FIBER CONTRACTION APPROACHES FOR IMPROVING CMC PROPORTIONAL LIMIT

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Introduction

The fact that the service life of ceramic matrix composites (CMC) decreases dramatically for stresses above the CMC proportional limit has triggered a variety of research activities to develop microstructural approaches that can significantly improve this limit. As discussed in a previous report (ref. 1), both local and global approaches exist for hindering the propagation of cracks through the CMC matrix, the physical source for the proportional limit. Local approaches include: (1) minimizing fiber diameter and matrix modulus; (2) maximizing fiber volume fraction, fiber modulus, and matrix toughness; and (3) optimizing fiber-matrix interfacial shear strength; all of which should reduce the stress concentration at the tip of cracks pre-existing or created in the matrix during CMC service. Global approaches, as with pre-stressed concrete, center on seeking mechanisms for utilizing the reinforcing fiber to subject the matrix to in-situ compressive stresses which will remain stable during CMC service. Demonstrated CMC examples for the viability of this residual stress approach are based on strain mismatches between the fiber and matrix in their free states, such as, thermal expansion mismatch and creep mismatch (cf. refs. 1 and 2). However, these particular mismatch approaches are application limited in that the residual stresses from expansion mismatch are optimum only at low CMC service temperatures and the residual stresses from creep mismatch are typically unidirectional and difficult to implement in complex-shaped CMC.

The general objective of the present research is to determine the technical feasibility for improving the CMC proportional limit by a strain-mismatch approach which is based on the high-temperature in-situ axial contraction of the reinforcing fibers. The theory and technical details of this concept are explained in Fig.1. The prime motivation for examining such an approach was the observation, during fiber research studies at NASA Lewis, that some polycrystalline ceramic fibers currently being utilized as CMC reinforcement will display large axial contractions under certain high temperature conditions (refs. 3 and 4). These contractions occur even under the application of high tensile stress, suggesting that they should also occur within CMC, even under the back-stresses provided by the matrix during compression. As an initial step toward understanding the feasibility of the fiber contraction approach, the objective of this study (Fig. 2) was to measure and model the effects of time, temperature, and tensile stress on the free-state axial contraction of SiC fibers by two mechanisms: (I) decomposition and densification and (II) anelastic creep recovery.

Contraction Mechanism I: Decomposition/Densification

The underlying theory for Mechanism I (Fig. 3) is the fact that due to their processing approach, some polymer-derived fibers contain unstable oxide impurity phases which are not eliminated at the maximum production temperatures for the fibers (typically near 1200°C). Thermally treating these fibers above this

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temperature will result in decomposition of these phases, mass loss by volatilization of carbon and silicon monoxide, densification of the resulting microstructure, and axial and radial contraction of the fiber. Using the experimental approach described in Fig. 4, the time- and temperature-dependent contraction strain results shown in Fig. 5 were obtained for multifilament tows of polymer-derived Hi-Nicalon and Nicalon fibers. For these data, the tows were held at effectively zero stress in an argon environment. Applying thermal activation theory (ref. 5), the contraction data for the lower oxygen-containing and thus more technically-viable Hi-Nicalon fiber were found to be closely modeled by the master contraction curve shown in Fig. 6. The fact that all the data do not fit this curve can possibly be explained by measurement difficulties during the initial, very rapid, decomposition stages at the higher temperatures.

Two primary concerns for applying Mechanism I to CMC are (1) concurrent creep of the fiber during contraction so that the matrix back-stresses could possibly negate the benefits of contraction, and (2) loss of significant fiber tensile strength due to the decomposition process. Fig. 7 for Hi-Nicalon fibers in single and tow form show that as long as tensile back-stresses do not exceed ~100 MPa, the fibers can indeed achieve a net contraction of ~0.1%, a minimum desirable level since CMC proportional limits are currently less than this value. But, as Fig. 8 shows, Hi-Nicalon tows treated in argon can lose approximately 50% of their initial room-temperature strength and that, for treatments in vacuum, the strength loss can be even worse under certain conditions. Thus, as discussed in Fig. 9, for optimum application of contraction Mechanism I using Hi-Nicalon fibers, the CMC should preferably contain a large volume fraction of fibers and a low modulus matrix in order to minimize effects due to matrix back-stresses and fiber strength degradation. Additional unknown concerns could be chemical alteration of the fiber-matrix interface by the fiber decomposition products, and alteration of the decomposition kinetics by the fiber interfacial coating or by the matrix.

Contraction Mechanism II: Anelastic Creep Recovery

The underlying theory for contraction Mechanism II (Fig. 10) is based on the transient creep behavior observed for all SiC fibers tested to date (ref. 6). This transient behavior indicates that during creep at a constant level of applied stress, internal stresses (associated with grain boundary sliding) build up in the fiber microstructure which may eventually fully oppose the applied stress, resulting in saturation of creep strain. When the creep stress is completely removed, it has been observed that these internal stresses drive the creep strain back towards zero at a rate dependent on time and temperature (anelastic behavior; cf. ref. 4). It has also been observed that under zero back stress, the amount of recovered strain is some fraction of the total creep strain and that this fraction decreases with increasing creep strain (ref. 7). Thus, as discussed in Fig. 11, if thermally-stable SiC fibers were pre-crept, for example, by tensioning devices during or after fiber production, these fibers with their internal stresses could then be inserted into CMC by use of matrix fabrication time-temperature conditions less than those used during the pre-creeping stage. The CMC could then be thermally treated above the matrix fabrication temperature to allow in-situ fiber contraction in which the fiber internal stresses act to overcome the matrix back-stresses. Thus high applied creep stresses are needed to more easily overcome matrix back-stresses; but they can also be beneficial for achieving a given creep strain in a cost-effective short time.

For those studies aimed at measuring and modeling Mechanism II, SCS-6 monofilaments were used to generate data for tensile creep and recovery. This large-diameter SiC fiber was chosen because bend data exist for its creep/recovery behavior and because this behavior should be typical of thermally-stable small-diameter SiC fibers which are more technically viable for complex-shaped CMC. The experimental approach (Fig. 12) focused on determining (1) whether time- and temperature-dependent creep-recovery models developed previously from bend tests on SCS-6 fibers also applied for tensile tests on SCS-6 and (2) whether Mechanism II could provide tensile contraction strains (i.e. recovered strains) greater than

0.1% after the application of a high applied creep stress (750 MPa). The recovered strain versus creep strain results shown in Fig. 13 pertain to both questions. First, the solid curves calculated from SCS-6 bend recovery data and an anelastic creep model (ref. 7) show that although the recovered strain (for zero back-stress) increases with increasing creep strain, its fraction of the creep strain decreases. However, at a given total creep strain, the recovered strain can be increased by increasing the stress applied during the creep stage. These curves should apply in a qualitative manner to all SiC fibers which display transient creep. The close agreement between the 800 MPa predicted curve and the two SCS-6 data points supports the use of this anelastic model to also predict the amount of tensile creep recovery after achieving a given creep strain level. To estimate the conditions needed to achieve this creep strain, one can use the empirical equation shown for the abscissa in Fig. 13. Using this equation, NASA studies have determined the empirical creep constants for all SiC fibers of current technical interest (ref. 6). For the second question, it can be observed in Fig. 13 that the recovered strains for the SCS-6 tensile data were ~ 0.3%, a value well above the level needed for possible CMC application of Mechanism II. Also since the fiber internal stresses associated with the 0.3% recovered strain were ~750 MPa, fiber contractions within CMC should be able to withstand high matrix back-stresses.

Concluding Remarks

The key results of this study are summarized in Fig. 14. Regarding general conclusions from the current study (Fig. 15), Mechanisms I and II appear to be feasible for increasing CMC proportional limits. To demonstrate this, models now exist for estimating the proper fiber and CMC treatment conditions for activating these mechanisms and also the maximum amount of free-state fiber contraction. Prime concerns for the applicability of Mechanism I with Hi-Nicalon fibers are low contraction under high matrix back-stress and tensile strength loss during contraction. On the other hand, Mechanism II with SCS-6 fibers does not appear to suffer from these issues. Nevertheless, there still remains concern that the required fiber pre-creeping stage may be difficult to implement at high applied stress, for example, because of a lack of adequate tensioning devices for continuous tows of small-diameter fibers or because of a high incidence of random fiber breaks in the tows. Finally, as detailed in Fig. 16, future research will attempt to demonstrate both mechanisms in mini-CMC using SiC matrices fabricated by chemical vapor deposition (CVI). This matrix type has many advantages: (1) fabrication temperatures below those of the contraction mechanisms, (2) capability for remaining elastic during fiber contraction, and (3) the existence of a large vendor base for CMC fabrication.

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CONCEPT OF INCREASING CMC PROPORTIONAL LIMIT BY FIBER CONTRACTION

- High-Temperature Mechanisms Exist Which Cause Fibers To Contract Axially Even Under The Application of High Tensile Stress. If This Contraction Is Allowed To Occur Within Consolidated CMC, It Should Provide A Compression of The Matrix Along The Fiber Directions.
- Since Matrix Fracture Strains In CMC Are ~0.1%, Small Fiber Contraction Strains At or Above This Level Should Significantly Improve The CMC Proportional Limit And Service Life.
- For Optimum Compression, Matrix Fabrication Temperatures Should Be Below The Fiber Contraction Temperatures. Thus Post-Thermal Treatment Of The CMC Will Generally Be Required To Implement Concept.
- Likewise, Treated CMC Should Be Utilized Under Service Conditions Where Fiber And Matrix Remain Elastic, In Order To Retain A Time And Temperature-Independent Compression Of The Matrix.

Fig. 1

OBJECTIVES

GENERAL

Investigate The Feasibility For Compressing CMC Matrices And Improving CMC Proportional Limits By The In-Situ Axial Contraction Of The Reinforcing Fibers

THIS STUDY

As An Initial Step, Measure And Model The Effects Of Time, Temperature, And Stress On The Free-State Contraction Of SiC Fibers By Two Mechanisms:

I. Decomposition/Densification
II. Anelastic Creep Recovery

Fig. 2

Mechanism I:
Fiber Contraction By Decomposition And Densification

Underlying Theory

- Polymer-Derived SiC Fibers, Like Nicalon And Hi-Nicalon, Are Typically Processed At Maximum Temperatures (~1200°C) Which Allow The Retention Of Unstable Oxide Phases And Porosity In The Microstructure Inherent In The Fiber Process

- Thermal Treatment Above The Maximum Processing Temperature Will Cause The Oxide Phases To Decompose And The Resulting Microstructure To Densify, Thereby Causing Fiber Axial And Radial Contraction

Fig. 3

Mechanism I:
Fiber Contraction By Decomposition And Densification

Experimental Approach

- Measure And Model Kinetics For Contraction Of Hi-Nicalon Fibers Under Unstressed And Stressed Conditions

- Determine Residual Strength Of Contracted Fibers At Room Temperature

- Test Conditions:
  - Specimens: Hi-Nicalon Tows (N = 500, Nippon Carbon)
  - Fiber Creep Facilities: Grip-Grip Length ~ 250 mm; Hot Zone ~ 120 mm
  - Temperatures (Constant): 1200 to 1700°C
  - Environments: Argon, Vacuum
  - Stress (Constant): 0.6 to 140 MPa
  - Strength Test (Tow): Gauge Length ~ 25 mm

Fig. 4

TYPICAL CONTRACTION CURVES FOR Hi-NICALON AND NICALON TOWS IN ARGON

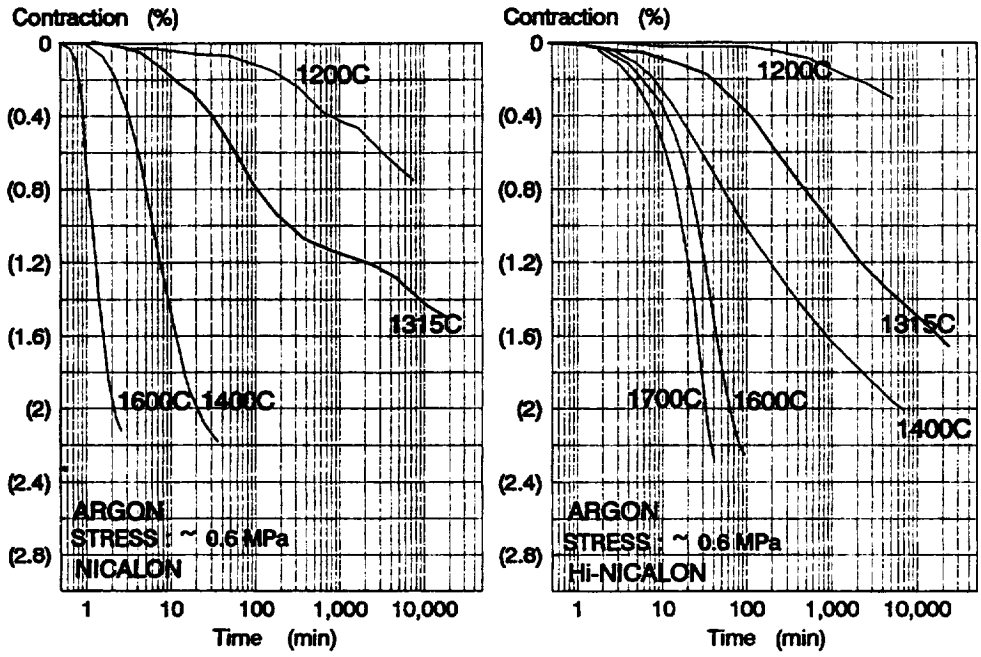


Fig. 5

MASTER CONTRACTION CURVE FOR Hi-NICALON TOWS IN ARGON USING ACTIVATION MODEL

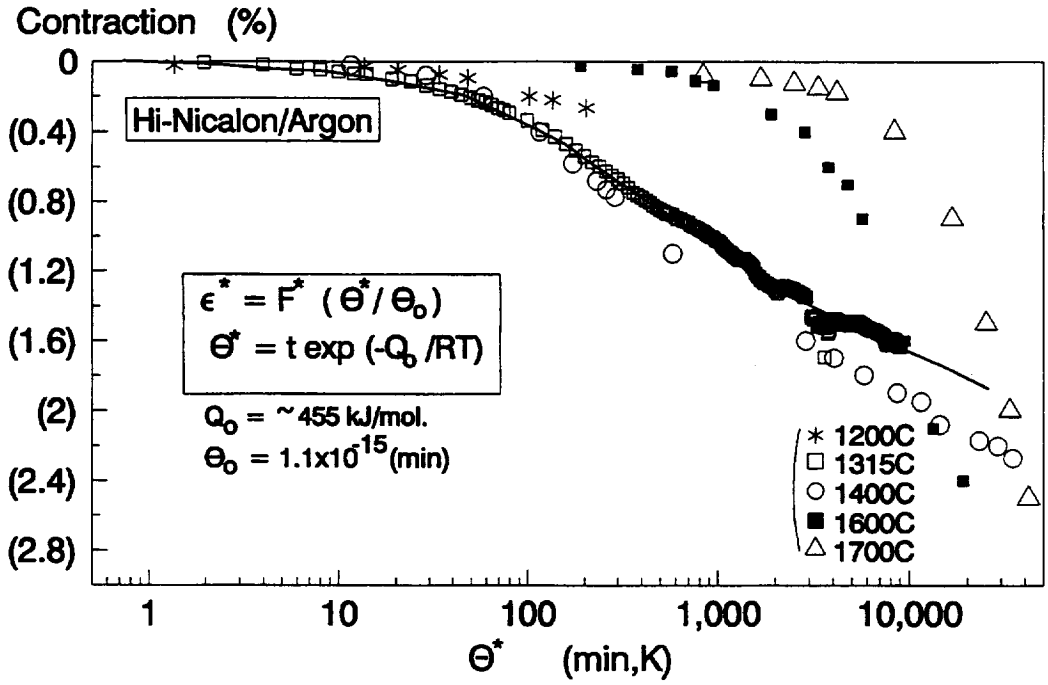


Fig. 6

STRESS EFFECTS ON THE CONTRACTION OF Hi-NICALON SINGLE AND TOW FIBERS

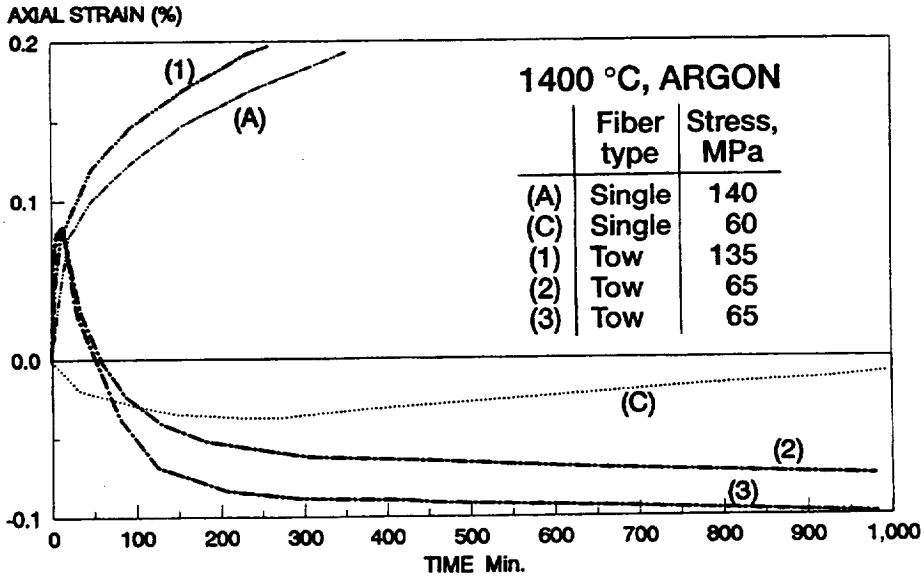


Fig. 7

R.T. TENSILE STRENGTH AFTER 100 HR CONTRACTION

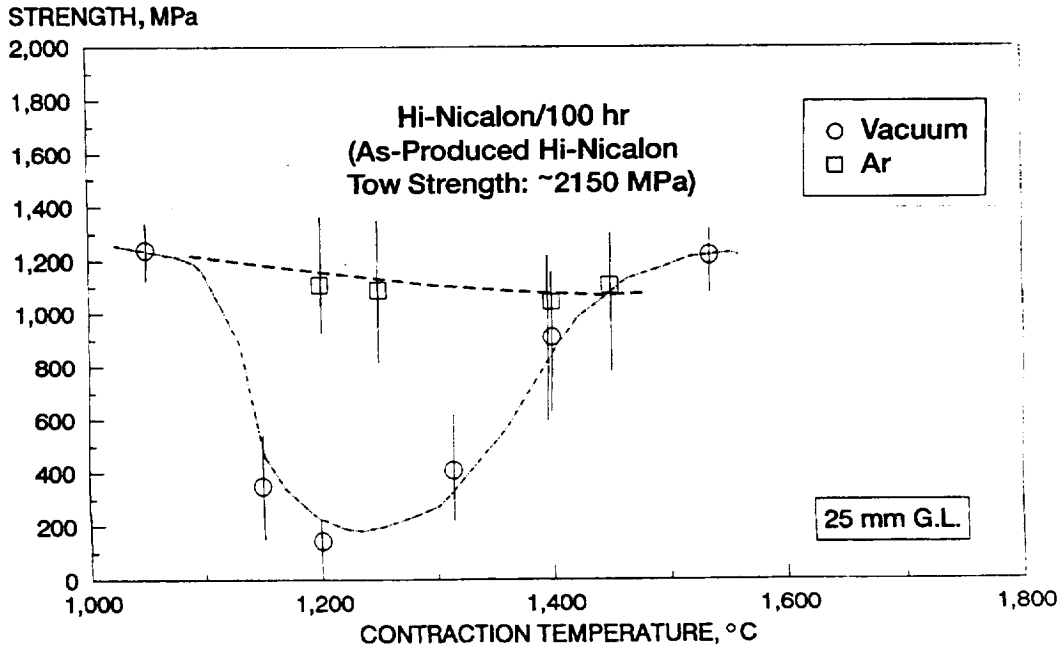


Fig. 8

Mechanism I:
Fiber Contraction By Decomposition And Densification

Possible Approach For CMC Application

- Use Fiber Preforms With High Volume Fraction And Matrices With Low Modulus In Order To Minmize Matrix Back-Stress

Potential Feasibility Issues

- Fiber Creep During Contraction
- Fiber Strength Degradation
- Fiber Decomposition Alters Interfacial Coating

Fig. 9

Mechanism II:
Fiber Contraction By Anelastic Creep Recovery

Underlying Theory

- All SiC Fibers Tested To-Date Display Large Transient Creep Behavior, Indicating The Buildup Of Internal Elastic Stresses During Grain Boundary Sliding

- Decreasing Temperature And Releasing Appled Stress Freezes Internal Stresses Within Fiber Microstructure

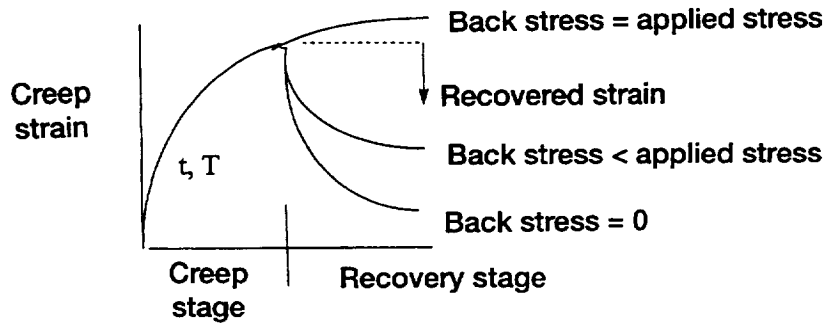
- Subsequent Thermal Treatment Of Fiber Allows Internal Elastic Stresses To Recover, Resulting In Anelastic Creep Recovery Or Fiber Contraction From The Crept Condition

Fig. 10

Mechanism II:
Fiber Contraction By Anelastic Creep Recovery

Potential Approach For CMC Application:

- Choose Stoichiometric SiC Fibers Which Are Thermally Stable And Creep At High Temperatures Above Typical Matrix Fabrication Temperatures
- Pre-Creep Fibers At High Stress Without Causing Rupture
  (At Fiber Vendor During Or After Fiber Production)
- Consolidate CMC And Post Treat To Allow In-Situ Recovery Of Fiber Creep Strain



- High Applied Creep Stresses Are Needed To Provide
  ---Resistance To Matrix Back-Stress During Fiber Contraction
  ---Short Creep Times For Cost-Effectiveness

Fig. 11

Mechanism II
Fiber Contraction By Anelastic Creep Recovery

Experimental Approach

- Determine And Model The Relationships Between Tensile Creep Recovery And Tensile Creep Using SCS-6 Monofilament Fibers

- Determine The Tensile Creep Conditions For Achieving Fiber Contraction Strains Greater Than 0.1%

- Test Conditions:
  - Fiber Creep/Recovery Facilities: Hot Zone ~ 120 mm
  - Environment: Argon
  - Creep Temperatures/Time: 1300 and 1400 °C / 1 Hour
  - Creep Stress: 750 MPa
  - Recovery Temperature/Time: 1500 °C / 10 Hours
  - Recovery Stress: < 1 MPa

Fig. 12

Mechanism II:
Fiber Contraction By Anelastic Creep Recovery

Results For Recovered Strain Vs Creep Strain

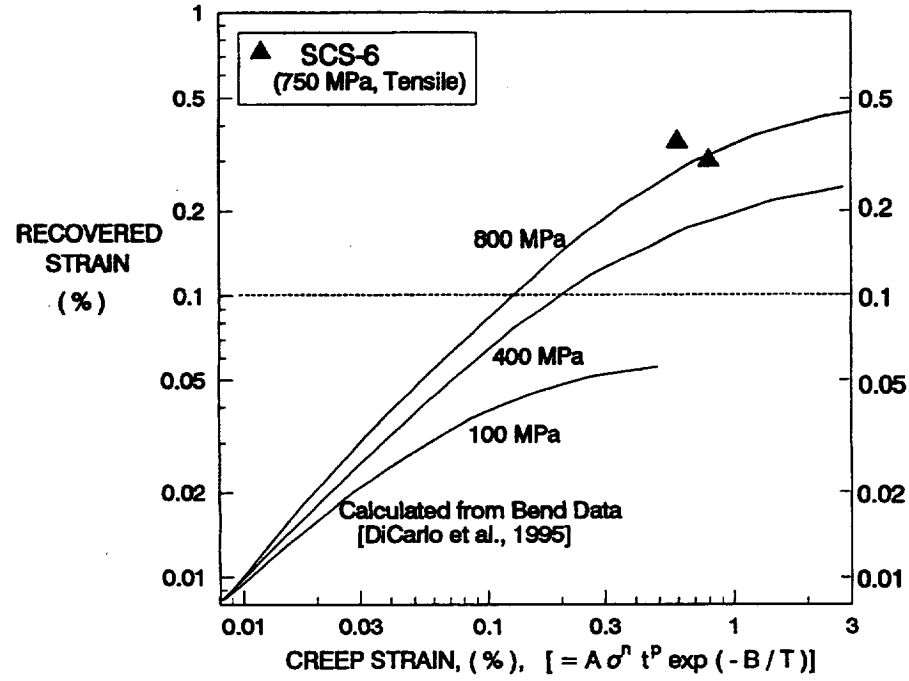


Fig. 13

SUMMARY OF RESULTS

- Measurements Have Been Made And Models Developed Which Describe The Effects of Time, Temperature, And Stress on The Axial Contraction Strain of SiC Fibers Which can Occur By Two Mechanisms:
  - I: Fiber Decomposition And Densification
  - II: Anelastic Strain Recovery After Fiber Creep

- For Mechanism I And Hi-Nicalon Fibers, Contraction Strains Well Above 1% Can Be Achieved, But At The Expense of Fiber Strength Degradation By ~50%. Maximum Back-Stresses For Hi-Nicalon Contraction Are ~ 100 MPa.

- For Mechanism II And SCS-6 Fibers, Contraction Strains Up To 0.3% Were Achieved At High Stress (~750 MPa) and Low Total Creep. Tensile Results Agree Closely With Anelastic Creep Recovery Model Developed From Fiber Bend Data.

Fig. 14

CONCLUSIONS

- Models Now Exist For Understanding And Predicting The Free-State Contraction Of Hi-Nicalon Fibers By Decomposition/Densification And of Thermally Stable SiC Fibers, Like SCS-6, By Anelastic Creep Recovery.

- Both Mechanisms Appear Feasible For Causing Sufficient Matrix Compression In CMC To Significantly Increase The Proportional Limit.

- Potential Issues For Using Hi-Nicalon Fibers And Mechanism I Are Fiber Strength Loss And Fiber Creep At The Decomposition/Densification Temperatures.

- Potential Issues For Using Mechanism II Appear To Be In The Pre-Creeping Stage, i.e., Stress Capability Of Fiber Tensioning Devices And Possible Random Fiber Fracture During Tensioning.

Fig. 15

FUTURE RESEARCH

- To Demonstrate the Feasibility of Fiber Contraction Mechanisms I and II, Mini-CMC Composites Will Be Fabricated Using CVI Matrices Reinforced By
  - Single Tows of As-Produced Hi-Nicalon Fibers
  - Single Fibers of Pre-Crept SCS-6 Monofilaments

- Initial Models Taking Into Account Matrix Back-Stress Effects Will Be Developed In Order To Estimate Best Conditions For Thermal Treatment of The Mini-CMC and For Creep of the SCS-6 Fibers.

- Changes In Matrix Cracking Behavior Will Be Monitored Using Tensile Stress-Strain Hysteresis And Acoustic Emission.

Fig. 16