REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS
BEFORE COMPLETING FORM

1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
ARO 23025.1-MS ✓		

4. TITLE (and Subtitle)	5. TYPE OF REPORT & PERIOD COVERED
Kinetics and Mechanisms of Primary and Steady State Creep in B- and Al-Containing Alpha Silicon Carbide	Final 85-11-15 through 89-07-25
	6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)	8. CONTRACT OR GRANT NUMBER(s)
Robert F. Davis Calvin H. Carter, Jr.	DAALD3-86-K-0013

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
North Carolina State University Dept. of Materials Science & Engineering Raleigh, NC 27695	

11. CONTROLLING OFFICE NAME AND ADDRESS	12. REPORT DATE
U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709	July, 1989
	13. NUMBER OF PAGES 12

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)	15. SECURITY CLASS. (of this report)
	Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

DTIC
ELECTE
AUG 0 2 1989
S D
D

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

NA

18. SUPPLEMENTARY NOTES

The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Creep	Silicon Nitride	Grain boundary sliding
Structural Ceramics	Mullite	Coble creep
Silicon Carbide	Niobium Carbide	Nabarro-Herring creep

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Please see next page

89 7 31 093

The steady state creep behavior of a number of high temperature structural ceramics have been measured and the results analyzed to determine the controlling mechanism.

Pure polycrystalline silicon carbide, devoid of sintering aids, creeps by dislocation motion and climb. Silicon carbide containing B- and Al- sintering aids, on the other hand, creeps by grain boundary sliding controlled by diffusion mechanisms (grain boundary diffusion – Coble creep – below 1920K; lattice diffusion – Nabarro-Herring creep–above 1920K). The difference in behavior is attributed to the high concentration of vacancies accompanying impurity substitution in the sintered silicon carbide.

Experimental measurements of grain boundary sliding offsets on polycrystalline silicon carbide have shown that the primary, transient, creep stage in this material is primarily due to plastic strain within the grains (90% plastic strain, 10% grain boundary sliding) and that the secondary, steady state, creep stage is primarily due to grain boundary sliding between the grains (90% grain boundary sliding, 10% plastic strain). Again, the dominant mechanism of steady state creep is grain boundary sliding.

The creep of single crystal and polycrystalline niobium carbide in the 1570–1850°K range is controlled by dislocation glide and climb.

Silicon nitride and mullite ceramics show little or no dislocation activity. The creep of hot pressed silicon nitride and mullite in the 1470–1800°K range is controlled by grain boundary sliding due to the amorphous phase present as a consequence of Y_2O_3 and Al_2O_3 sintering aids. Furthermore, it is found that the addition of silicon carbide whisker reinforcement has no beneficial effect on the creep resistance of Si_3N_4, whereas, in the more easily deformed mullite, silicon carbide whisker reinforcement does result in a reduced steady state creep rate. It is presumed that the whiskers are carrying some of the load during creep in the mullite material.

Accesion For		
NTIS CRA&I	☑	
DTIC TAB	☐	
Unannounced	☐	
Justification		
By		
Distribution /		
Availability Codes		
Dist	Avail and / or Special	
A-1		

Kinetics and Mechanisms of Primary and Steady State Creep in B- and Al-Containing Alpha Silicon Carbide

Final Report

Robert F. Davis

Calvin H. Carter, Jr.

July 1989

North Carolina State University
Department of Materials Science & Engineering
Box 7907
Raleigh, NC 27695-7907

I. Statement of the Problem Studied

The development of structural ceramics for high temperature applications in high performance engines and gas-turbines, heat exchangers and high temperature reactors requires a complete understanding of the high temperature mechanical behavior of ceramic systems. The reliability of these systems depends on their stability over long hours of stress at high temperatures in a corrosive environment. In particular, the mechanical creep behavior has become a critically important factor in high temperature applications.

The objectives of this research project were to determine the kinetics and mechanisms involved in the creep of a number of high temperature structural ceramics. The studies were far more wide ranging than implied by the title of the project. They covered the behavior not only of α-SiC, but also niobium carbide, silicon nitride and mullite ($2SiO_2 \cdot 3Al_2O_3$) and selected silicon carbide whisker reinforced ceramic composites.

Studies were conducted to obtain new knowledge on the materials listed above. The research was original because the materials were new and not generally available and because the facilities at North Carolina State University were unique with temperatures and stress ranges not available elsewhere. These results complement previous research conducted at NCSU. Together they have been compared with published results on the creep behavior of other high temperature structural ceramics to provide a total overview of the field.

II. Summary of the Most Important Results

A. Overview

The significant results from this broad range investigation can be summarized first in general statements describing the creep processes which occur, and second in specific statements for the respective ceramic materials.

With respect to creep mechanisms we have found:

(i)   The different creep mechanisms involve strain within the grains and/or displacement at the grain boundaries. Grain strain occurs by dislocation motion and climb. Grain boundary sliding is accommodated either by diffusion or cavitation. The diffusion is controlled either by grain boundary diffusion (Coble creep) or by bulk diffusion (Nabarro-Herring creep).

(ii)   The dominant creep mechanism varies from ceramic to ceramic. There is no universal creep behavior which characterizes all high temperature structural ceramics.

(iii)   Furthermore, for a given ceramic the dominant creep mechanism depends on the stress and temperature range but even more significantly on the processing steps and the resultant microstructure.

(iv)   Before a ceramic can be used in an application requiring high temperature mechanical stability, the creep behavior under the specific operational conditions must be determined.

With respect to specific materials we have found the following:

B. Silicon Carbide

B.1 Reaction Bonded (RB) SiC and Chemical Vapor Deposited (CVD) SiC

Activation energy and stress exponent analysis of steady–state creep in these two silicon carbide materials in the 1800–2000°K temperature range plus transmission electron microscopy confirms that the controlling mechanisms are dislocation climb (RB-SiC)[1,3] and dislocation glide (CVD-SiC)[2,3]. Dislocation motion must overcome significant structural barriers (the Peierls stress) or must climb past obstructions. Grain boundary sliding mechanisms make no measurable or identifiable contributions to the total creep strain in these two materials.

The CVD material is also strongly textured, with the growth direction perpendicular to [111]. (The dominant ($\approx$60 vol%) polytype in this materials is the cubic β form; thus cubic indicies denoting crystallographic directions and planes have been used.) Consequently, samples loaded in the growth direction are not oriented for creep by glide over the (111) plane, and there is no creep at all even at the highest temperature (2073°K) and the highest stress (220 MPa) available when the materials is stressed in this orientation. This remarkable creep resistance makes this material ideally suitable for loading platens for other high temperature creep resistance studies. Creep was only achieved by cutting the samples such that the (111) surface plane was 45° to the stress axis.

B.2 Sintered Silicon Carbide Containing B- and Al-Sintering Aids

It is concluded that there are two independent contributions to creep in this material.[4-7] They are plastic strain and grain boundary sliding. Plastic strain occurs within the grains due to dislocation motion. At low temperatures (1673°K) the dislocations are impeded by their interaction with numerous and very small ($\approx$20 nm) B_4C precipitates,[4-6] but at high temperatures (2073°K) many of the precipitates coalesce (some dissolution also occurs) and the dislocation motion becomes easier.[5,6] At the same time grain boundary sliding is

occurring. Below 1920°K grain boundary sliding is accommodated by Coble creep and above 1920°K by Nabarro-Herring creep.

Direct measurement of grain boundary offsets[7] has enabled an estimation to be made of the relative contributions of these two components, dislocation glide and grain boundary sliding, to the primary, or transient creep, and the secondary, or steady-state, creep stages of the total creep strain. It is found that primary creep is 90% dislocation glide—10% grain boundary sliding, secondary creep is 90% grain boundary sliding—10% dislocation glide, with contributions to the total strain averaging 67% grain boundary sliding, 33% dislocation glide.

As reported in the preceding section, there is no grain boundary sliding in pure CVD silicon carbide. Dislocation glide is the sole mechanism in pure SiC. Since grain boundary sliding is dominant in these doped materials, it is concluded that the existence of B- and Al in the grain boundary regions must generate a high concentration of excess (charge compensating) vacancies to facilitate diffusion which results in grain boundary sliding.

References: (1) C. H. Carter, Jr., R. F. Davis and J. Bentley, "Kinetics and Mechanisms of High Temperature Creep in Silicon Carbide: I, Reaction Bonded," J. Amer. Cer. Soc. **67** [6], 409-17 (1984).

(2) C. H. Carter, Jr., R. F. Davis and J. Bentley, "Kinetics and Mechanisms of High Temperature Creep in Silicon Carbide: II, Chemically Vapor Deposited," J. Amer. Cer. Soc. **67** [11] 732-40 (1984).

(3) R. F. Davis, C. H. Carter, Jr., and J. Bentley, "High Temperature Creep in Reaction-Bonded and CVD Silicon Carbides," in Proc. Japan–U.S. Seminar on Structural Ceramics, S. Somiya and R. C. Bradt, eds., 1985, pp. 220-235.

(4) K. L. More, C. H. Carter, Jr., J. Bentley, W. H. Wadlin, L. Gunderson and R. F. Davis, "The Occurrence and Distribution of B-containing Phases in Sintered Alpha Silicon Carbide," Jour. Am. Ceramic Soc., **69**, 695 (1986).

(5) J. E. Lane, C. H. Carter and R. F. Davis, "Kinetics and Mechanisms of High Temperature Creep in Silicon Carbide: III, Sintered Alpha," J. Am. Ceram. Soc. **71** [4] 281–95 (1988).

(6) R. D. Nixon, J. B. Posthill, R. F. Davis, H. R. Baumgarner and B. R. Rossing, "Correlation of Steady State Creep and Changing Microstructure in Polycrystalline SiC Sintered with Powder Derived Via Gaseous Reactants in an Arc Plasma," J. Mater. Res. **3** [5] 1021–30 (1988).

(7) R. D. Nixon and R. F. Davis, "Kinetics and Mechanisms of High Temperature Creep in Silicon Carbide: IV, Differentiation of the Contributions of Grain Boundary Sliding and Dislocation Glide in Sintered Alpha Silicon Carbide," Submitted to Jour. Amer. Ceram. Soc., (1989).

C. Niobium Carbide

Niobium carbide, like silicon carbide, is a ceramic material in which dislocation motion can be readily observed at high temperatures.[1-3] Dislocation glide also plays a prominent role in the high temperature creep of this material. Among the high temperature carbides, niobium carbide enjoys the further distinction that glide occurs on <110> {111} slip systems.[3] These slip parameters are identical to those for face centered cubic metals. Indeed the dislocation substructures generated by the high temperature creep of niobium carbide single crystals between 1570 and 1850°K are similar to the cell structures developed in face centered cubic metals (e.g., copper) around room temperature.

Steady-state creep in both niobium carbide single crystals and polycrystalline material has been found to be controlled by the dislocation glide and climb mechanism. Grain boundary sliding does not play any measurable or observable role.

References: (1) R. D. Nixon, R. F. Davis and J. Bentley, "Kinetics and Mechanisms of Creep in Hot Isostatically Pressed Niobium Carbide," in *Defect Properties and Processing of High Technology Nonmetallic Materials*, Mater. Res. Soc. Symp. Proc., Vol. 60, Y. Chen, W. D. Kingery, R. J. Stokes, eds., Materials Research Society., Pittsburgh, PA, 1986, pp. 153–162.

(2) R. D. Nixon, S. Chevacharoenkul, and R. F. Davis, "Steady State Creep Behavior of Hot-Isostatically Pressed Niobium Carbide," Materials Research Bulletin, **22**, 1233, (1987) (Special Issue honoring M. Koizumi).

(3) S. Chevacharoenkul and R. F. Davis, "Dislocation Mechanisms, Diffusional Processes and Creep Behavior in NbC_x," Acta. Metallurgica **37**, 417–27 (1989).

D. Silicon Nitride

D.1 Hot Pressed Silicon Nitride Containing Y_2O_3 and Al_2O_3 Sintering Aids

Unlike the two previous high temperature ceramics, polycrystalline silicon nitride shows no dislocation glide activity. Dislocations have not been seen in transmission electron micrographs of crept samples. Steady-state creep in the temperature range 1470–1720K is controlled by sliding in the grain boundary region that contains an amorphous phase.[1-4] Below 1570K the sliding is accommodated solely by viscous flow via the amorphous phase. Above 1570K cavitation also contributes to the deformation. Crystallization of the amorphous phase did not result in any significant change in the viscous flow characteristic of this material.

D.2 Hot Pressed Silicon Nitride Containing Silicon Carbide Whiskers and Y_2O_3 and Al_2O_3 Sintering Aids

An extensive study has been conducted on whisker reinforced silicon nitride composites.[2-4] The general conclusion from these studies is that whisker reinforcement has minimal effect on the creep behavior. The creep rate, the kinetics and the viscous grain boundary sliding mechanisms controlling creep are basically unchanged. Thus, we conclude that reinforcing silicon nitride with SiC whiskers presents no advantage for high temperature structural applications.

References: (1) R. F. Davis and C. H. Carter, Jr., "A Review of Creep in Silicon Nitride and Silicon Carbide," in *Fine Ceramics*, Shinroku Saito, ed., Ohmsha Ltd., Tokyo, 1987, pp. 95–126.

(2) R. D. Nixon, D. A. Koester, S. Chevacharoenkul and R. F. Davis, "Steady State Creep of Hot-Pressed SiC Whisker-Reinforced Silicon Nitride," submitted to Journal of Composite Science and Technology.

(3) R. D. Nixon, S. Chevacharoenkul, M. L. Huckabee, S. T. Buljan and R. F. Davis, "Deformation Behavior of SiC Whisker Reinforced Si_3N_4," in *Advances in Structural Ceramics*, Materials Research Soc. Proc., Vol. 78, P. F. Becher, M. V. Swain and S. Somiya, eds., Materials Research Soc., Pittsburgh, PA, 1987, pp. 295–302.

(4) D. A. Koester, R. D. Nixon, S. Chevacharoenkul and R. F. Davis, "High Temperature Creep of SiC Whisker-Reinforced Ceramics," in Proceedings of the International Conference on Whisker- and Fiber-toughened Ceramics, ASM International, Metals Park, OH, 1988, pp. 139–45.

E. Mullite

E.1 Hot Pressed Mullite (3Al$_2$O$_3$, 2SiO$_2$)

Mullite, like silicon nitride, shows little or no dislocation activity during high temperature creep.[1,2] The behavior is also controlled by grain boundary sliding and cavitation. This material exhibits three distinct regions of behavior between 1500 and 1700K. Around 1500K, steady-state creep occurs by grain boundary sliding accommodated by diffusion through the amorphous grain boundary phase, at higher temperatures the grain boundary sliding results in cavitation at multi-grain boundary junctions, around 1700°C the viscosity of the amorphous phase is sufficiently low to relieve intergranular sliding without cavitation. While these mechanisms are qualitatively similar to those outlined for silicon nitride, mullite is much less creep resistant and shows a higher rate of viscous flow than silicon nitride.

E.2 Hot Pressed Mullite Containing Silicon Carbide Whiskers

In contrast to silicon nitride there is a beneficial effect of whisker reinforcement in mullite.[1,2] The composite shows a significantly reduced steady-state creep rate. There are no significant changes in the basic mechanisms involved from those described for unreinforced mullite (E-1), except that cavitation in the middle temperature range, around 1600K, is confined to the whisker-mullite interface, and not the intergranular junctions. It is suggested that the whiskers carry an increasing fraction of the load during viscous creep, thereby accounting for the reduced creep rate, and the beneficial effects of whisker reinforcement on the creep resistances of this material.

References: (1) D. A. Koester, R. D. Nixon, S. Chevacharoenkul and R. F. Davis, "High Temperature Creep of SiC Whisker-Reinforced Ceramics," in Proceedings of the International Conference on Whisker- and Fiber-toughened Ceramics, ASM International, Metals Park, OH, 1988, pp. 139–45.

(2) R. D. Nixon, S. Chevacharoenkul, R. F. Davis and T. N. Tiegs, "Creep of Hot-Pressed SiC Whisker Reinforced Mullite," to be published in the *Proceedings of the International Workshop on the Science and Technology of Mullite*, S. Somiya, R. F. Davis and J. A. Pask, eds., American Ceramic Society, 1988.

3. List of all Publications on this Project

K. L. More, C. H. Carter, Jr., J. Bentley, W. H. Wadlin, L. Gunderson and R. F. Davis, "The Occurrence and Distribution of B-containing Phases in Sintered Alpha Silicon Carbide," Jour. Am. Ceramic Soc., **69**, 695 (1986).

R. D. Nixon, S. Chevacharoenkul, M. L. Huckabee, S. T. Buljan and R. F. Davis, "Deformation Behavior of SiC Whisker Reinforced Si_3N_4," in *Advances in Structural Ceramics*, Materials Research Soc. Proc., Vol. 78, P. F. Becher, M. V. Swain and S. Somiya, eds., Materials Research Soc., Pittsburgh, PA, 1987, pp. 295–302.

D. A. Koester, R. D. Nixon, S. Chevacharoenkul and R. F. Davis, "High Temperature Creep of SiC Whisker-Reinforced Ceramics," in Proceedings of the International Conference on Whisker- and Fiber-toughened Ceramics, ASM International, Metals Park, OH, 1988, pp. 139–45.

J. E. Lane, C. H. Carter, Jr., and R. F. Davis, "Kinetics and Mechanisms of Creep in SiC III-Sintered Alpha Silicon Carbide," Jour. Am. Ceram. Soc. **71**, [4], 281–95 (1988).

R. D. Nixon, J. B. Posthill and R. F. Davis, "Correlation of Steady-State Creep and Changing Microstructure in Polycrystalline SiC Sintered with Powder Derived Via Gaseous Reactants in an Arc Plasma," Jour. of Materials Research, **3** [5], 1021–30, (1988).

S. Chevacharoenkul and R. F. Davis, "Dislocation Mechanisms, Diffusional Processes and Creep Behavior in NbC_x," Acta. Metallurgica **37**, 417–27 (1989).

R. F. Davis, C. H. Carter, Jr. and J. E. Lane, "Deformation Behavior of Reaction-Bonded Chemically Vapor Deposited and Sintered Silicon Carbides at Elevated Temperatures," in *Ceramic Transactions*, Vol. 2, Silicon Carbide, 1987, J. D. Cawley and C. E. Semler, eds., American Ceramic Society, Westerville, OH, 1989, pp. 253–74.

R. D. Nixon, S. Chevacharoenkul, R. F. Davis and T. N. Tiegs, "Creep of Hot-Pressed SiC Whisker Reinforced Mullite," to be published in the *Proceedings of the International Workshop on the Science and Technology of Mullite*, S. Somiya, R. F. Davis and J. A. Pask, eds., American Ceramic Society, 1989.

R. D. Nixon, D. A. Koester, S. Chevacharoenkul and R. F. Davis, "Steady State Creep of Hot-Pressed SiC Whisker-Reinforced Silicon Nitride," to be published in the Journal of Composite Science and Technology, (1989).

R. D. Nixon and R. F. Davis, "Kinetics and Mechanisms of High Temperature Creep in SiC: IV–Differentiation of the Contributions of Grain Boundary Sliding and Dislocation Glide in Sintered Alpha Silicon Carbide," Submitted to Jour. Amer. Ceram. Soc., 1989.

4. List of All Participating Scientific Personnel Plus Advanced Degrees Earned While Employed on the Project.

Jay E. Lane	PhD, 1988
Sopa Chevacharoenkul	PhD, 1988
Robert D. Nixon	Ph.D., 1989
David A. Koester	M.S. Candidate, 1989

Calvin H. Carter, Jr., Research Assistant and Co-principal Investigator
Robert F. Davis, Professor and Principal Investigator