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AD-A260 440

DOCUMENTATION PAGE

Form Approved  
OMB No 0704-0188



Information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

2. REPORT DATE 8 Dec 92	3. REPORT TYPE AND DATES COVERED Final 1 Nov 88 - 31 Aug 92
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4. TITLE AND SUBTITLE Crystal Chemistry of Ceramic/Mineral Systems	5. FUNDING NUMBERS 0
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93-03123

DTIC

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)  
U. S. Army Research Office  
P. O. Box 12211  
Research Triangle Park, NC 27709-2211

S ELECTE FEB 18 1993 D

SPONSORING/MONITORING AGENCY REPORT NUMBER  
26246.3 -ms

11. 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.

12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.	12b. DISTRIBUTION CODE
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13. ABSTRACT (Maximum 200 words)  
Crystallochemical and mechanical property relationships of refractory materials were investigated including thermal expansion and the friction and wear of refractory ceramics. Continuous x-ray diffraction techniques as a function of temperature were developed.

14. SUBJECT TERMS Thermal Expansion, x-ray diffraction, ceramic wear, MgO, SiC, B4C, BN	15. NUMBER OF PAGES
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL
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## Crystal Chemistry of Ceramic/Mineral Systems

Robert R. Reeber

The objectives of this research were threefold:

a. make measurements of diffraction intensities and thermal diffuse intensities as a function of temperature from cryogenic temperatures to temperatures near the Debye Characteristic temperature for selected refractory ceramic materials;

b. semiempirically relate these data to the higher temperature mechanical and physical properties of the materials including melting point, thermal expansion, crystal anisotropy, and elastic moduli;

c. develop computer programs to interpret data from the traveling Laue Camera (TLC).

### Project Summary

MgO was considered an excellent model material because of the large body of previous work with other techniques. We were able to obtain a large number of MgO crystals from the UNC physics Department. These had been grown at Oak Ridge National Laboratory during the 70's. X-ray work was carried out with these MgO crystals from room temperature to 550K. Initially we had planned to carry out low temperature experiments to 77K in a dewar obtained several years earlier from Dr. Lefkowitz. Unfortunately this dewar was internally corroded and had to be discarded. A new metal dewar suitable for a range of experiments down to 77K was designed and built locally. During the course of the work a densitometer was set up, calibrated and MgO film intensities were measured. Intensity changes over the temperature range observed, room to 550K, were not large enough to determine Debye parameters and were complicated by unexpected indications of deviations from cubic symmetry and phase transitions. The preliminary evaluation of our results indicate that the MgO crystals we have were grown at high temperature and are contaminated with carbon. Carbon distorts the lattice and causes non-reversible phase changes in the material. Heating this material causes outward diffusion and oxidation of the carbon. The crystallographic changes associated with these effects are not intrinsic to MgO or reproducible as other workers have proposed. A paper was presented at the 1992 annual meeting of the American Ceramic Society and work is continuing on a journal article relating to this effort. X-ray Debye intensity data for MgO was difficult to evaluate because of the unexpected additional effects, cooling water effects on x-ray tube current stability, and the unavailability of low temperature capabilities early enough in the project.

Several furnaces were assembled in which crystal growth of aluminum diboride crystals from aluminum melts was also accomplished at temperatures of 850C and 920C. Other than x-ray characterization and metallographic examinations no further work was completed with these boride crystals. A variety of techniques were tried to remove these crystals from the aluminum matrix including partial melting, dilute HCl etching at room temperature and dilute HCl in anhydrous ether etching at 0 degrees C. All these methods were in general unsatisfactory, with slightly improved results obtained from the last method. A cooperative effort with the Physics Department and Dental Research Center resulted in a new method for lubricating boron carbide through surface process controlled phase transition of boron carbide to a composite boron carbide/boron nitride surface. The work was published and patented.

#### Computer Program Development:

Thermal expansion fitting with multiple Einstein frequencies was accomplished on an IBM compatible computer with code compiled in Microsoft Fortran 5.0. A detailed analysis of thermal expansion data for polymorphs of SiC was carried out. The work was presented as a poster paper for the Fall 1991 American Ceramic Society meeting.

Significant progress was made in determining random crystal orientations for crystals of any crystal system from forward reflection Laue photographs. Three programs; LAU20, PAIR, and SIXANG1 have been written and debugged. These programs determine sets of four diffraction spots with self-consistent indices and interplanar angles. Additional programming is required to check crystallographic consistency of each set and from the results then calculate the indices and degree of fit of all diffraction data.

A program was written to calculate interplanar angles as a function of temperature and statistically minimize errors in the diffraction data obtained from travelling Laue x-ray films.

#### Publications/presentations:

1. Reeber, R.R., Kusy, R.P., Yu, N. and Chu, W.K. " Formation of a Solid Lubricant in Boron Carbide by Nitrogen Ion Implantation and Laser Annealing." Abst. MRS meeting Nov. 1989, Appl. Phys. Let. 56 (11), 12 March 1990.
2. Reeber, R.R., Kusy, R.P. Yu, Ning and Culbertson, R. "Tribological Properties of Nitrogen implanted Boron Carbide" Presented at 10th International Conference on Boron, Borides and Related Materials Albuquerque, N.M. August 26, 1990. Volume 231 AIP Proceedings 1991.

3. Reeber, R.R., "Thermal Expansion of Silicon Carbide". Abstract Bull. Amer. Ceram. Soc. 1991 presented at Fall 1991 Basic Sciences Section Meeting of the American Ceramic Society.

4. Reeber, R.R. and A. Zingg, "Phase Transition Anomalies in MgO," Abstract : Bull. Amer. Ceram. Soc. 1992 presented at Spring 1992 Annual Meeting of the American Ceramic Society.

5. Reeber, R.R., "Surface Engineering of Structural Ceramics," Review Manuscript Accepted for publication in the Journal of the American Ceramic Society February 1993.

Patents:

1. U.S. Patent, #5075130, "Surface Modification of Boron Carbide to Form Pockets of Solid Lubricant" issued Dec. 24, 1991.

Army Interactions: Dr. Robert Culbertson and Dr. James Hirvonen from the Army Materials Technology Laboratory and Dr. Lawrence Mizerka from the Center for Night Vision were cognizant of aspects of this work. Dr. Culbertson was a coauthor on one of our publications.

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