December 18, 1991

DOE/ER/45305--5

DE92 006416

PROGRESS REPORT: GRANT DE-FG02-87ER45305

"High Resolution Energy Loss Research: Si Compounds and Ceramics"
For the period January 2, 1991 to January 1, 1992,
for continuation funding from 6/1/92 to 5/31/93

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1. Experimental Results

(a) Materials

Our current investigation of the structure and chemistry of whisker/matrix interfaces and matrix grain boundaries in SiC whisker reinforced Si_3N_4 composites has been completed. We examined these interfaces and boundaries in four composites whose starting materials and processing were identical except for the SiC whiskers themselves, which were from four different sources: American matrix, Nikkei, Huber and Tokai. Thus, differences in interfaces among the composites are attributable to differences in the whiskers. The results showed that oxygen-rich amorphous interfacial layers were discontinuous in all whisker/matrix interfaces and continuous in all matrix grain boundaries. Further, we used position-resolved high spatial resolution electron energy loss spectroscopy to show that the "chemical interface width" is much wider than the "geometric or structural interface width" at both types of interfaces in all four composites. The geometric interface widths were determined from high resolution TEM images of edge-on interfaces. Enclosure 1 illustrates these results for composites synthesized with American Matrix and Nikkei composites. These results are part of the Ph.D. thesis of K. Das Chowdury and the research was done in collaboration with Dr. W. Braue of DFVLR, Koln, FRG. A comprehensive paper describing these results is being prepared for publication.

Fresnel fringes were observed in TEM images of whisker/matrix interfaces at positions along the interfaces where no oxygen was detected by EELS. Fresnel fringes along grain boundaries in out of focus TEM images of ceramic grain boundaries have historically been accepted as a definitive indicator of the presence of a thin amorphous oxygen-rich layer at the boundary. We repeated this experiment at a Σ=13(510) grain boundary in a silicon bicrystal, in a boundary region for which oxygen was undetectable by EELS, and again observed Fresnel fringes. Fundamental considerations show that Fresnel fringes in interface or boundary images result from a sharp change in mean inner potential at the boundary or interface plane. Such changes can result not only from a different layer composition at the interface joining the grains, but also from a difference in atom density in the grain boundary plane due to the presence of dislocations or imperfect atom matching. We calculated the reduction in Si atom density in the Σ=13 boundary relative to the bounding perfect crystals, based on our high resolution analysis of its structure, and used the corresponding difference in mean inner potential at the boundary to theoretically simulate the experimental Fresnel images, under rather restrictive experimental conditions. A good match of these preliminary calculations with experimental results was obtained.

We concluded that Fresnel fringes at TEM boundary/interface images are a necessary but not sufficient condition to establish the presence of a thin chemically segregated layer there. These results are given in Enclosures 2 and 3.

We have completed an experimental investigation of low temperature (500 to 900°C) oxidation of SiC in air, to determine whether silicon oxycarbide exists as part of the oxidation product. It does not. We investigated the oxidation product and the product/SiC interface using high resolution electron imaging and electron energy loss. This data extends knowledge of the oxidation reaction to below 1000°C for the first time. These results are being prepared for publication.

Experimental investigation of the microstructure of a monolithic silicon oxynitride (Si_3N_2O) ceramic synthesized from SiO_2 and Si_3N_4 with small Al additions was completed. We observed that Si_2N_2O undergoes mass loss during small probe EELS experiments, with the loss rates of oxygen and nitrogen being different and non-linear with dose. A preliminary report of these important results has been published.

(b) Instrumentation

Our analysis of the current distribution in focussed filed emission probes in a TEM/STEM analytical microscope is complete. This is the first analysis of the topic, and is shown in Enclosure 4. This analysis defines the important electron optical parameters for small probe formation and shows their effect on probe current density distributions for both the coherent and incoherent approximations, and shows that experimentally measured probe current distributions can be accurately reproduced theoretically. The best electron optical conditions for nanoprobe spectroscopy are defined. This paper is especially timely now, since a new generation of field emission TEMs is just beginning to become available. These considerations have been extended in the paper of Enclosure 5, to include the effects of parallel EELS detectors, signal to noise ratios and the specimen itself, as well as electron optical parameters on a quantitative definition of microanalytical performance. A computer system to provide digital control of the Philips field emission analytical electron microscope itself and of EELS and X-ray spectrum collection was designed and constructed here in our Center. It is described in the preprint of Enclosure 6, already submitted for publication. This unit provides the capability for position and time-resolved nanospectroscopies essential for our research. Our general policy is to buy necessary equipment from the usual vendors, but in this case no equipment was available commercially that would perform the functions we required. This equipment development venture was successful and cost effective and four more similar units have been constructed for use with other microscopes here, based on this first unit.

2. Theory

(a) Spectroscopy

Use of EELS for study of chemical composition and bonding at important lattice defects such as the Σ=13 Si boundary noted above required understanding of spectrum fine structure from perfect crystals before embarking on detailed study of spectra from defects. Our most recent analysis of aspects of Si-$L_{2,3}$ edge fine structure (Enclosure 7) shows that valence band electron relaxation before the 2p core hole is filled by valance electrons has very little effect on X-ray emission spectra or on the excitonic effect for EELS spectra.

The ground state valence electron wavefunctions should be used for calculating the excitonic effect for EELS spectra. Our earlier results showed the Random Phase Approximation is sufficiently accurate for use in these calculations, and that the dipole approximate is valid for EELS collection angles up to collection half-angles of ~12mr. This information provides sufficiently detailed understanding to justify experimental investigation of EELS fine structure from Σ=13 grain boundaries in Si.

We have formulated a new unified scheme of CNDO/2 parametrization applicable to heavy atom systems. The exponents ξ_μ and electronegativities $X(_\mu)$ of atomic orbitals are corrected by the relativistic Dirac-Fock (RDF) expectation values of atomic orbital radii and energy level. This leads to the possibility of calibrating the β° parameters directly by the equilibrium geometric configuration of molecules. The parametrization for hydrogen, halides and rare earth series as well as some test calculations for compounds of these elements have been carried out to show the utility of the scheme. The results demonstrate that the present scheme can give satisfactory MO levels and ionization potentials as well as correct molecular geometry. A manuscript describing these results has been submitted for publication, by G.S. Wu, H. Ma and S.H. Lin.

(b) Interfaces

Atom positions in Σ=13 grain boundaries can be determined with relatively good accuracy by HREM (see Enclosure 2). We have begun an investigation of theoretical methods to predict these boundary structures from first principles. Conventional procedures such as as the Embedded Atom Method (EAM) rely on empirical potential functions. After reviewing these, we decided to investigate the Quantum Molecular Dynamics (QMD) method, which may relieve dependence on empirical functions. The theoretical foundation of QMD, is the density functional theory within the local density approximation and the nonlocal pseudo potential scheme. It relies on a total energy minimization scheme, based on lattice kinetic energy, electron interaction with the ionic and nonlocal pseudo potentials, electron-electron Hartree interaction, exchange-correlation within the local density and inaction, and ion-ion interaction. First results are promising and justify further effort.

R.W. Carpenter, DE-FG02-87ER45305
December 1991

Enclosures with Progress Report

1. A comparative high-resolution study of interface chemistry in silicon-nitride-based ceramic matrix composites reinforced with silicon carbide whiskers, K. Das Chowdhury, R.W. Carpenter and W. Braue, galley proof of article for Ultramicroscopy.

2. Structure and precipitation on a Σ=13 tilt grain boundary in silicon, M.J. Kim, R.W. Carpenter, Y.L. Chen and G.H. Schwuttke, Galley Proof copy for article on Ultramicroscopy.

3. Analysis of Interfaces by Fresnel Fringe Technique, K. Das chowdhury, R.W. Carpenter, and M.J. Kim, preprint, submitted.

4. A study of small electron probe formation in a field emission gun TEM/STEM, J.K. Weiss, R.W. Carpenter and A.A. Higgs, Ultramic. 36, 319-329 (1991).

5. Factors limiting the spatial resolution and sensitivity of EELS microanalysis in a STEM, J.K. Weiss and R.W. Carpenter, Galley proof of article for Ultramicroscopy (1991).

6. A Computer System for Imaging and Spectroscopy in Analytical Electron Microscopy, J.K. Weiss, Peter Rez and A.A. Higgs, preprint for Ultramicroscopy.

7. Ab initio study of the valence-electron relaxation effect on x-ray-emission spectra and the excitonic effect on electron-energy-loss-spectra of the Si-$L_{2,3}$ edge, H. Ma, S.H. Lin, R.W. Carpenter and O.F. Sankey, Galley proof from article in Phy Rev B.

Other publications not listed are refereed conference abstracts.

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3/3/92