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Progress Report: Grant DE-FG02-87ER45305

"High Resolution Energy Loss Research: Si Compounds and Ceramics"

For the period June 1, 1987 to January 1, 1988, for continuation funding from June 1, 1988 to May 31, 1989.

By: R.W. Carpenter and S.H. Lin

1. Experimental Results

(a) Materials

Experimental work that began when the proposal leading to this grant was being reviewed yielded useful experimental results. Preliminary findings have been published in conference proceedings, and regular papers for submission to journals are in preparation.

(1) Liquid-Phase Reaction Zones in Wurtzite SiC Alloys.

These alloys are based on the pseudo ternary SiC-Al_2OC-AlN system, which is reported to have the wurtzite structure. Interest in the system is based on using Al_2O_3 and Al_4C_3 (which form a eutectic at about 1850°C) for sintering aids, which will then react to form the solid solution noted above and result in a strong structural ceramic without amorphous grain boundary phases. Our preliminary results (see Attachment #1) showed that reaction in grain boundary regions does occur, and that most grain boundary regions are crystalline, not amorphous. This remarkable result is much different than all other SiC structural ceramics, which contain amorphous phases.

(2) Energy Loss and X-ray Analysis of Major Constituents in Silicon Oxynitride Ceramics.

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Silicon oxynitride is an orthorhombic phase that has often been observed in Si_3N_4 ceramics, probably resulting from reactions between sintering aids, impurities, sintering atmospheres and Si_3N_4 itself. The differences between the EELS spectra of Si_2N_2O, Si_3N_4 and SiO_2 are up to now unexplored, and no information was available on differences in electronic structure. Our preliminary results (Attachment 2) show typical core loss spectra for Si-L, N-K and O-K in Si_2N_2O. These experimental results, and corresponding theoretical calculations, showed that the local electronic structure of Si in Si_2N_2O is more like Si in SiO_2 than Si in Si_3N_4, despite the fact that three of the nearest neighbors of Si in Si_2N_2O are N, and only one is O.

(b) Instrumentation

Several types of measurements to characterize the focussed electron probe at the specimen in a field emission source analytical electron microscope have been completed. These include probe current, probe size, and the effect of aberrations of the final probe forming lens on probe current and size. The SEMPER program, obtained from Dr. O. Saxton of Cambridge University, has been found suitable for accurate, detailed simulation of high resolution probe images, and will be used to compute probe current distributions as a function of microscope operating parameters.

2. Theory

(a) Electron Energy Loss Core Edge Theory for Crystals.

We have developed a method for band structure calculations for ceramic compounds based on the semiemperical CNDO/2R (complete neglect of

differential overlap) scheme. This method has been applied to calculate the inelastic electron scattering cross sections of solids (i.e. EELS core loss edges). We tested the method by calculating Si-L edges for crystalline Si, and compared the results to experimental data, and to our previous calculated results using the extended Huckle methods. The results were favorable, and give improved information about local electronic structure for crystals (see Attachment 3).

(b) Electronic Structure of Amorphous Solids.

To properly describe the amorphous or glass state we are developing the classical and quantum Monte Carlo methods. The classical method is well known, but the quantum Monte Carlo method is just beginning to attract attention. We have applied the path integral formulation to develop the quantum Monte Carlo method. To test this method, it has been used to calculate the quantum partition function. This theoretical method can be be used to calculate the properties of materials systems with many degrees of freedom, like amorphous solids. For these types of materials, the usual methods of solving the time independent Schroedinger equation by use of a basis set expansion fails, because there are too many degrees of freedom (see Attachment 4).

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"High Resolution Energy Loss Research: Si Compounds and Ceramics"

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1. Progress for June 1, 1987 to January 1, 1988

   a. Materials

   Analytical electron microscopy research on SiC ceramics made by liquid phase reaction leading to formation of crystalline grain boundary phases has shown that this amorphous grain boundary phases can be largely eliminated by this technique.

   Electron energy loss experiments have shown that the characteristic core loss spectra of silicon oxynitride, Si_2N_2O, is similar to SiO_2 and therefore the electronic structure of Si in Si_2N_2O is similar to that in SiO_2.

   b. Instrumentation

   Focussed probe size and current measurements have been made for a field emission source analytical transmission electron microscope. The SEMPER program is being used to simulate these results.

   c. Theory

   A new computation method, CNDO/2R, is being used to calculate the EELS spectra core edges for crystalline materials such as Si, SiC, and Si_3N_4. This method was shown to be an improvement over the earlier extended Huckel method.

   A quantum Monte Carlo computational method is being developed to compute the electronic structure of amorphous solids, for comparison with experimental EELS results.

2. Proposed Research for JUNE 1, 1988 TO MAY 31, 1989.

A. MATERIALS

Amorphous Si_3N_4 and amorphous SiC will be examined by electron energy loss spectroscopy to examine the differences that occur in the spectra when crystalline order is not present. High resolution microscopy will be used to establish that microcrystals are not present.

Ceramic/Ceramic composites composed of SiC/Al_2O_3 and SiC/Si_3N_4 will be examined by electron energy loss spectroscopy and high resolution imaging to determine the geometric and chemical structure of the interfaces.

b. Instrumentation

Computations of field emission probe images at the specimen as a function of spherical and chromatic aberration of the probe forming lenses and defocus of the final probe forming lens will be done. A method to include the aberrations of the field emission gun itself in these calculations will be developed.

A parallel detection system for electron energy loss spectroscopy will be installed and brought into operation on a field emission analytical electron microscope. This system will permit collection of spectra from areas about 20Å in diameter in less than 1 second, and enable analysis of interfaces with much higher spatial resolution than presently possible.

A new JEOL-2000FX analytical electron microscope will be brought into operation for use on this project. This instrument was not part of the instrumentation originally proposed for this research. It is a thermionic source instrument for operation at 200kV, with 2.8Å point resolution, fitted with a parallel electron energy loss spectrometer and a

1 atmosphere compatible energy dispersive characteristic x-ray spectrometer. The availability of this microscope is expected to materially increase the rate of progress of the research.

c. Theory

The CNDO/2R computational method will be applied to core shell absorption edges for EELS spectra of Si, SiO_2, Si_3N_4, SiC and Si_2N_2O to yield improved understanding of the electronic structure of these materials. The quantum Monte Carlo method will be developed for application to EELS spectra from amorphous SiC and Si_3N_4.

Development of computational methods for interpretation of EELS spectra from interfaces in ceramic/ceramic composites will begin.

3. Graduate Students supported.

a. Jon Karl Weiss, B.S. Physics

Mr. Weiss is carrying out the calculations of field emission probes in TEM/STEM analytical microscopes. His thesis will present those results and some applications to ceramic materials. He is expected to complete work for the Ph.D. in January or June, 1989.

b. Karnoketu Daschowdhury, B.S. Engineering

Mr. Daschowdhury is just finishing his course work for the Ph.D. and will begin his dissertation research in the summer of 1988. His thesis will deal with experimental and theoretical investigation of interfaces in ceramic/ceramic composites. He is expected to finish his Ph.D. in January of June 1990.

c. Philip R. Rice, M.S. Physics

Mr. Rice will be beginning graduate study toward a Ph.D. in January, 1988. He is an experienced EELS researcher. His thesis will deal with

the experimental aspects of high spatial resolution EELS investigation of ceramic/ceramic interfaces. His Ph.D. work should be finished in June, 1990.

d. Hong Ma, B.S. Chemistry

Mr. Ma is the main student contributor to the CNDO/2R computations for electron energy loss spectra core edge shape. He will apply these results and quantum Monte Carlo methods to crystalline and amorphous Si, SiC, Si_3N_4 and SiO_2, all compounds of fundamental and technological importance, for his dissertation. He is expected to complete his dissertation between January and June, 1989.

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