibers containing TiO_2 had been experimentally manufactured previously at Schuller (Manville). Three fiber samples (two compositions) were obtained as follows:

Fiber Number	SiO_2 , wt %	Al_2O_3 , wt %	TiO_2 , wt %	ZrO_2 , wt %
236, 237	48.6	41.4	10	
238	28	50	19	3

It was suggested that some Fe_2O_3 might be present as an impurity. This would lower the melting point. The composition data shown in Table A5.7 was obtained using the x-ray microanalysis capability (EDS) associated with the SEM. No Fe was found. The area surveyed during each EDS measurement was approximately $400 \mu\text{m}^2$.

Table A5-7: Composition of Al_2O_3 - SiO_2 - TiO_2 (- ZrO_2) Fibers Based on EDS.

Fiber Number	Al_2O_3 , wt %	SiO_2 , wt %	TiO_2 , wt %	ZrO_2 , wt %
236	35.92	54.28	9.80	-
237	35.67	56.74	7.59	-
238	41.53	40.11	16.12	2.24

SEM micrographs were obtained at the same time as the EDS analysis. It was observed that the fibers were smooth and that there was a variation in shot content and morphology of shot particles between the fibers. Shot is the spherical material that is formed at the "head" of each fiber as it is formed off of the spinning wheel. The formation of shot is undesirable for several reasons. Its presence means that less of the material has been made into fibers. Shot is much larger in size than the diameter of the fibers and increases the bulk density of a fiber blanket. It was seen in the micrographs that there is relatively little shot in the 236 and 237 fibers, but that there is a lot of shot of larger size and varying shape in the 238 fiber.

A5.2.1.2 Experimental Methods Specific to the Study of Ti-Containing Fibers

The goal in studying the Ti-containing fibers was to observe the course and speed of crystallization with the idea of making glass-ceramic fibers. Because of the presence of nucleating agents, it was expected that significant crystallization should occur in a fairly short time. A heat-treatment time of 15 min. was chosen to minimize the effects of sample heat-up time in the furnace. Two temperatures were chosen based on the upper and lower temperatures studied by Lo [1991] and were expected to show some differences in nucleation and growth rates. Nucleation rates are greater at lower temperatures and growth rates are greater at higher temperatures. Phases present in the heat-treated fibers were studied with x-ray diffraction and reference to the applicable phase diagrams indicated that crystallization was not complete after 15 minutes. Therefore, a longer time, 4 hours, was chosen. In addition, a combined treatment consisting of 4 hours at the lower temperature and 4 hours at the higher temperature was chosen with the expectation that nucleation

would occur at the lower temperature and then grain growth would occur at the higher temperature. A 24 hour heat-treatment was performed in an attempt to produce completely crystallized material for determining percent crystallization and, also, because it would be desirable to have nearly equilibrium crystallization in the glass-ceramic fiber to reduce shrinkage.

A5.2.1.3 Discussion and Results of Heat Treatments and XRD Study of Ti-Containing Fibers.

The fiber compositions 236 and 237 lie in the mullite/cristobalite/ Al_2TiO_5 phase triangle. From the phase diagram, [Agamawi 1951], the equilibrium solid composition would be 27.7 wt % mullite, 26.7 wt % Al_2TiO_5 , and 45.5 wt % cristobalite (SiO_2). Mullite is expected to crystallize first. Most likely, Al_2TiO_5 would crystallize next. This was not observed. In fact, Al_2TiO_5 was not observed in any of the XRD charts. Table A5.8 includes a summary of all of the XRD results on fibers 236, 237 and 238.

Since there is only 2.24 % ZrO_2 in fiber 238, it seems likely that the phases should be similar to those observed in the Al_2O_3 - SiO_2 - TiO_2 ternary, but with some additional Zr-containing phase. However, this was not observed in the XRD results. Rutile (TiO_2) crystallized after mullite and no cristobalite was observed. The additional Zr-containing phase that is present in the heat-treated fibers is ZrTiO_4 . It is obvious from an examination of the components that a SiO_2 -containing phase, most likely cristobalite, must eventually crystallize. The SiO_2 - TiO_2 - ZrO_2 phase diagram [McTaggart and Andrews 1957] shows a possible crystallization path with rutile and ZrTiO_4 crystallizing and ending in a eutectic reaction producing cristobalite. Equilibrium solid phases are likely to be mullite (57.85 wt %), ZrTiO_4 (3.68 wt %), rutile (14.67 wt %), and cristobalite (23.80 wt %). The alternative to cristobalite crystallization is that the SiO_2 exists in a glass phase. Based on this discussion, it seems likely that a glass phase exists even in the 24 hour and 1 week, 1430°C samples.

A week-long (168 hr) heat treatment was performed at 1430°C. Fibers 236 and 237 shrank greatly and formed dense, solid masses. Fiber 238 retained a somewhat looser structure, but still sintered to form a single chunk of crumbly material. SEM was used to observe the structure of the fibers subjected to week long heat-treatment at 1430°C. (See Figures 6.20 through 6.24.) All fibers had large, elongated crystals with random orientation. The crystals were approximately 0.5 to 1 μm by 3 to 4 μm in size. A great deal of flow was observed at the contact points.

The TiO_2 -containing fibers 236 and 237 sintered to form chunks so solid that it was difficult to break them by hand. The high degree of sintering indicated by this and the SEM micrographs is very undesirable in a refractory fiber because thermal conductivity is greatly increased. Similarly, the amount of shrinkage, although not quantified, was great enough to disqualify them for use as commercial insulation. The study of these fibers was discontinued.

Table A5.8: X-Ray Diffraction Results after Heat Treatment of $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-TiO}_2$ (ZrO_2) Fibers

Fiber Number	Heat-Treatment		X-Ray Diffraction Observations
	Time	Temp. °F	
236, 237	As received	As received	Mostly amorphous, some rutile
	15 min	1800	Some amorphous, mullite nucleation
	15 min	2600	Some amorphous, mullite
	4 hr	1800	Mullite nucleation
	4 hr	2600	Some amorphous, mullite, some cristobalite
	4hr	1800	Some amorphous, mullite, very little cristobalite
	4hr	2600	
	24 hr	2600	Little amorphous, mullite, cristobalite
	1 week	2600	Little amorphous, mullite, cristobalite
238	As received	As received	Partly amorphous, some mullite nucleation
	15 min	1800	Some amorphous, mullite nucleation
	15 min	2600	Mullite, some rutile, some ZrTiO_4
	4 hr	1800	Some mullite and rutile
	4 hr	2600	Very little amorphous, mullite, rutile, some ZrTiO_4 , no cristobalite
	4 hr	1800	Mullite, rutile, ZrTiO_4
	4 hr	2600	
	24 hr	2600	Mullite, rutile, ZrTiO_4 , no zircon or cristobalite
	1 week	2600	Mullite, rutile, ZrTiO_4 , no zircon or cristobalite

A5.2.2 Glass-Ceramic Fibers Through Post-Fiberization, Pre-Use Processing

A5.2.2.1 Experimental Development of Glass-Ceramic Study

The ultimate goal is to make a refractory fiber that exhibits little shrinkage during use at high temperatures. To achieve that goal, a series of compositions was chosen based on the commercial ASZ fiber with small amounts of additives. The additives chosen were known nucleating agents. Since direct use after production did not produce a more refractory residual glass phase. These modified ASZ fibers were used to investigate the possibility of creating glass-ceramic fibers through post-fiberization, pre-use processing in which crystallization is complete or nearly complete before the fiber is put into use as a refractory insulator. This would "pre-shrink" the fibers and also should decrease viscous sintering occurring while the fibers were in use. In effect, the result would be a glass-ceramic fiber produced by the melt-spinning process, but incorporating

a nucleation heating-cycle into the production process. This might involve heating to a nucleation temperature, holding to produce nucleation sites, and then raising the temperature to grow crystals. If growth could be achieved at a lower temperature than sintering, it might be possible to pre-shrink the fibers by devitrification and prevent, or reduce, later thickness shrinkage by sintering during use. This additional processing would increase the cost of the fibers somewhat, but should hold the price down relative to sol-gel produced fibers.

Determining possible heating cycles is the first step needed to create such a glass-ceramic fiber. Differential thermal analysis (DTA) was used to determine the first temperature of crystallization upon heating. DTA scans were obtained for each fiber on heating from room temperature to 1200°C or 1400°C. All of the scans showed a peak in the DTA at approximately 1035°C. Such an exothermic peak should indicate the onset of crystallization. Therefore, heating cycles were devised to investigate the phases present at temperatures above and below this peak, and to try to take advantage of prolonged crystallization at a minimum temperature to maximize nucleation and create a glass ceramic. These heating cycles are shown in Figure A5.6. Fibers were chosen which had exhibited the lowest shrinkage or which were hoped to show the greatest improvement, Table A5.9.

Table A5.9: Fibers Chosen for Glass-Ceramic Study

Fiber	Composition, wt %	Reason Chosen
1022A	48 SiO ₂ , 32 Al ₂ O ₃ , 19 ZrO ₂	Baseline Composition
1025A	Baseline + 2.4 WO ₃	Low Shrinkage
1027A	Baseline with 1.9 Cr ₂ O ₃	Low Shrinkage
1027C	Baseline + 0.6 TiO ₂ + 7.4 Cr ₂ O ₃	Combination of classic nucleating agents
1023B	Baseline + 3.6 La ₂ O ₃ + 2.7 TiO ₂	High shrinkage and sintering

In addition to the heating cycles designed to investigate devitrification, another series of heating cycles was chosen to investigate the progression of shrinkage. The fiber chosen for this series of tests was fiber 1023B, which had previously exhibited the most shrinkage and sintering and should, therefore, be the most obvious indicator. Diagrams of these heating cycles are shown in Figure A5.7.

A5.2.2.2 Results of Glass-Ceramic Study

As discussed previously, the x-ray analysis of the heat-treated fibers were reported in a qualitative form for analysis. The peak intensities of the largest peak for each phase present were ranked from weak to strong and tabulated. (See Table A5.10 and Table A5.11.) Additionally, the data from the continuously heated fibers (modified ASZ fibers) were included for comparison where appropriate. Shrinkage measurements and bulk density changes are listed in Table A5.12 and Table A5.13 for the heating cycles shown in Figure A5.6.

Figure A5.6 Heating Cycles to Investigate Nucleation Crystallization Effects

Figure A5.7 Heating Cycles to Investigate Nucleation Effects on Shrinkage

Table A5.10: Qualitative X-Ray Analysis of Fibers in Glass-Ceramic Studies Heating Cycle Recipe 10

Fiber	Heat Treatment	Cristobalite	Mullite	Zircon	t-ZrO ₂
1022A	10-1	-	-	-	-
	10-2	-	vw	-	mw
	10-3	vw	w	-	s
	15 min @ 1427°C	-	mw	-	s
	10-4	ms	mw	-	vs
	4 hr @ 1427°C	ms	mw	vw	vs
1025A	10-1	-	-	-	-
	10-2	mw	w	-	vs
	10-3	w	w	w	w
	15 min @ 1427°C	w	w	vw	s
	10-4	w	w	w	w
	4 hr @ 1427°C	ms	mw	mw	ms
1027A	10-1	-	-	-	-
	10-2	-	-	-	vs
	10-3	vw	w	vw	w
	15 min @ 1427°C	w	w	vw	ms
	10-4	w	w	vw	mw
	4 hr @ 1427°C	m	w	w	ms
1027C	10-1	-	-	-	mw
	10-2	-	-	-	vs
	10-3	w	w	-	w
	15 min @ 1427°C	m	w	-	ms
	10-4	w	w	vw	w
	4 hr @ 1427°C	m	w	w	ms

Notes to Table A5.10

Heat Treatment	Time-Temperature Relationships
10-1	600 to 900°C at 20°/min
10-2	10-1 + 900°C to 1040°C @ 14°/min, hold 30 min
10-3	10-2 + 1040°C to 1400°C @ 24°/min, hold 15 min
10-4	10-3 + hold at 1400°C for 4 hrs

Table A5.11: Qualitative X-Ray Analysis of Fibers in Glass-Ceramic Studies Heating Cycle Recipe 25

Fiber	Heat Treatment	Cristobalite	Mullite	Zircon	t-ZrO ₂
1022A	25-1	-	vw	-	mw
	25-2	m	mw	-	s
	15 min @ 1427°C	-	mw	-	s
	25-3	s	mw	vw	vs
	4 hr @ 1427°C	ms	mw	vw	vs
1023B	25-1	-	-	-	mw
	25-2	w	m	m	m
	15 min @ 1427°C	vw	w	w	s
	25-3	w	s	s	vw
	4 hr @ 1427°C	w	ms	ms	vw

Notes to Table A5.11

Heat Treatment	Time-Temperature Relationships
25-1	830 to 1030°C in 30 min, hold for 1.5 hr
25-2	25-1 + 1030 to 1430°C in 25 min, hold at 1430°C for 15 min
25-3	25-2 + hold at 1430°C for 3.75 hours (4 hours total)

Table A5-12: Effect of Nucleation Cycle on Shrinkage Heating Cycle Modified Recipe 25

Fiber	Heat Treatment	Shrinkage, %	
		Length/Width	Thickness
1023B	Modified 25-A	46.1	80.5
1023B	Modified 25-B	37.3	88.6

Notes to Table A5.12

Heat Treatment	Time-Temperature Relationships
Mod. 25-A	830 to 1030°C in 0.5 hr, hold 1.5 hr, 1030 to 1430°C in 0.25 hr, hold at 1430°C
Mod. 25-B	1430°C for 4 hr

Table A5.13: Effect of Nucleation Cycle on Shrinkage No ID# Heating Cycle

Fiber	Heat Treatment	Shrinkage, %	
		Length/Width	Thickness
1023B	No ID-A	7-11	21-35
	No ID-B	17-25	68

Notes to Table A5.13

Heat Treatment	Time-Temperature Relationships
No ID-A	20 min at 1030°C
No ID-B	No ID-A + 1030°C to 1400°C in 6 hrs

A5.2.2.3 Discussion of Results of Glass-Ceramic Studies.

Sample 1022A 10-1 shows the condition of the fiber at a temperature below the DTA peak to be completely amorphous. This does seem to indicate that the DTA peak marks the onset of crystallization.

When sample 1022A 10-2 is compared with fiber 1022A heated at 1035°C for 1.5 hr to determine effects of holding at assumed nucleation temperature (DTA peak), it is observed that the x-ray charts are virtually identical. Both contain broad mullite and t-ZrO₂ peaks with approximately the same intensity. The only difference is the existence of slightly more mullite with longer time at the nucleating temperature.

Sample 1022A 10-3 can be compared with fiber 1022A heated at 1427°C for 15 min to determine effects of heating through the nucleation temperature on fibers with short-term use. Again, the x-ray charts are virtually identical. The only difference is a small amount of cristobalite in the "nucleated" sample.

Sample 1022A 10-4 can be compared with fiber 1022A heated at 1427°C for 4 hours to determine effects of heating through nucleation temperature on fibers with slightly longer use. As in Samples 2 and 3, the x-ray charts are virtually identical. The only difference is a very small amount of zircon in the "non-nucleated" sample.

Samples 1025A, 1027A, and 1027C can be subjected to a similar analysis. However, strangely, any effect observed from the nucleation cycles seems to be the opposite to that anticipated. Specifically, the amounts of advanced crystalline phases (cristobalite and zircon) present at 15 minutes and 4 hours appear to be less than the amounts observed in the continuously heated fibers as studied in the previous section. Certainly, this indicates that these heating cycles are not performing the desired function for these fibers. However, it may indicate further avenues of study for the retention of refractory residual glass phases as studied in the previous section.

The recipe 25 experiment was intended to show any difference achieved with a nucleation cycle most dramatically since fiber 1023B originally had the most shrinkage and sintering of all of the modified ASZ fiber series. For fiber 1023B after 1.5 hours at 1030°C, the only crystalline phase present is t-ZrO₂. The x-ray peak is very broad, indicating small crystalline size. Crystallization does appear to be more advanced in sample ID 25-2, the 15 min 1430°C sample with the nucleation cycle, than without the nucleation cycle (more zircon, less ZrO₂), but this effect is lost by 4 hours at 1430°C. Direct examination of the x-ray trace for 1023B at 4 hours with a 1.5 hour, 1030°C nucleating cycle reveals it to be almost identical to the sample without the nucleation cycle. Additionally, the quantitative shrinkage comparison (modified recipe 25) which was performed, while it revealed a more uniform shrinkage with the nucleation cycle, did not show a large enough decrease in thickness shrinkage to indicate that sintering was being prevented. The additional shrinkage experiment showed a large thickness shrinkage even without prolonged exposure to high temperatures.

Gani and McPherson [1977] performed a series of experiments similar in concept to the recipe 10 series, although more detailed and extensive, on the binary SiO₂-Al₂O₃ system and found a similar peak DTA for the crystallization of mullite. They found, by x-ray analysis, that cristobalite formed at 1400°C although they did not observe an exothermic DTA peak up to the 1500°C limit of their apparatus. However, in this study of ternary or quaternary systems, based on the XRD data, it was inconclusive as to what the exothermic peak represented. The apparently uncorrelated changes in position and intensity of the exotherm make conjecture difficult. Various compositions appeared to crystallize mullite and t-ZrO₂, only; or mullite, t-ZrO₂, and cristobalite within the same temperature range without any correlated shift in the exotherm. The appearance of cristobalite at such a low temperature was surprising in fiber 1025A. Equally surprising was the absence of mullite upon crystallization, while the DTA showed a strong peak. It is possible that the effect of multiple phases crystallizing is causing the confusion in the DTA interpretations. Takemori and Roy [1973] state, "The simultaneous appearance of more than one type of crystal after one rapid exothermic reaction... may indicate cooperative motion of the atoms in their rearrangement during crystallization...."

It should be recalled that the goal of this method was to create a glass-ceramic fiber. Notwithstanding the interest that a puzzling DTA correlation (or non-correlation) holds, the absence of any substantial differences between the "nucleated" and "non-nucleated" samples, or even decrease in advanced crystalline phases in the nucleated samples relative to the non-nucleated samples, and the absence of any dramatic decrease in shrinkage or sintering indicates that insufficient advantage has been achieved by this method. The results might be useful in the continued study of the retention of refractory residual glass in fibers 1025A and 1027A if shrinkage were small enough to warrant that.

A5.3. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

The TiO₂-containing fibers sintered so greatly, and shrank so much, that their use as a commercial insulation is not recommended. Future study with that goal is not warranted.

The modified ASZ fibers, when continuously heated at the target use temperature (1427°C), devitrified to more advanced phases and shrank more than the baseline ASZ composition with no added oxides. These fibers are not recommended for direct use as refractory insulation.

When the modified ASZ fibers were heated after manufacture, but supposedly before use, with the idea of creating glass-ceramic fiber, some possibly interesting results were obtained. There was no

substantial differences between the "nucleated" and "non-nucleated" XRD results, when heated at the target temperature, for the baseline ASZ composition. However, when the fibers with added oxides were subjected to pre-use heating at temperatures thought to increase crystal nucleation, a decrease in advanced crystalline phases in the nucleated samples relative to the non-nucleated samples of that same fiber was observed. Unfortunately, those fibers had greater shrinkage in the target temperature shrinkage tests, and there was no dramatic decrease in shrinkage or sintering observed in the glass-ceramic tests. The experiments performed here did not achieve a sufficient advantage to be able to recommend the use of any of these fibers as high temperature insulation. The results might be useful in the continued study of the retention of refractory residual glass in fibers 1025A and 1027A, or similar fibers, if shrinkage were small enough to warrant.

Future work should concentrate on either eliminating any added oxides to the ASZ system and increasing the refractoriness of the fiber by using a composition in that system which has a higher liquidus or crystallizes to a higher invariant point, or on studying the pre-treatment heating process for use as a method of retaining a glass phase during fiber use. The first option is the more likely to succeed. It was not attempted in this work, because it would require altering the manufacturing process to accommodate a lower melt viscosity.

A5.4 REFERENCES

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