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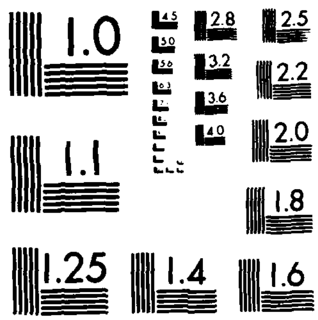

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This report describes the status of a transmission electron microscopy system that was purchased through a grant ~~(AFOSR-87-0078)~~ entitled "Request for a High Voltage/High Resolution Scanning Transmission Electron Microscope." The microscope purchased is a Philips EM 430T; accessories bought with the microscope are an energy-dispersive x-ray spectrometer (EDS) and an electron energy loss spectrometer (EELS). The tests at all modes of analysis have been completed and the results indicate that the instrument and its peripherals operate at their expected performance.

The system has already proven to be an indispensable tool in ~~our DoD-supported~~ projects on the development of advanced materials and it is expected that it will serve as a primary characterization tool in future projects.

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FINAL REPORT

on the

ACQUISITION OF A HIGH VOLTAGE/HIGH RESOLUTION TRANSMISSION ELECTRON MICROSCOPE

submitted to

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

by

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August 1988

Contents

1.0 SUMMARY

This report describes the status of a transmission electron microscopy system that was purchased through a grant (AFOSR-87-0078) entitled "Request for a High Voltage/High Resolution Scanning Transmission Electron Microscope." The microscope purchased is a Philips EM 430T; accessories bought with the microscope are an energy-dispersive x-ray spectrometer (EDS) and an electron energy loss spectrometer (EELS). The tests at all modes of analysis have been completed and the results indicate that the instrument and its peripherals operate at their expected performance.

The system has already proven to be an indispensable tool in our DoD-supported projects on the development of advanced materials and it is expected that it will serve as a primary characterization tool in future projects.

2.0 BACKGROUND

There is a strong relationship between the microstructures and phase assemblages which are developed during the processing of materials. The crystallographical, morphological, and compositional variations in materials which affect their properties can take place in small dimensions and quantities. Therefore, it is necessary to fully and accurately characterize these materials in order to understand and predict material properties and to design new and improved materials for advanced technological applications. The transmission electron microscope is a unique system which permits the study of materials (metals, ceramics, composites, etc.) in all modes of analysis including imaging, diffraction, and spectroscopy at the highest spatial resolution possible in one instrument (Figure 1).

The purchased transmission electron microscope (the Philips EM 430T) fulfills many of the requirements for the high spatial resolution analysis of materials.

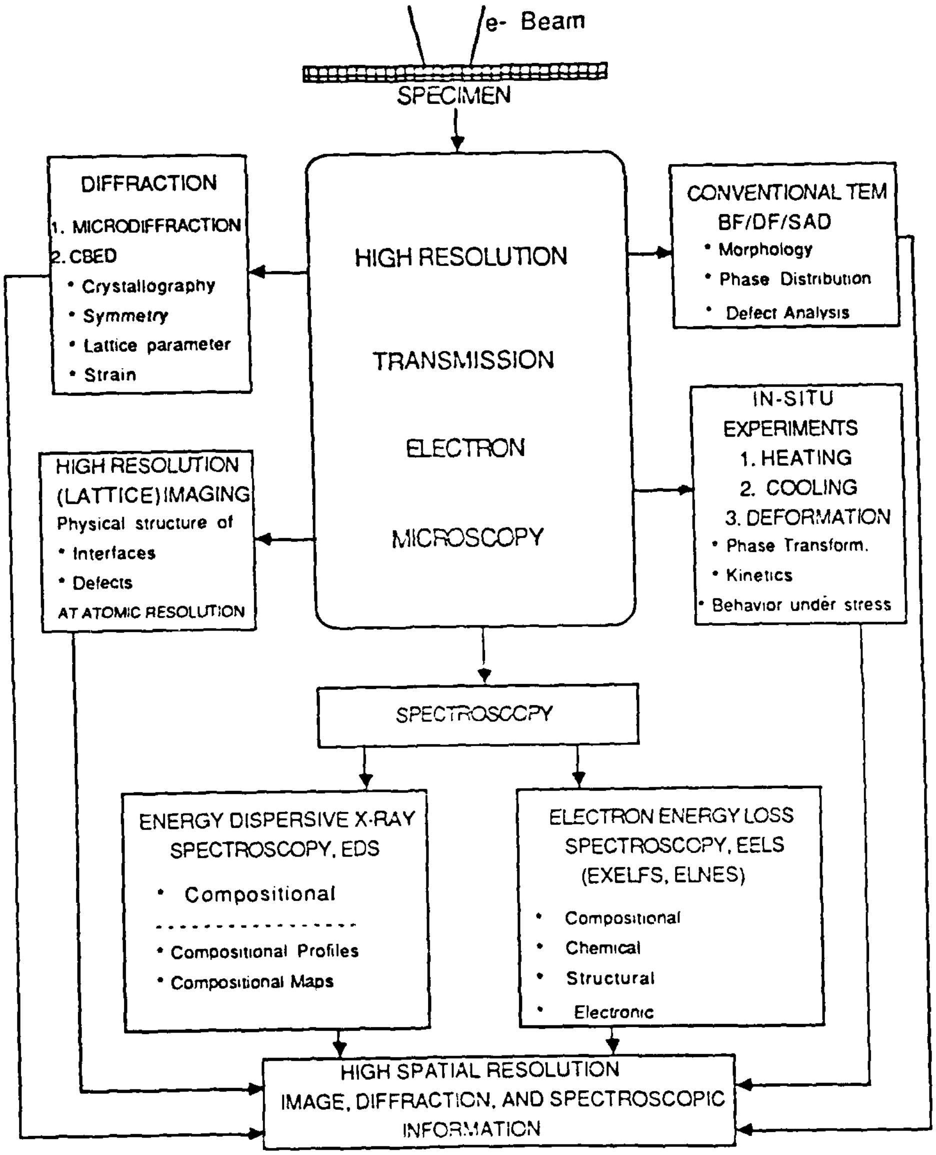

Figure 1: Schematic illustration of TEM techniques

The Philips EM 430T has the following features:

- A maximum operational voltage of 300 kV.

- Peripheral devices consisting of a scanning transmission electron microscopy unit, an energy dispersive x-ray spectrometer, and an electron energy loss spectrometer.

- Small probe-forming capabilities.

- Special specimen holders used for various analytical purposes.

The short descriptions of the system and its attachments are given below.

2.1 The Transmission Electron Microscope, TEM

The transmission electron microscope is a Philips EM 430T model TEM/STEM instrument which can be used for high resolution imaging and the formation of small electron probe, used in diffraction and spectroscopic applications. It displays images formed by the transmitted electrons on a phosphorous screen. The operating voltage can be varied from 0 to 300 kV at 1 eV steps with an external controller. Maximum magnifications on the photographic plate are 750,000 ×, 650,000 ×, and 550,000 × at voltages of 100, 200, and 300 kV, respectively. The smallest probe size that can be formed in the TEM mode is about 40 Å, and image resolution is 2.0 Å as confirmed by HREM (see Section 3.1).

The TEM and all the attachments (except EELS) were purchased from the North American Philips Co., Philips Electronic Instruments, 1381 McCarthy Boulevard, Milpitas, CA 95035; contact person: Mr. W. R. Turnquist, (408) 263-7000.

2.2 Scanning Transmission Electron Microscopy Unit, STEM

This unit has a separate detection system for scanned and transmitted electrons and operates at all comparable voltages of the TEM. In the image mode, the maximum image magnification is 400,000 ×, and the image is displayed on a cathode ray tube (CRT). In the diffraction mode, the minimum probe size is 20 Å. The STEM unit has independent focussing and astigmatism correction features. Its main use is the formation of small electron probes, principally for compositional analysis using EDS.

2.3 Energy Dispersive X-Ray Spectrometer, EDS

This unit includes a Si(Li) solid state detector horizontally mounted to the microscope column at the sample level and it is mainly used for quantitative elemental analysis. It has a thin beryllium window and windowless options; both features are used for the detection of characteristic x-rays that are produced during interaction of incoming electrons with the thin TEM foil. The detector is attached to a minicomputer and a multichannel analyzer for the storage, manipulation, and display of spectra. Hard copy of the spectra as well as tables of elements can be obtained from a line printer and plotter.

2.4 Electron Energy Loss Spectrometer, EELS

This spectrometer, located beneath the microscope, detects, counts, and displays the energy loss electrons which have undergone excitations during their passage through the TEM foil. EELS is mainly used for elemental analysis of low atomic weight elements (down to Li, $Z = 3$) and their electronic and bonding configurations. It is, therefore, the highest spatial resolution spectrometer available. It has a unique construction and a photodiode array allowing the acquisition and display of EELS spectra within 1 to 10 secs, rather than detecting and displaying energy loss electrons channel by channel as in conventional EELS, where sequential detection is done (in 100 to 1000 secs). The acquisition times are thereby decreased 100-fold and the efficiency is increased.

EELS is the only attachment that is bought separately through the Washington Technology Center support. The vendor is: GATAN, Inc., 6678 Owens Drive, Pleasanton, CA 94566; contact person: Mr. Dana Clough, (415) 463-0200.

2.5 Specimen Holders

There are four specimen holders and each is used for a specific purpose. These are described below.

2.5.1 Single Tilt Holder

With this holder, the sample can only be tilted in one direction, but the holder has high mechanical stability. Also, sample loading is straightforward. It is mainly used for high resolution imaging of small suspended particles on an amorphous TEM grid (e.g., on a carbon film).

2.5.2 Double Tilt Holder

Tilting can be performed in two orthogonal directions by $\pm 30°$ and $\pm 45°$. Its main use is conventional microscopy and crystallography studies (through high-angle diffraction).

2.5.3 Tilt-Rotation Holder

Both tilting ($\pm 45°$) and rotation (between $0°$ and $360°$) can be performed with this holder. Its main usage is in crystallographic analysis.

2.5.4 Low Temperature-Low Background Holder

This holder can be cooled to -175°C by liquid nitrogen, which reduces thermal vibration in the sample. It also has a low x-ray background feature and is, therefore, heavily used in EDS analysis. For beam-sensitive materials, such as superconducting ceramics or bioparticles, this holder can be used for diffraction, EDS, and EELS studies since it reduces the radiation damage to the sample.

3.0 Performance Tests

The microscope can be operated at four analysis modes of advanced transmission electron microscopy. These are: high resolution imaging, converging beam electron diffraction, energy dispersive x-ray spectroscopy, and electron energy loss spectroscopy. This section describes the tests that have been undertaken in each of these modes to establish the performance of the microscope at respective operation modes.

3.1 High Resolution Electron Microscopy

HREM imaging is a technique in which thin samples with periodic arrangements of atoms (crystals) are imaged in a projection in the direction of the electron beam. Therefore, it is an atomic resolution imaging revealing the atomic packing of matrix and its defect structures, structures of boundaries, interfaces, and small particles. The instrumental resolution of the microscope, d_r, is dictated mainly by the optical defect in the objective lens (i.e., by C_s, which is the spherical aberration coefficient of the objective lens) and by the kinetic energy of the incoming electrons (i.e., by the acceleration voltage, or by the wavelength, λ, of electrons) through the Shertzer formula,[1]

$$d_r = 0.7\, C_s^{1/4} \lambda^{3/4}$$

The value for C_s for the Philips EM 430T is 2.0 mm and at 300 kV accelerating voltage (λ = 0.0197Å), the theoretical resolution becomes 2.3 Å.

The resolution tests have been performed by imaging colloidally prepared gold particles suspended on a thin (50 Å) and amorphous carbon film. Figure 2 is an image from such a sample. It reveals the atomic arrangements in several gold particles projected in various orientations. As can be seen in particle A, both 111 (d_{111} = 2.35 Å), and 200 (d_{200} = 2.04 Å) fringes are resolved (the image was taken at a defocus value lower than the Shertzer value producing a reverse contrast, i.e., atoms appear "bright" in the image).

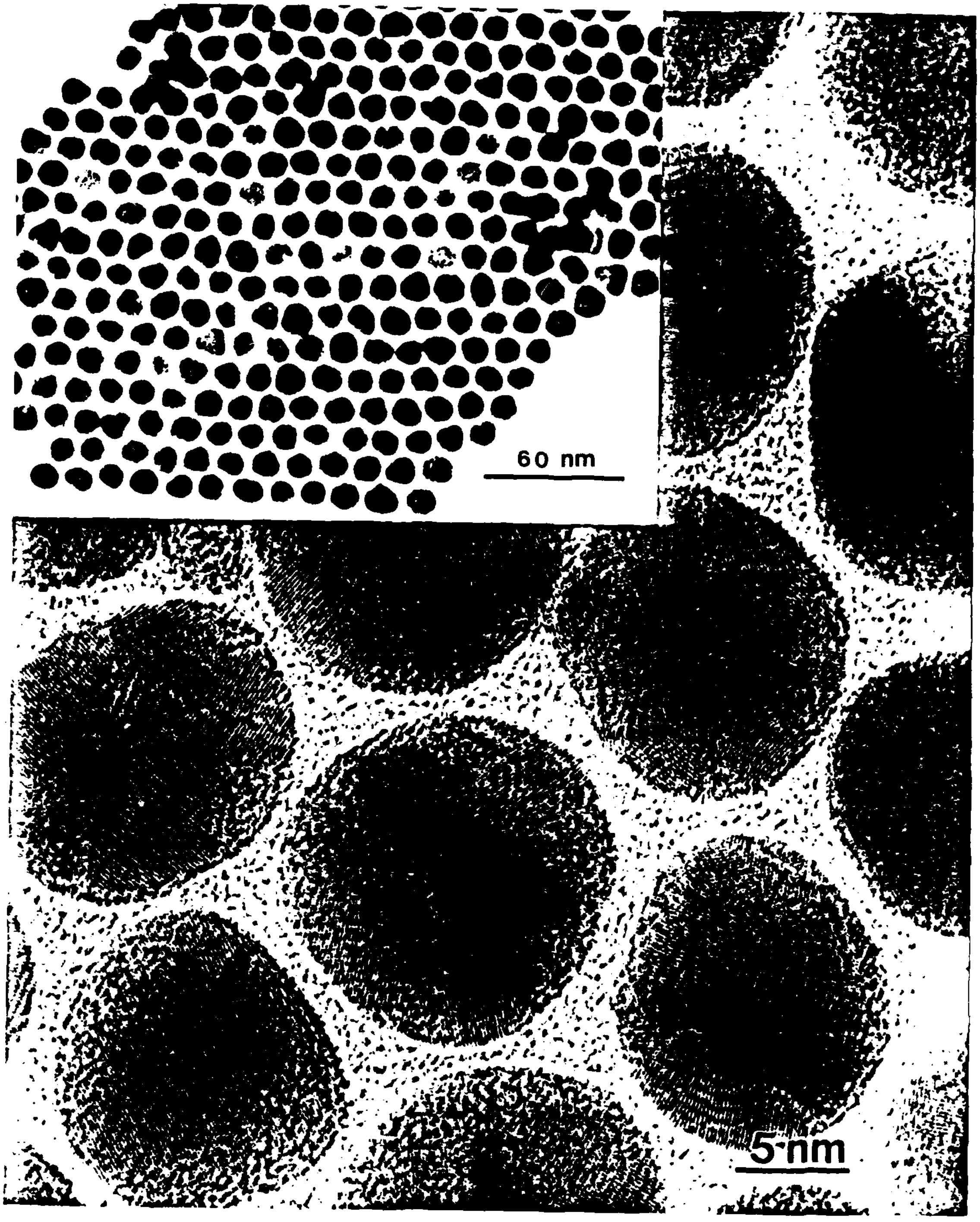

Figure 2. HREM image of gold particles suspended in a carbon film. Note several particles imaged in a zone axis orientation revealing atomic positions in the fcc lattice of gold.

3.2 Convergent Beam Electron Diffraction, CBED, and Microdiffraction

Because of the twin lens arrangement of the objective lens, i.e., the upper and lower pole pieces of the objective lens about the sample, small electron probes can be formed. This is done mainly by the excitation of the upper pole piece of the objective lens. The theoretical probe sizes that can be formed under different condensor-1 (C1) excitations and condensor aperture (CA) sizes in the TEM and STEM modes are listed in Table I.

Selector position	LM range (μm)	M and SA range (μm)	M and SA range (nm)
	set to MICROPROBE	set to MICROPROBE	set to NANOPROBE
C1 OFF	2	0.39	108
1	2.2	0.44	40
2	1.1	0.22	24
3	0.6	0.11	14
4	0.25	0.05	6
5	0.1	0.02	2.6
6	0.05	0.01	1.4

Table I. Probe sizes in microprobe and nanoprobe modes in the TEM

The formation of electron probes was tested both in microdiffraction and CBED modes. In the former, small (~100 – 500Å) magnetite (fcc-Fe_3O_4) particles are used (see Section 4.1.2). These particles, produced by *Aquaspirilum magnetotacticum* bacteria, are magnetic and are used by the bacteria as a compass in their search for food.[2] The interest in microdiffraction was to find out the orientation relationship between the particles formed along the longitudinal direction of the bacteria. As shown in Figure 3b, microdiffraction pattern is given in a zone axis orientation. The conditions for probe formation were: C1 at position 6 (theoretical probe diameter 100 Å); CA = 50 μm; TEM mode; E_o = 200 kV (accelerating voltage); CL = 450 mm (camera length). This test indicates that probes as small as 100 Å can be formed in the microdiffraction mode and easily be placed on the small particles (200-500 Å diameter) which are then tilted to near a zone axis to obtain microdiffraction patterns.

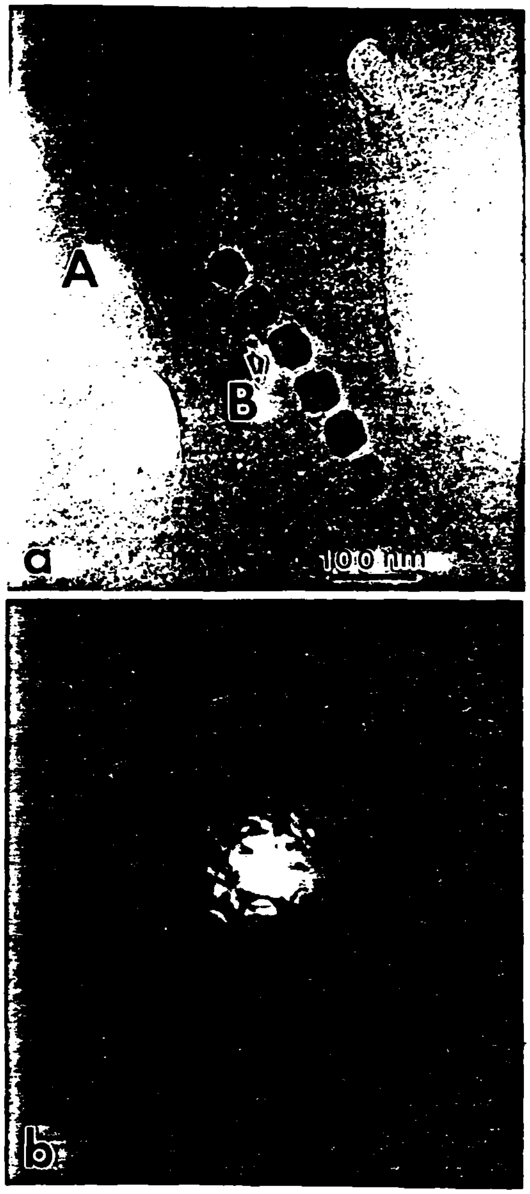

Figure 3. Bright field (a) and microdiffraction pattern (b) taken from the magnetic particle indicated by *B*.

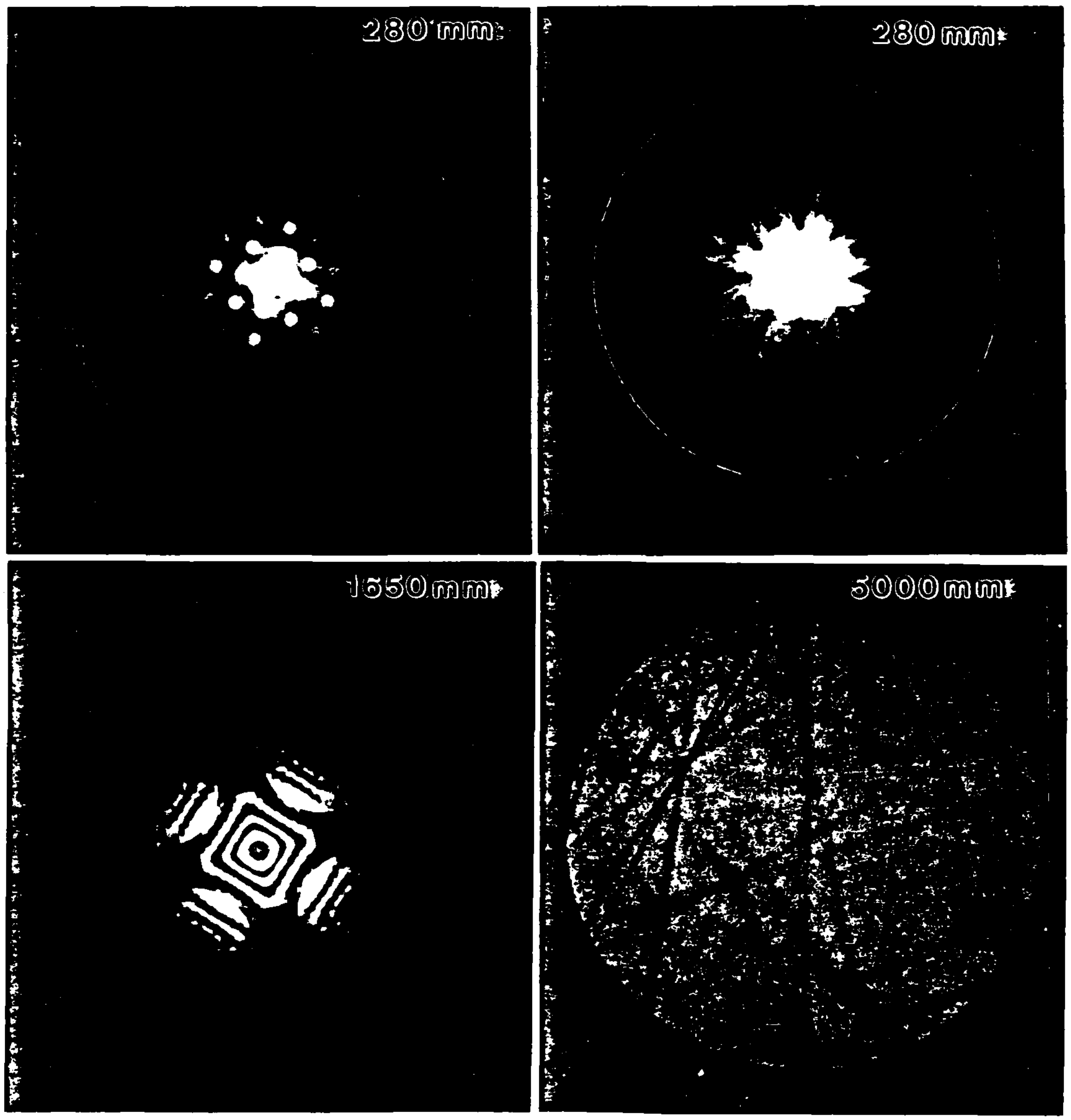

Figure 4. CBED patterns, at various camera lengths to reveal the details of the CBED patterns. Sample Si, $E_0 = 200$ kV, crystal orientation [001].

Convergent beam experiments were done by using single crystal Si (dc, a = 5.4309 Å). The experiments were performed to check the stability of the electron probe during the recording of the CBED patterns and to reveal high order Laue zone (HOLZ) lines located in the forward scattered beam. In order to decrease the thermal vibrations and increase the sharpness of the diffraction lines, experiments were done by using the low temperature holder (specimen temperature equalled was -170°C). Figure 4 exhibits CBED patterns at various camera lengths to reveal symmetry and diffraction features in the whole pattern, in the zero layer, and in the bright field disc.[3] The revelation of HOLZ lines in the BF disc by [100] orientation, which have low scattering amplitudes, is especially interesting and can only be done by using the low temperature holder.

3.3 Energy Dispersive X-Ray Spectroscopy, EDS

The EDS technique is primarily used in compositional analysis of TEM foils.[4] With the present detector (which has both windowless and thin window options) elements between boron (B, $Z = 5$) and uranium (U, $Z = 92$) can be detected and quantified. For illustration, an experiment performed on the orthorhombic phase of the $YBa_2Cu_3O_{7-x}$ phase is included here. The purposes of the experiment were twofold. Firstly, to check the stability of the sample under a condensed beam and to establish conditions for EDS acquisition. Secondly, to check the performance of the quantitative analysis software provided by the manufacturer of the EDS system.

The samples used for EDS analysis were $YBa_2Cu_3O_{7-x}$ which were produced in this research group (cf. Section 4.1.4 and Appendix IV) and they superconduct near 90K. The elemental ratios in the stoichiometric samples are Y:Ba:Cu = 1:2:3. Table II below displays the quantitative analysis as performed by using the automatic "Thin Foil Quantification" package. Within ±3% error, the analysis resulted in the stoichiometric composition and it was found to be within acceptable limits of quantification. Analysis by using standards, high counting statistics, including absorption and fluorescence correction, and performing more careful background subtraction, should increase the accuracy to within ±1%. The experimental conditions established for the analysis of the sample of interest includes: the analysis in the TEM mode, a 30° tilt angle of the sample toward the detector, use of the low temperature holder (with a specimen temperature of -170°C), accelerating voltage ≤ 200 kV, probe sizes (d_p) ≤ 500Å, and condenser aperture size, (CA) ≤ 100μm. A characteristic spectrum displaying Y, Ba, and Cu peaks is shown in Figure 5a as a reference. The spectrum shown in Figure 5b. is from an intergranular phase which was identified as cuprous oxide (Cu_2O) (see Appendix).

LABEL = 1-2-3							
A. 362.630 LIVE SECONDS				B. 74.469 LIVE SECONDS			
ELEM	CPS	BKGD	P/B	ELEM	CPS	BKGD	P/B
Y-L	17.086	4.936	3.461	Y-L	38.956	10.206	3.817
Ba-L	51.234	3.673	13.948	Ba-L	120.305	8.634	13.933
Cu-K	85.914	2.427	35.403	Cu-K	197.666	6.002	32.931

LABEL: 1-2-3			LABEL = 1-2-3		
C. 362.630 LIVE SECONDS			D. 74.469 LIVE SECONDS		
ELEM	CPS	AT % ELEM	ELEM	CPS	AT % ELEM
Y-L	17.086	16.626	Y-L	38.956	16.394
Ba-L	51.234	31.418	Ba-L	120.305	31.907
Cu-K	85.914	51.956	Cu-K	197.666	51.699
Total		100.000	Total		100.000

Table II. Quantitative analysis of the superconducting $YBa_2Cu_3O_{7-x}$ phase. A and C are elemental ratios, D and C are peak-to-background, P/B, ratios.

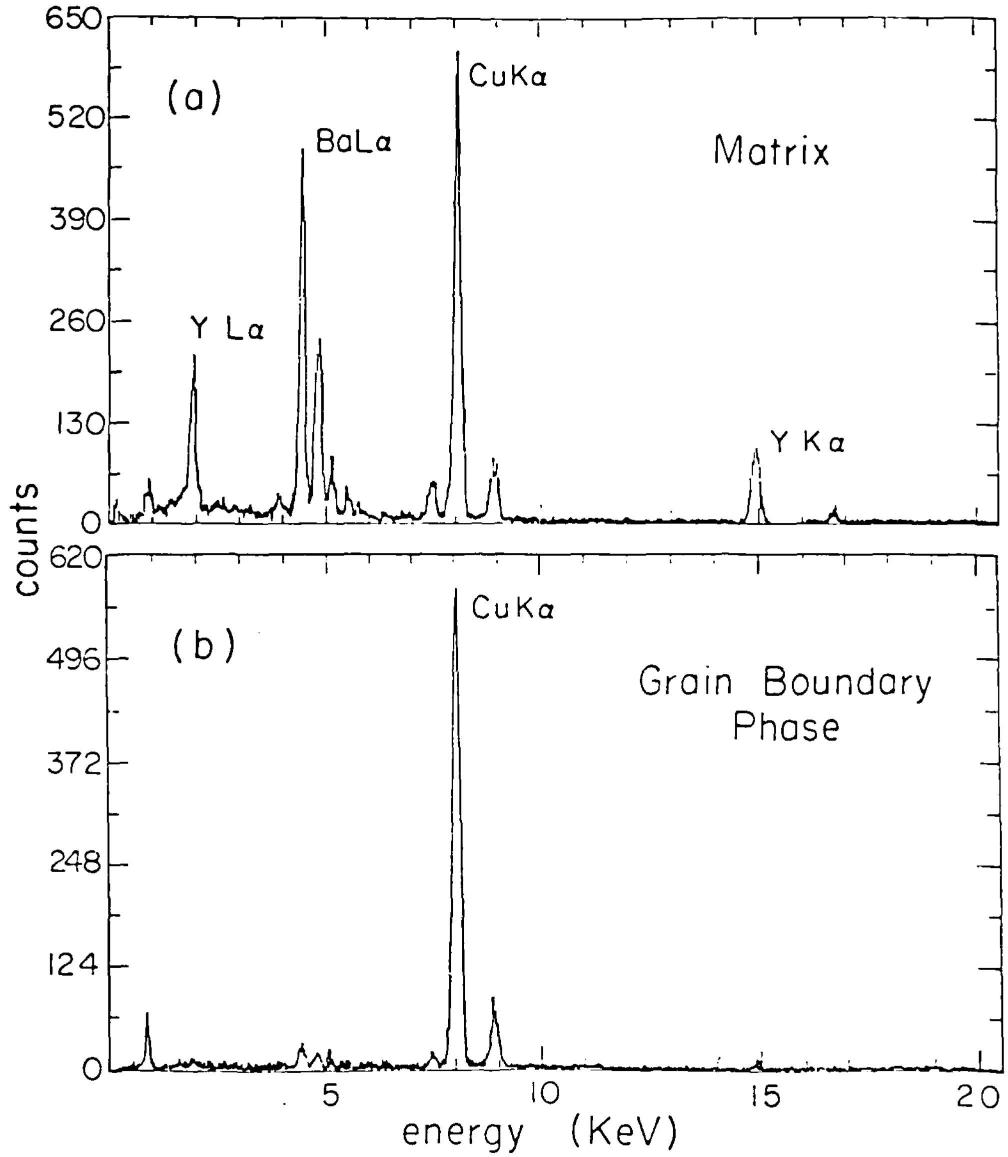

Figure 5. EDS spectra of 1:2:3 phase (a) and of intergranular phase (b). Note that in (b), there are only peaks corresponding to Cu. The intergranular phase has been identified to be cuprous oxide (Cu_2O) (see Appendix for the *J. Amer. Soc.* paper on this subject).

3.4 Electron Energy Loss Spectroscopy (EELS)

The EELS is the study of energy distribution of electrons which have interacted with a specimen.[5,6] The number of electrons which have lost a certain amount of energy from their primary value (the ordinate) is plotted with respect to their respective energy loss, ΔE (abscissa) in an energy loss spectrum (Figure 6a). The EEL spectrum, in this respect, resembles an x-ray absorption spectrum with edges corresponding to absorption edges.[6] Both the intensity under each edge (after background subtraction and multiple scattering effects are excluded), as well as the detailed shape and the energy threshold of each edge, are used for compositional and atomic binding information.

EELS technique is particularly useful for the detection and quantification of low atomic number elements, such as Li ($Z = 3$), Be, B, C, N, O, and F (9), and in this respect, complementary to EDS analysis, where higher Z elements are analyzed.

A uniqueness of the spectrometer, i.e., GATAN 666 Parallel Detection System, that is installed on the Philips 430T is that the energy loss electrons are detected in parallel, i.e., the whole spectrum is collected at once.[7] This is in contrast to traditionally used serial systems where the electrons at each channel are collected in serial (channel-by-channel) basis. So, for example, for 1000 channels, the acquisition times for the parallel detection system decreases an order to two orders of magnitude. This feature of the new parallel EELS system is extremely important in the high resolution spectroscopic characterization of beam sensitive materials, such as ceramics, nanocrystals, biomaterials, and polymers. Therefore, PEELS is opening up new possibilities in the characterization of these important new classes of materials.

A sample spectrum is given in Figure 6b taken by PEELS from a Si sample, using a total acquisition time of 15 seconds. It displays the Si-K edge at the edge energy of 1839 eV. It clearly outlines the threshold of the edge, as well as the near edge and extended edge fine structure which all are essential information sources on the electronic structure of atomic species which make up the materials and atomic bonding. These studies will be pursued in our current and future research.

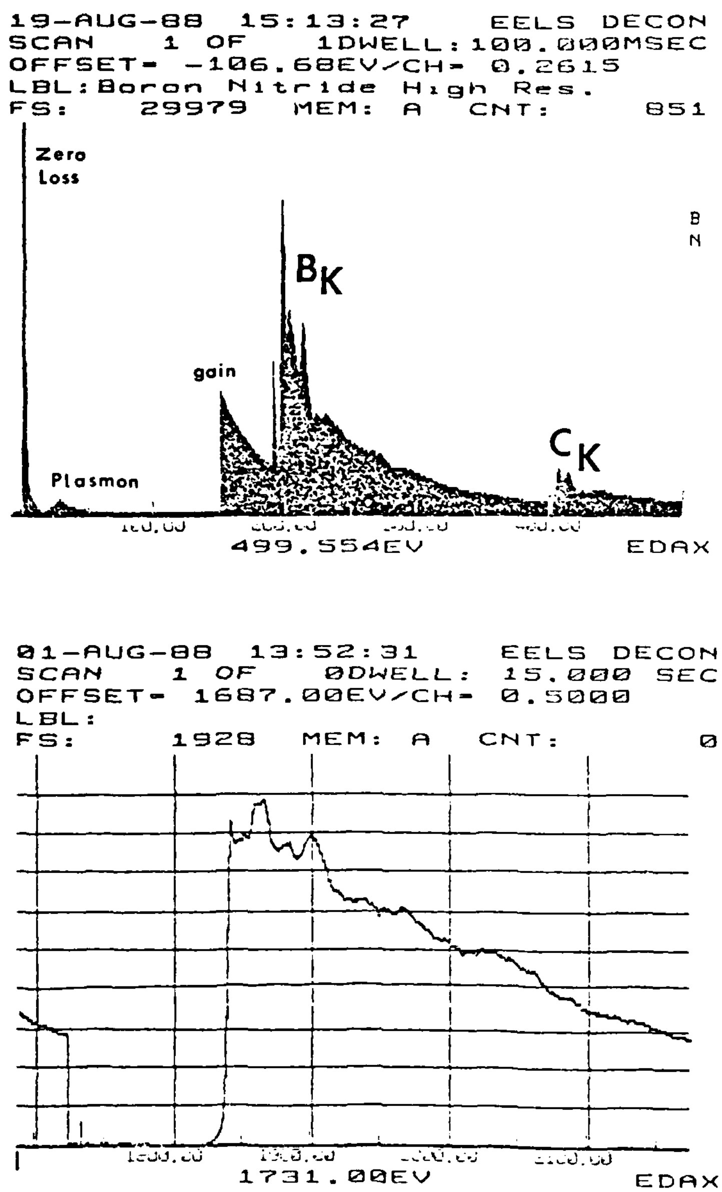

Figure 6. (a) A spectrum from a BN sample displaying the essential features of an EEL spectrum. (b) EEL spectrum from a Si-K edge displaying the details of the edge. The spectrum was taken at E_o = 300 kV, t = 15 seconds, in the image mode.

4.0 Research Projects

4.1 Current DoD Supported Research

4.1.1 Microdesigning of Lightweight/High Strength Ceramic Materials

I.A. Aksay
Sponsor: AFOSR/DARPA; Program Manager: D. R. Ulrich
Amount: $410,000/yr.; Duration: 7/1/1987 - 6/31/1990

This research program is concerned primarily with the processing and characterization of complex ceramic matrix composite systems. The emphasis is placed on developing processing schemes for whisker-reinforced ceramic matrix composites and additional studies deal with B_4C-Al ceramic/metal composites. In each case, material purity and microstructural features can significantly affect the macroscopic properties of the material.[8] Special techniques are being developed to allow the efficient design of microstructural features during processing. Work is underway on dispersion, consolidation, and sintering of ceramic powders and ceramic-forming gels, in an effort to identify key processing parameters that affect the microstructure of the composite material.[8-9] Considerable continuous effort is also being spent on the fabrication, mechanical testing, and high resolution electron microscopy analysis of B_4C-Al composites, so that the relationship between microstructure, composition, and mechanical properties may be determined. Lastly, theoretical models of particle-particle interaction, particle-polymer interaction, and colloidal suspension stability are being developed, based upon statistical mechanics and interparticle potential analysis to provide the foundation for developing a more fundamental understanding of colloidal systems in various configurations.[8-12]

In the following paragraphs, only two aspects of the project related to imaging and analysis will be described to emphasize the significance of the instrumentation and its impact on this and other projects summarized in this report.

4.1.1.1 Fundamental Studies in Processing. The major effort of this portion of the research program is concerned with the processing of ceramic matrix composite systems made from ultrafine (submicron) ceramic particles. In particular, the work seeks to develop a fundamental understanding of the important parameters involved in the dispersion, consolidation, and sintering of particles in the size range of 10^{-9} to 10^{-3} m. These particles may be spheroidal, platelike, or rodlike, and may form a highly dispersed or agglomerated suspension. Surfactants or polymers may be added to a suspension to improve the consolidation step, resulting in the tailored packing of the particles in the green microstructure. Densification may take place with the addition of heat and/or pressure. This program studies each of these areas in detail in order to improve upon current processing methodology in designing and producing desired microstructural features.

In the high density consolidation of nanosized particles with surfactants (synthetic or biopolymers, refer to Section 4.1.2), control of the evolution of the structures is of great importance. Therefore, direct observation of the cluster structures is necessary. Structures of clusters or aggregates of small particles can be studied directly by transmission electron microscopy techniques (Fig. 7).[12]

Fig. 7. A transmission electron microscopy image of a cluster of gold particles (diameter 15 nm). The cluster is a fractal object; the fractal dimension can be determined by a digital image analyzer using a projection such as this one.

In some colloidal systems the structure of the aggregates are found to be fractal objects. The Housdorff fractal dimension D is generally defined by the following relation:[13]

$$N(r) = (r / r_o)^D \tag{1}$$

where $N(r)$ is the number of particles within a sphere of radius r and r_o is the radius of the particles. Therefore, by counting the number of particles in the micrograph, the fractal dimension D can be calculated easily.

More generally, the space correlation function can be studied:

$$C(r) = \frac{1}{N} \sum_{r'} \varphi(r')\varphi(r + r') \tag{2}$$

where N is the number of particles and $\varphi(r)$ is the probability that a particle can be found at position r. For fractal objects, the space correlation function (or the pair correlation function $g(r)$) is directly related to the fractal dimension D and particle diameter d:

$$C(r) \sim r^{D-d} \ . \tag{3}$$

The main difficulty in obtaining fractal dimension and correlation function is the need for a large sampling. This difficulty can be solved readily with the help of a digital image analyzer utilized concurrently with electron microscopy imaging (Figure 7). A factor that influences the results is the edge effect, but this can be avoided by more elaborate procedures that are planned to be developed with an image analyzer.

4.1.1.2 Processing and Characterization of B_4C-Al Cermets. The primary focus of this study of B_4C-Al ceramic/metal ("cermet") composite materials is the processing and mechanical testing, and the microstructural analysis and characterization of these composite materials.[14-16] The composite is formed by first heating the consolidated B_4C powder above 2000°C to form a porous "skeleton," and then by infiltrating aluminum into the porous skeleton at 1100°C. The objective of the initial portion of this work has been to study the effect of controlled modifications in the microstructure upon the elastic and fracture properties of the B_4C-Al cermet. Special emphasis has been given to the response of the tailored microstructure to static and dynamic loading. (This portion of the work is underway in collaboration with Los Alamos

National Laboratories where the dynamic testing is being conducted.) The goal of the second portion of the work has been to use high resolution TEM imaging techniques to correlate structure, composition, and mechanical properties of phases and interphases in the B_4C-Al ternary system. Because chemical reactions during high temperature processing may produce up to fifteen phases, and because the resulting microstructure can affect mechanical behavior, such TEM studies provide fundamental information regarding the interrelationship between mechanical properties and microstructural and compositional variations. It is planned to continue to perform general phase and composition analysis with the EDS and to use high resolution TEM for analysis requiring high spatial resolution, such as atomic structures of interfaces.

4.1.2 Processing of Ceramics by Biopolymers

M. Sarikaya, J.T. Staley, D.M. Dabbs, and I.A. Aksay
Sponsor: AFOSR; Program Manager: A.J. Matuszko
Amount: $100,000/yr; Duration: 2/1/1988-1/31/1991

As the high performance components for advanced uses such as in electronic and aerospace applications become smaller, the trend in the production of these components leans toward the utilization of newly emerging engineering methods in which the microstructural design starts at the nanometer level. One such method is colloidal processing of materials with ultrafine particles in which particle-particle interactions play the most important role in controlling the aggregate structure.[8] Therefore, in addition to particle size, these particle interactions have to be controlled if "tailor-made" microstructures with controlled defect size and distribution are to be achieved. The use of surfactants and lubricating polymers offers possibilities in developing particle surface properties leading to control of the aggregate structures.[9-12] The primary purpose of this proposal is to initiate a program to first synthesize biologically produced lubricating polymers and then investigate their possible applications in the colloidal processing of ceramics with ultrafine particles. Afterwards, nanometer-sized particles will be synthesized and subsequently used in ceramic processing through biomimetic and bioprocessing routes.

Structural development of the samples prepared by using various unusual biopolymers is being investigated by well-established methods. The new approach to characterization introduced in this proposal is the elucidation of the mechanisms of biopolymer-mediated particle formation and biogenic particle formation in bacteria: the technique involves the use of a TEM on thin-sectioned samples and a scanning tunneling microscope to image freeze-fracture replicas of biopolymers.[20]

4.1.3 New Catalytic Routes to Polysilazanes

Richard M. Laine
Sponsor: ONR; Program Manager: K. Wynne
Amount: $119,000; Duration: 1/1/1988-12/31/1988

The development of optimal, high strength, lightweight ceramic and metal matrix composites (CMC and MMC) is an important directive of the Strategic Defense Initiative (SDI) because of the significant impact these materials will have in improving the design, performance and protection of space-based satellites, their propulsion systems, and general methods of payload delivery.[21-23] The fabrication of high quality silicon nitride (Si_3N_4) and silicon-carbide-nitride (SiCN) fibers for CMCs and MMCs will greatly facilitate progress in this direction. Advances in the development of Si_3N_4 and SiCN fibers have produced materials with tensile strengths of 300 ksi and moduli of 3×10^4 ksi.[21] Unfortunately, the cost of manufacture is still high and no process is as yet commercial. Considerable time and effort must still be invested to realize technically and commercially viable fibers. In the last four years (since 1984), in work sponsored by the Strategic Defense Sciences Office through the Office of Naval Research (Contract Nos. N00014-84-C-0392 and N00014-85-C-0668) we have demonstrated the feasibility of preparing novel polymer precursors to Si_3N_4 and SiCN using transition metal catalyzed reactions of silanes with amines.[24-26] We have further demonstrated that these polymers can be used: (1) to form strong ceramic coatings on various metals, glasses and ceramics; (2) as binders for Si_3N_4 powder. We also have preliminary evidence that with proper viscoelastic properties, thin (10 μm) precursor fibers can be formed.

We proposed to extend our studies to develop new improved catalytic methods of preparing preceramic polysilazanes, transforming them into ceramic products, and characterizing the chemical and material properties of these products. The objective of the last task area is to extend our studies on the effect of variations in pyrolysis conditions on ceramic yields, composition, and structure. In particular, we plan to emphasize in-depth analytical characterization of the ceramic products in terms of imaging at all levels of resolution (from optical to atomic resolution) by direct spectroscopy (EDS, EELS, WDS, as well as NMR) and diffraction (both electron and x-ray diffraction). The imaging and analysis system on TEM will greatly enhance our studies. It will enable us to perform systematic and efficient analysis of structural and compositional evolution of the transitory and final ceramic products, and will allow us to design processing routes to control the final product.

4.1.4 Processing, Fabrication, and Characterization of High-T_c Superconducting Oxides

I.A. Aksay, R.M. Laine, M. Sarikaya, and E.A. Stern
Sponsor: AFOSR/DARPA; Program Manager: D. R. Ulrich
Amount: $505,000/yr. (subcontracted from Boeing Aerospace Co.);
Duration: 9/1/1988-8/31/1989

This project is a comprehensive program on the processing, fabrication, characterization, and device demonstration of Y-Ba-Cu-O containing superconducting oxides which exhibit transition temperatures at or above 90 K and which have high current carrying capacities in large magnetic fields. In this program Boeing Aerospace Company (BAC) will guide and contribute to the work performed by each team member to ensure the successful development of superconducting materials systems for aerospace applications.

The basic program objectives include: (i) the use of advanced ceramic processing techniques including sol-gel, organometallics, sputtering, and plasma deposition to produce fibers, thin films, and monoliths applicable to high current and electromagnetic screening devices;[27] (ii) the fabrication of superconducting samples at experimental and device levels which are fully dense and have tailor-made microstructures to produce sharp transition temperatures and high critical current capacities in magnetic fields, and which are structurally, mechanically, and cryogenically stable;[27] (iii) the development of an understanding of the thermodynamics of the phase equilibria in this system and the production of new and more stable compounds with potential application to superconducting devices; (iv) the ultrastructural characterization of the superconducting samples, which includes nano- and micro-structures, lattice structures and defects, and local structures and electronic states.[28-29] We will also undertake detailed modeling and theoretical studies which will facilitate optimization of material systems; and (v) the demonstration of the above technologies, along with contact development and optimization, in *both a high and a low current* (Meissner region) superconducting device. Emphasis will be on the high current device.

The subject of high temperature superconducting oxides is of great scientific interest and is of significant value to future aerospace applications. We have established a consortium between two universities (University of Washington and Washington State University) and a government laboratory (Battelle, Pacific Northwest Laboratories) to more efficiently and effectively achieve the program objectives. Scientific completion of this program will result in the material and process information required to produce conductors and thin films with optimized properties for application in devices such as solenoids and coatings for electromagnetic screening.

4.1.5 Hierarchically Clustered Structures

I.A. Aksay and R. Kikuchi
Sponsor: ARO; Program Manager: George Meyer
Amount: $322,868; Duration: 6/1/1985-5/31/1988

This project deals with the sintering of submicron size particles consolidated by colloidal techniques. It is known that hierarchically clustered structures form during colloidal consolidation. Both experimental and theoretical methods have been used to characterize the formation and development of the structures. Based on these findings, two objectives have been (i) developing experimental techniques of tailoring microstructures through colloidal consolidation techniques, and (ii) developing a methodology for predicting how these consolidated structures will evolve during sintering.

Advances have been made in understanding the stability of a colloidal suspension which depends on control of the interparticle binding energy. Like in atomic systems, the stability regimes of the colloidal fluid and solid states are outlined in a phase diagram.[30] It has also been shown that the size and spatial arrangement of particle clusters, and thus of the associated voids, can be varied simply by changing the colloidal solidification path in the phase diagram. It has also been shown that varying solidification rates form a variety of hierarchically clustered structures with first, second and third order voids. Further work is under way to establish a fundamental understanding of the parameters that affect nucleation and growth of particle clusters that result in such structures, and of the role which the structures subsequently play in microstructural evolution during sintering.

4.2 Planned Research

4.2.1 Development of Lightweight Ceramic Particulate Reinforced High Strength Al-Li Alloys

M. Sarikaya, I. A. Aksay, and R. Kikuchi
Sponsor and Program Manager: not yet known
Amount: ~$320,000/3 years; Duration: 1988-1991

Precipitation and dispersion are particular methods of hardening a material by the introduction of obstacles to deformation and crack propagations.[31-33] This concept of strengthening a matrix by the introduction of discrete obstacles which are particles of a phase with a higher yield strength and lower ductility is the basis of a wide variety of applications. The purpose of this program is to develop light ceramic particulate reinforced Al alloys for improved mechanical properties. An important aspect of the program is to increase the strength while decreasing the overall density of the material. For this reason, it is proposed that additions of non-conventional low density ceramic dispersoids be made to Al-Li alloys.

In this proposed program, we will rely on our earlier success in developing low density B_4C-Al cermets with strong ceramic/metal interfaces. For dispersoids, additions of B_4C, AlB_2, and newly discovered Al_4BC phases will be made into an Al-Li matrix. The use of thermodynamically stable dispersed ceramic phases with strong interfaces, coupled with solute-solution and precipitation strengthening, is proposed as the most promising route in achieving higher strength in these technologically important materials. Both experimental and theoretical analyses of the effects of dispersoids on the deformation behavior of the matrix will be performed. The experimental analysis will constitute standard mechanical tests and in-situ heating and straining studies in the transmission electron microscope. The theoretical analysis will be based on computer models of particle-defect interactions. In this analysis, a special emphasis will be given to the effect of particle/matrix interface structures, and to the determinations of property microstructure relationships through mechanical testing and high spatial resolution imaging and spectroscopy.

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APPENDIX

Copies of Publications Related to Transmission Electron Microscopy

(From June 1987--date of installation of the TEM--to July 1988, present time)

APPENDIX

Copies of Publications Related to Transmission Electron Microscopy

(From June 1987--date of installation of the TEM--to July 1988, present time)

APPENDICES

Appendix - I

"Microstructural Characterization of $YBa_2Cu_3O_{7-x}$"

M. Sarikaya, B. L. Thiel, and I. A. Aksay, W. J. Weber, and W. J. Frydrych

J. Mater. Res. **2** (6) Nov/Dec, 736 (1987)

Microstructural characterization of $YBa_2Cu_3O_{7-x}$

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(Received 8 July 1987; accepted 24 August 1987)

A detailed characterization study on polycrystalline specimens of $YBa_2Cu_3O_{7-x}$ that were prepared by solid-state reaction techniques has been carried out. In the samples studied, magnetization and resistivity measurements indicate superconductivity onset temperatures of up to 89 K. Transmission electron microscopy (TEM) techniques have been used to facilitate direct microstructural characterization. It is shown that the planar defects on (001) planes form during the ion milling of the samples and are not directly connected with superconductivity. Laser Raman spectroscopy has revealed that these materials are sensitive to environmental degradation.

I. INTRODUCTION

Superconductivity above 30 K was first reported by Bednorz and Müller[1] in a La–Ba–Cu–O compound. A number of other related compounds were found that exhibited superconductivity with layered-like structural packing similar to K_2NiF_4.[2,8] Through improved sample preparation techniques,[3,5,9] changes in chemical constituents,[5] and applied pressure,[4] the transition temperature T_c was raised above 30 K, and the transition width was reduced. It is now possible to prepare nearly pure phase RE–Ba–Cu–O compounds (RE = Y, Nd, Sm, Eu, Gd, Ho, Er, and Lu) that show T_c between 90 and 95 K and that show bulk superconductivity.[5] The most recent studies indicate that the critical temperature has risen to 155 K in compounds where O is partially replaced by F[10] and to 240 K in compounds that contained the same atomic species as in the original Y–Ba–Cu–O samples but in different amounts.[11(a),(b)] However, neither the exact composition nor the crystal structure or other structural features of these new phases are yet known. As more experimental information is accumulated about these compounds, T_c may be expected to rise to even higher temperatures.

The reports made in the literature[3,5] and the results of diffraction and transmission electron microscopy (TEM) studies in our laboratory[12] indicate that the original high-T_c samples consisted of more than one phase. Subsequent studies have determined that the high-T_c superconductor can be produced in a single phase with a composition $YBa_2Cu_3O_{7-x}$.[13,14] These compounds have either tetragonal[5,15] or orthorhombic crystal structures,[3,6,9,12–14,16] as determined by x-ray and neutron diffraction. Although some models have been developed on the atomic packing of these crystals that are supported by theoretical and experimental studies through the bulk measurements,[3,6,16] these models have not all agreed with one another on the actual arrangements of the atoms and the relationships of atomic layers within the lattice. In some recent atomic resolution electron microscopy studies,[17(a)–(c)] not only was the lattice of the 90 K phase (pseudo-orthorhombic) successfully imaged, directly in (100) orientation revealing the position of the atomic species, but also some unexpected lattice defects were found. The effect of these defects on the superconductivity in these samples is not yet known. Only limited information has been reported in the literature on the micro- and nano-structural variations in polycrystalline high-T_c superconducting samples.

Presently, what is needed is the use of techniques that would (i) allow the revelation of the phase that produce superconductivity at high temperatures; (ii) that would provide information about their spatial distribution, crystal structure, and composition; and (iii) that would provide direct spectroscopic information. This article focuses on the morphology and crystallography of superconducting $YBa_2Cu_3O_{7-x}$ as studied by high-resolution TEM techniques. During the preparations, unprecedented modifications may be introduced to the thin sections used for TEM observations. This could lead to erroneous interpretations. Therefore the purpose of this report is twofold: first, to explain the techniques used in the preparation of electron transparent sections for TEM observations, and second, to perform microstructural and spectroscopic analyses of polycrystalline samples.

II. EXPERIMENTAL PROCEDURE

A. Sample preparation

Samples of $YBa_2Cu_3O_{7-x}$ were prepared for this study by the solid-state reaction of Y_2O_3, BaO_2, and

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Appendix - II

"Local Structural Variations in $YBa_2Cu_3O_{7-x}$"

M. Sarikaya and E. A. Stern

Phys. Rev. B, 37 (16), June, 1988

Local structural variations in $YBa_2Cu_3O_{7-x}$

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(Received 11 January 1988)

Electron microscopy investigations at 120 K utilizing microdiffraction and selected area diffraction on isolated single-crystal grains of the orthorhombic phase of $YBa_2Cu_3O_{7-x}$ reveal local variations in $\Delta a/a$. Here $\Delta a/a$ is the percentage difference between the a and b dimensions of the orthorhombic structure. The microscopic values of $\Delta a/a$ vary from zero to more than twice the macroscopic value over typical spatial dimensions of 1000 Å. The results are consistent with the sample being in the spinodal decomposition region as predicted by Khachaturyan *et al.* We show an approximate linear relationship between macroscopic values of $\Delta a/a$ and T_c and use this to argue that appropriate processing may be able to raise T_c to 220 K.

INTRODUCTION

In spite of the intensive investigations that have been made since the discovery of the copper oxide high-T_c ceramic superconductors,[1,2] the basic mechanism that leads to such high T_c has not been elucidated. However, some detail of the properties of superconductors have been determined.[3-9] Our interest will focus on the class of superconductors with the highest T_c around 90 K. The structure of these materials is fundamental to their understanding and there has been much experimental evidence relating their superconductivity properties to the one-dimensional Cu–O chains at the Cu(I) site (using the notation of Ref. 3). These chains occur because of the ordering of O vacancies in the Cu(I) plane. When these vacancies are most ordered the superconductivity appears to be most enhanced. The 90-K superconductors such as $YBa_2Cu_3O_{7-x}$ (1:2:3 phase) have an orthorhombic structure related to the perovskitelike structures.[3,9] The Cu–O chains are directed along the b direction introducing the main asymmetry to expand the b-lattice constant above that of the a direction. The c-lattice constant is very closely three times that of b.

The crystal structure determinations in the literature are done by diffraction techniques on powdered samples which measure an average structure.[3-5,8,9] There have been electron microscopy studies which show that even within a single-crystal grain the 1:2:3 superconductors are not homogeneous. On the 1000-Å scale, twinning occurs along the {110} family of planes which interchange the a and b directions in the a-b plane.[10-13] On the 100-Å scale, high-resolution electron microscopy studies indicate different domains which have been interpreted as regions of superstoichiometry and substoichiometry of O atoms about the value of seven.[14]

On the theoretical side, it has been suggested that for nonzero values of x the 1:2:3 phase may be a spinodal decomposition mixture of two different oxygen stoichiometry phases implying a microscopic variation of O composition within the sample.[15,16] What we show in this paper is that there exist regions within single-crystal grains where wide variations of $\Delta a/a$ occur over spatial dimensions of 1000 Å. Here $\Delta a/a = 2(b-a)/(a+b)$ is the measure of the deviation from tetragonality of the orthorhombic phase. We find the range of the variation to be between $0 \leq \Delta a/a \leq 4.0\%$, as compared to the 1.8% value found for $x=0$ by x-ray diffraction.[17]

EXPERIMENTAL PROCEDURES AND METHODOLOGY

Bulk samples were prepared by hand grinding with a mortar and pestle of the stoichiometric mixture of Y_2O_3, CuO, and BaO_2 powders which were dispersed in ethanol for complete mixing. The ethanol was driven off and the dried powder was die-pressed into pellets at 20000 psi. Heat treatment was performed in a Thermolyne Type 600 furnance. The sample was brought to 950 °C at a rate of 5 °C/min, held there one hour and cooled at 1 °C/min to room temperature. The samples were almost entirely single phase with a grain boundary phase of Cu_2O which constituted only 0.5% by volume of the microstructure. The samples were measured by four-probe resistivity measurement to have T_c values at 92 K with a transition width of about 2 K.

Thin foils for transmission electron microscopy (TEM) studies were prepared by hand on dry lapping disks to avoid contamination and reduce mechanically induced defects. It is now well established that ion milling induced defects into the microstructure.[12] Extreme precaution was taken both during the ion milling and during the TEM observations to reduce or eliminate damage to the samples. 40–50-μm thick disks were ion milled in a cold stage (liquid-nitrogen temperature) with a dual ion miller (GATAN 600) at an angle of 20–25° with a specimen current of 0.4 A using 6 kV in an argon gas. Samples

Appendix - III

"Structure and Formation of Twins in the Orthorhombic $YBa_2Cu_3O_{7-x}$"

M. Sarikaya, R. Kikuchi, and I. A. Aksay

Physica C, **152**, 161 (1988).

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STRUCTURE AND FORMATION OF TWINS IN THE ORTHORHOMBIC $YBa_2Cu_3O_{7-x}$

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Received 19 January 1988

Structure and formation of twins in the orthorhombic phase of $YBa_2Cu_3O_{7-x}$ samples, exhibiting bulk superconductivity at 90 K, are studied by transmission electron microscopy and modeling. Twinned domains with {110} twin boundaries form with separation λ which is dictated by energetic and geometrical requirements. Both of these requirements are related to $\Delta a=b-a$, where b and a are lattice parameters of the orthorhombic phase. Geometrical requirement leads to the estimate that the stable values of λ are integer multiples of $d=ab/(\sqrt{2}\Delta a)$. In some samples λ's are regular, in others not. Deviation of λ from theoretically expected stable separations is interpreted as due to local variation of oxygen ordering and/or local elastic strain. The twin boundary has a structure different from the bulk orthorhombic phase and electron micrographs suggest that it has a width of 30-50 Å. In bulk samples twinned domains can be present at different stages of the growth process. These substructural variations suggest that samples are at metastable equilibrium and are consistent with samples being in the superconducting glassy state.

1. Introduction

Recently, there is a growing interest in the possible effects of substructural variations, i.e., various lattice defects and inhomogeneities at nanometer range, to the superconducting properties of $YBa_2Cu_3O_{7-x}$ phase. For example, some latest measurements perfomed on high-T_c oxides on susceptibility and magnetization [1] and microwave absorption [2] have been interpreted to be due to these compounds being in a superconducting glassy state, as discussed by Deutscher and Müller [3]. Furthermore, it was suggested that single-crystal critical current measurements [3] are consistent with the disappearance of the glassy behavior, which may be caused by twins, at low temperatures [4]. In relation to twin formation in these compounds, it was found that there are local structural variations and that $\Delta a/a$, where $\Delta a=b-a$ (b and a being the lattice parameters of the orthorhombic phase) varies between zero and 4.0%, while the values measured from the bulk samples for a (3.826 Å) and b (3.891 Å) correspond to $\Delta a/a$ equal to 1.8%. The variation in $\Delta a/a$ was attributed to variations in the local oxygen content with samples being in a metastable condition and having various states of oxygen ordering. These structural variations at the 100 Å scale are consequently suggested to cause variations in the superconducting critical temperatures below and above 90 K, which corresponds to the value of 1.8% for $\Delta a/a$ of the bulk material and, therefore, substantiates the suggestion of superconducting glassy state [5].

The metastability of the samples around 90 K as suggested by Sarikaya and Stern [5] is consistent with the prediction that there may be a spinodal decomposition region as related to oxygen ordering in the phase diagram at low temperatures predicted by Khacharuryan et al. [6] although this has not been proven yet. It has been found that careful annealing treatments can produce a bulk superconducting phase with oxygen content $0.3<x<0.4$ in $YBa_2Cu_3O_{7-x}$ which exhibits T_c around 60 K [7]. Furthermore, it has been observed by high-resolution transmission electron microscopy that there are isolated domains at 100 Å scale with sharp boundaries which have been attributed to regions of super- and sub-stoichiometry of O atoms about the value of seven [8]. It appears that there is a need for more quantitative analysis of structural variations in orthorhombic samples, especially in conjunction with the formations of twins which are the dominant substructural features of both single and polycrystalline samples. In this paper we

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(North-Holland Physics Publishing Division)

Appendix - IV

"Identification of Intergranular Cu_2O in Polycrystalline $YBa_2Cu_3O_{7-x}$"

M. Sarikaya and B. L. Thiel

J. Am. Ceram. Soc. 71 (6), June, C305-C309 (1988)

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J. Am. Ceram. Soc., 71 [6] C-305-C-309 (1988)

Identification of Intergranular Cu_2O in Polycrystalline $YBa_2Cu_3O_{7-x}$ Superconductors

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The presence of intergranular Cu_2O has been identified in polycrystalline $YBa_2Cu_3O_{7-x}$ superconducting samples (T_c ~90 K) which are prepared by dry-powder processing techniques. Transmission electron microscopy was employed to determine the crystal structure of the phase while energy-dispersive analysis provided the composition. The intergranular Cu_2O, as indicated by XRD and shown by optical microscopy, is concentrated around pores and extends back along grain boundaries adjacent to these pores. Analysis performed on samples sintered in a furnace atmosphere at 950°C, with and without a post-oxygen anneal at 450°C, gave similar results.

THE observation of a high critical superconducting temperature in a $YBa_2Cu_3O_{7-x}$ compound (where x varies between 0 and 1, also called the 1:2:3 compound) has spurred research on the origin of superconductivity at high temperatures and on the production of this compound in useful forms. To date, no one has reliably produced polycrystalline samples of high-T_c superconducting oxides in the form of a "single phase," that is, with complete absence of an extraneous phase such as a bulk secondary phase or some grain-boundary phases (see papers in Refs. 1 and 2). The presence of extraneous phases in the 1:2:3 compound is important from both an academic and a technological point of view. First, most of the characterization studies which are directed toward the understanding of the origin of superconductivity in 1:2:3 compounds are performed by surface-sensitive techniques (such as Raman, XPS, AES, and EXAFS).[3] In these studies, the spectroscopic information is collected from the surfaces of fractured specimens; hence, a grain-boundary phase several nanometers thick could produce irrelevant spectroscopic results and cause erroneous interpretations.

Technologically, the identification of intergranular phase(s) is also important since the processing of chemically stable polycrystalline 1:2:3 samples is required for practical applications. Furthermore, polycrystalline samples with high current-carrying capacities and with sharp transition temperatures can only be achieved by the elimination of grain-boundary phase(s). In addition, it is thought that the mechanical properties of the samples are directly affected by the presence of "weak" phases at grain boundaries.[3]

Many research groups have already identified various grain-boundary phases that are mostly sensitive to and produced as a result of a particular processing technique applied in the production of ceramic monoliths. Some of these phases identified include CuO,[4-7] $BaCuO_2$,[4,5] Cu_2O,[8] $BaCO_3$,[9] and Y_2CuO_5.[10] When these phases were analyzed, conclusions were mostly drawn from qualitative spectroscopic results and from the stoichiometry achieved on the basis of the thermodynamical equilibria of the existing bulk phases in the microstructure. In this paper, the presence of the Cu_2O phase at the boundaries of 1:2:3 grains was confirmed by imaging, diffraction, and spectroscopic analysis in the transmission electron microscope in samples which were prepared under a furnace atmosphere with and without post-oxygen annealing.

EXPERIMENTAL PROCEDURE

Two samples were prepared for the analysis of the grain-boundary phase. The sample for the furnace atmosphere was prepared by grinding the stoichiometric mixture of Y_2O_3, CuO, and BaO_2 powders by hand with mortar and pestle and dispersing the powder in ethanol for complete mixing. The ethanol was driven off and the dried powders were die-pressed into pellets at

CONTRIBUTING EDITOR — T. O. MASON

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*Member, the American Ceramic Society.

Appendix - V

"Local Structural Variations and Formation of Twins in the Orthorhombic $YBa_2Cu_3O_{7-x}$"

M. Sarikaya, E. A. Stern, R. Kikuchi, and I. A. Aksay

Proc. MRS. Conf. Symp. on High Temperature Superconductors, D. W. Capone II, W. H. Butler, B. Batlogg, and C. W. Chu (Eds.), Spring (1988)

LOCAL STRUCTURAL VARIATIONS AND FORMATION OF TWINS IN THE ORTHORHOMBIC $YBa_2Cu_3O_{7-x}$

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INTRODUCTION

In addition to atomic configuration and electronic structure in the $YBa_2Cu_3O_{7-x}$ phase, micro- and nano-structures are fundamental to the understanding of high temperature superconductivity. Recently there has been a growing interest in the possible effects that substructural variations in these compounds may have on the superconducting properties. One prominent substructural feature is the formation of twins on {110} planes, parallel to [001], which result as a consequence of the need for the accommodation of stresses created during the tetragonal to orthorhombic transformation. [1-4] The lattice parameter change is due to the ordering of oxygen atoms along the [010] direction of the orthorhombic phase which causes elongation of $\vec{b}$ and contraction of $\vec{a}$ with respect to these directions in the tetragonal phase.

Some measurements made on the superconducting properties [5-6] indicate that these oxides may be in the superconducting glassy state which is attributed to inhomogeneities in the microstructure. [7] In the literature, the crystal structures are determined from bulk samples by techniques which measure average structures. [8-9] Even on single crystals, these measurements indicate some variations in structure. [10, 11] On the 100 Å scale, high resolution electron microscopy imaging and simulations reveal domains with super- and sub-stoichiometry of oxygen about the value of seven. [12] Experimental [13] and theoretical [14-15] phase diagram determinations indicate that several phases may be present in these samples. In conjunction with twin formation and their possible effects in creating inhomogeneities in the structure, [16] it was found that there are local structural variations from tetragonal to highly orthorhombic regions. [17] These variations may indicate that the samples are at a metastable state in agreement with phase diagram studies. In this extended abstract, we summarize our findings on these local structural variations and discuss the structure and formation of twins.

STRUCTURE OF THE TWIN BOUNDARY

Across a twin boundary, the lattices on two sides are mirror images. The projection of atomic configuration along [001] direction is shown in Fig. 1. In the idealized picture, Cu atoms are located on the twin boundary, and vacancy-vacancy and oxygen-oxygen pairs are created across the interface. In a more realistic picture, the position of Cu and O atoms and vacancies will shift or redistribute near the center of interface. Two unit cells are outlined in Fig. 1 by rectangles for the bulk orthorhombic region and the twin boundary region where two dimensional point group projection symmetries are given by 2mm and 1m respectively. Microdensitometer traces across the twin boundaries from electron micrographs indicate an average width of about 30-50 Å. Although claims have been made that superconductivity may be localized near twin boundaries [18], the above analysis suggests that twin boundaries may be acting as insulating layers because of lack of oxygen ordering

Appendix - VI

"Synthesis and Characterization of $YBa_2Cu_3O_{7-x}$ Superconductors"

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Advanced Ceramic Materials **2** (3B) Special Issue, 471-479 (1988).

SYNTHESIS AND CHARACTERIZATION OF $YBa_2Cu_3O_{7-x}$ SUPERCONDUCTORS

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ABSTRACT

Polycrystalline specimens of $YBa_2Cu_3O_{7-x}$ have been prepared by solid state reaction of the constituent metal oxides. The superconducting nature of the specimens has been characterized by magnetization, resistivity, and eddy current measurements. Onset temperatures for superconductivity exceed 88K. X-ray and electron diffraction results confirm the orthorhombic crystal structure. Characteristic features have been observed by laser Raman spectroscopy. Copper valency has been determined by thermogravimetric analysis, iodometric titration, and x-ray photoelectron spectroscopy. Additional evidence suggests that these materials are extremely sensitive to environmental conditions and handling.

INTRODUCTION

The discovery by Bednorz and Mueller [1] of superconductivity at about 30K in the La-Ba-Cu-O system initiated a resurgence in superconductivity research, which ultimately led to the discovery by Wu et al. [2] of superconducting transition temperatures exceeding liquid nitrogen temperature in the multiphase Y-Ba-Cu-O system. The superconducting phase was soon after identified as $YBa_2Cu_3O_{7-x}$ with an orthorhombic, oxygen deficient perovskite structure [3-5]. Since then, high-temperature superconductivity in other related Cu-based oxide systems have also been reported [6-8]. These events prompted the initiation of a collaborative research program at the Pacific Northwest Laboratory and University of Washington on the synthesis and characterization of the $YBa_2Cu_3O_{7-x}$ material. The broad scope of our activities in this area is reported in this paper.

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Appendix - VII

"Synthesis and Colloidal Processing of Superconducting $YBa_2Cu_3O_{7-x}$"

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in ***Proceedings of the Society for the Advancement of Materials and Process Engineering***, Seattle, June 16-17 (1988).

SYNTHESIS AND COLLOIDAL PROCESSING OF SUPERCONDUCTING $YBa_2Cu_3O_{7-x}$

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Abstract

Synthesis, processing and characterization of high temperature superconducting $YBa_2Cu_3O_{7-x}$ samples were performed. Ceramic precursors with varying degrees of homogeneity were prepared using microemulsions (at the nanometer level) and by organometallics precursors (molecular solutions). The advantage these routes offer over conventional oxide powders (micrometer scale) is control over microstructural and compositional homogeneities. The formation of extraneous phases was eliminated and the presence of grain boundary phases (such as Cu_2O) was brought to a minimum (0.5 vol %) through proper control of the microstructural development by colloidal processing and by careful densification techniques. The importance of the heating schedule was emphasized in terms of oxygen intake, particularly in conjunction with cooling rates.

1. INTRODUCTION

Recent advances in the discovery of high temperature superconducting ceramics[1-6] have focused research activity on the synthesis and fabrication of these materials into complex shapes. Various approaches are presently being used to process monolithic forms,[7], thin films,[8], and fibers.[9] As with the pioneering work in this area,[1-6] powder consolidation and sintering continues to be the most popular approach for fabricating monolithic shapes. Problems encountered in this approach center around (i) the elimination of porosity and (ii) the time required to complete the chemical reactions during the sintering. If chemical reactions cannot be completed during one sintering cycle, grinding and reconsolidation of the powder followed with a second and even a third sintering cycle must be used to form more homogeneous microstructures.[1-6]

Appendix - VIII

"Substructural Variations in $YBa_2Cu_3O_{7-x}$"

M. Sarikaya, R. Kikuchi, E. A. Stern, and I. A. Aksay

in ***Proceedings of Society for the Advancement of Materials and Process Engineering***, Seattle, June 16-17 (1988).

SUBSTRUCTURAL VARIATIONS IN $YBa_2Cu_3O_{7-x}$

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Abstract

Structural characterization of high temperature superconducting $YBa_2Cu_3O_{7-x}$ compounds have been made by transmission electron microscopy imaging and diffraction techniques. As a consequence of the tetragonal to orthorhombic transformation, twins form with {110} twin planes and with varying twin boundary spacings. Microdiffraction analysis at the 10 nm scale indicates local variations of $\Delta a / a$, where Δa is the difference between $\vec{a}$ and $\vec{b}$ directions of the orthorhombic phase. These studies indicate a significant spatial variation in the orthorhombicity in a single grain and, hence, nonhomogeneous distribution of regions with insulating character. The possible effects of these variations on the superconductivity will be discussed.

I. INTRODUCTION

In the quest for the explanation of high temperature conductivity in the perovskite-like oxides, notably in $YBa_2Cu_3O_{7-x}$, the effects of substructural features on the magnetic behavior of these oxides are gaining interest. This interest is further intensified by the fact that the electronic and magnetic properties measured in various laboratories yield differing and unexpected results, for example the frequent announcements of higher superconducting critical temperatures well above 90K, or even at room temperature or above. More reliable experiments do indicate an improvement of T_c which is associated with possible structural changes in the $YBa_2Cu_3O_{7-x}$ phase, related to oxygen ordering.[1] In addition, measurements

Appendix - IX

"Spinel Phase Formation During the 980°C Exothermic Reaction in the Kaolinite-to-Mullite Reaction Series"

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J. Am. Ceram. Soc., 70 [11] 837-42 (1987)

Spinel Phase Formation During the 980°C Exothermic Reaction in the Kaolinite-to-Mullite Reaction Series

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With the use of differential thermal analysis, X-ray diffraction, and transmission electron microscopic techniques, we showed that γ-Al_2O_3 type spinel phase is solely responsible for the 980°C exotherm in the kaolinite-to-mullite reaction series. Transmission electron microscopic characterization indicated that the spinel formation is preceded by a phase separation in the amorphous dehydroxylated kaolinite matrix. Chemical analysis of the spinel phase by energy dispersive X-ray spectroscopy revealed a nearly pure Al_2O_3 composition.

I. Introduction

THE kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$)-to-mullite ($3Al_2O_3 \cdot 2SiO_2$) reaction series has been the subject of various studies for nearly a century,[1] and still retains its active status as evidenced in most recent publications.[2-7] However, these studies have not resolved the questions concerning the issue of which phase formation is responsible for the exothermic reaction commonly observed at around 980°C.

The first step in the reaction series is the formation of an amorphous dehydration product identified as metakaolinite ($Al_2O_3 \cdot 2SiO_2$) after an endothermic reaction at ≈550°C. In the next step, the formation of crystalline product(s) from this amorphous intermediate phase results in a prominent exothermic reaction at ≈980°C. In most studies[3-17] dealing with this reaction series, the key issue has been the identification of the reaction product that results in this exothermic reaction.

The reaction mechanisms proposed for the 980°C exotherm can be classified into two general groups. In the first group, the common feature is the formation of a γ-Al_2O_3 type spinel phase and its association with the exothermic reaction.[3-5,8,9,13-17] The differences reported are mainly concerned with the composition of the spinel phase and whether the mullite phase (through a parallel reaction) also contributes to the exotherm.[3,14,16] In contrast to these spinel-based models, the second group proposes the formation of mullite without any spinel phase.[10-12] In view of the convincing evidence presented in recent studies,[3,14-16] the validity of this second mechanism can now be disputed.

With respect to the spinel-based mechanisms, however, two key problems still remain on the issues of (1) whether the spinel or the mullite phase is responsible for the exothermic reaction at 980°C and (2) how much silicon, if any, is present in the spinel phase. In this paper, we provide the answer to the first of these questions. We show that the spinel phase alone is responsible for the exothermic reaction. We also provide a partial solution to the second question, showing that this spinel contains <10 wt% silica and is probably very close to being pure alumina.

II. Experimental Procedure

Well-crystallized kaolinite was used in all our experiments. Based on chemical analysis and structural analysis by X-ray diffraction, 1.39 wt% TiO_2 was identified as the main impurity.

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*Now with Advanced Materials Division, Flow Industries, Inc., Kent, WA 98032

Georgia Kaolinite (KGa-1), Georgia Kaolin Co., Elizabeth, NJ

Appendix - X

"In-Situ Preparation of Silica Within Hydrogels"

B. Tarasevich, I. A. Aksay, and M. Sarikaya

in ***Atomic and Molecular Processing of Electronic and Ceramic Materials: Preparation, Characterization, and Properties***, Proceedings of the MRS Conference held August 30-September 2, 1987, University of Washington, Seattle, Washington, USA. Edited by I. A. Aksay, G. L. McVay, T. G. Stoebe, and J. F. Wager, (Materials Research Society, Pittsburgh, 1987) pp. 115-125.

IN SITU PRECIPITATION OF SILICA WITHIN HYDROGELS

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ABSTRACT

In situ precipitation of ceramic precursors within preformed polymer matrices is being investigated as a potential processing method for ceramic composites. In this study, silica is precipitated within polymer hydrogel matrices by diffusion and reaction of tetraethoxysilane (TEOS). The rate of precipitation depends on the hydrogel pore size which can be varied by varying the polymer concentration and the hydrogel pH. Silicate microstructures can be controlled by the hydrogel structures on one scale as well as the reaction chemistry (relative rates of hydrolysis and condensation) on a smaller scale. Matrices with as much as 65 v/o silica can be formed and dried without cracking.

INTRODUCTION

There is much interest in processing ceramic composite materials for electronic, magnetic, optical, and structural applications. Current trends are directed toward tailoring composite microstructures to have features and control over phase heterogeneities in the nanometer scale size range (0.1 to 0.001 microns).[1] It is difficult to control microstructures on such a fine scale, however, as conventional powder processing methods for structural materials often result in composites with large inhomogeneities and low densities.[2] Present additive and subtractive methods using vapor deposition and photolithography for electronic materials result in, at best, spatial resolutions of 0.5 microns. It is important to develop new processing methods to engineer structures on the molecular level in order to obtain higher degrees of microstructural control on the nanometer scale.

High ceramic contents, fine scale microstructures, and microstructural control are well known in mineral components of biological organisms.[3] In these systems, nanostructures are developed by the precipitation of calcium carbonate and calcium

Appendix - XI

"Characterization of Interfaces in Ceramic-Metal Composites by High Resolution Transmission Electron Microscopy"

M. Sarikaya, D. L. Milius, and I. A. Aksay

in ***Atomic and Molecular Processing of Electronic and Ceramic Materials: Preparation, Characterization, and Properties***, Proceedings of the MRS Conference held August 30-September 2, 1987, University of Washington, Seattle, Washington, USA. Edited by I. A. Aksay, G. L. McVay, T. G. Stoebe, and J. F. Wager, (Materials Research Society, Pittsburgh, 1987) pp. 167-173.

CHARACTERIZATION OF INTERFACES IN CERAMIC-METAL COMPOSITES BY HIGH RESOLUTION TRANSMISSION ELECTRON MICROSCOPY

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ABSTRACT

The properties of polycrystalline materials depend largely on the characteristics of the interfaces. This is especially true in the case of ceramic-metal composites where undesirable structures can form between the metal and ceramic phases. This paper presents high resolution electron microscopic information on various interfaces formed in B_4C-Al cermets to illustrate that the formation of atomically clean ceramic-metal interfaces results in superior mechanical properties.

BACKGROUND

Ceramics are strong and metals are tough; ceramic-metal composites (cermets) are designed to combine these properties into one system. Thermodynamically compatible classical systems, such as WC-Co and TiC-Ni, have been successfully developed over many decades and illustrate the principle benefits achieved from cermets.[1, 2] Recently, attempts have been made to process low density, thermodynamically incompatible cermet (e.g., B_4C-Al) systems.[3-5] Traditionally, failure in the processing of these systems was identified as insufficient wetting of the ceramic component by the metal or extensive chemical reactions that result in the depletion of the metal phase before the completion of sintering.[3, 4] Ceramic-metal interfaces are expected to play an important role in dictating the mechanical properties of cermets or metal matrix composites. At these boundaries, two phases with different chemistries and structures are joined together making up a heterophase boundary where one phase is mainly covalent/ionic and the other is metallic. Neither the chemistry of the bonding across the interface nor the physical structure of the interface are adequately known.

The methodology to overcoming the problem of processing a thermodynamically incompatible B_4C-Al cermet in terms of its wetting characteristics of the ceramic phase

Appendix - XII

"Characterization of Advanced Materials by High Resolution Transmission Electron Microscopy"

M. Sarikaya

in ***Atomic and Molecular Processing of Electronic and Ceramic Materials: Preparation, Characterization, and Properties***, Proceedings of the MRS Conference held August 30-September 2, 1987, University of Washington, Seattle, Washington, USA. Edited by I. A. Aksay, G. L. McVay, T. G. Stoebe, and J. F. Wager, (Materials Research Society, Pittsburgh, 1987) pp. 211-226.

CHARACTERIZATION OF ADVANCED MATERIALS BY HIGH RESOLUTION TRANSMISSION ELECTRON MICROSCOPY

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ABSTRACT

High resolution transmission electron microscopy (HREM) techniques provide invaluable information for structural and compositional characterization of advanced materials. These techniques involving imaging, diffraction, and spectroscopy can be used in one combined instrument at atomic resolution for practical applications. This paper outlines the important HREM techniques and presents examples to illustrate their applications in metal-matrix composites, superconducting materials, and ceramics.

INTRODUCTION

The properties of materials are structure sensitive, and phase assemblages and compositions are determined by processing which involve thermal treatments. It is essential to characterize microstructures quantitatively in terms of morphology, composition, and crystal structure of the component phases in order to understand the behavior of the samples of experimental and production materials, and to design new and improved materials. Since compositional and structural variations are present in small dimensions and low concentrations, complete characterization requires the use of several modes of analysis, i.e., imaging, diffraction, and spectroscopy, all at adequately high resolution levels. An analytical transmission electron microscope is a very powerful tool that fulfills these requirements.

The capabilities offered by a modern TEM is summarized schematically in Figure 1. Conventional TEM techniques (CTEM) involve bright field (BF) and dark field (DF) imaging, and selected area diffraction (SAD). These are used for morphological

Appendix - XIII

"Structural Control with Ultrafine Particles"

J. Liu, M. Sarikaya, and I. A. Aksay

in ***Proceedings of the 46th Annual Meeting of the Electron Microscopy Society of America***, edited by G. W. Bailey (San Francisco Press, San Francisco, 1988), pp. 716-717.

G. W. Bailey, Ed., *Proceedings of the 46th Annual Meeting of the Electron Microscopy Society of America*

STRUCTURAL CONTROL WITH ULTRAFINE PARTICLES

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Interest has increased in using ultrafine particles for structural control at the nanometer scale in making materials with improved properties.[1] This study illustrates the possibility of controlling the structural development of nanosized particle aggregates by using surfactants to monitor the surface characteristics of particles. Both conventional and high resolution TEM are used to characterize the morphology of packing and the interfacial structures of particles. Experiments are carried out using both gold and silica particles, and the microscopy is performed with a Philips EM 430T at 300 kV.

Stable colloidal gold suspensions are produced by reducing gold chloride with sodium citrate at 100°C which produces gold particles that are approximately spherical with diameters of about 15 nm.[2] High resolution images reveal that they are not single crystals, but contain fine substructures, including low angle grain boundaries and twins (Figs. 1 and 2). TEM samples are prepared by transferring a small amount of suspension onto a thin carbon film on TEM copper grid. Experiments are performed in a similar way with colloidal silica (DuPont Ludox colloidal silica) to illustrate ceramic processing.

It is desirable to pack particles closely to control pore size and distribution.[3] However, this is difficult with ultrafine particles mainly because of highly reactive surfaces which result in flocculated particles with ramified, non uniform and low density structures (Fig. 1a). The high resolution image in Fig. 1b reveals a considerable neck growth at the contact points of particles and lattice fringes which are continuous across some of the interfaces. These morphological features are indications that the particle surfaces are very active, and lead into the formation of low density packings.

Dense packing can be achieved when particle surfaces are coated with a layer of surfactant (Fig. 2a). In this case, surfactant has two functions: (1) to protect the active particle surfaces from forming strong bonding, and (2) to provide a low shearing strength between the particles allowing relaxation to take place.[3] A separation of about 2 nm, twice the size of surfactant, is maintained througnout the structure (Fig. 2b).

Similar studies are also carried out with ceramic and composite particles. Fig. 3 illustrates a tendency for high density packing in silica with the use of a surfactant. Packing with surfactants is directly applied to ceramic processing where green densities in excess of 65% have been readily achieved.[3] The use of surfactants in packing ultrafine ceramic-metal composite particles is also illustrated with a mixture of gold and silica particles (Fig. 4). As seen in this figure a uniform distribution of two types of particles is achieved without any phase segregation in a structure which is essentially a nanocomposite.[4]

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4. This work was jointly supported by AFOSR and DARPA under Grant No. AFOSR-87-0114.

Appendix - XIV

"Geometry and Formation of Twins in $YBa_2Cu_3O_{7-x}$"

M. Sarikaya, R. Kikuchi, and I. A. Aksay

in ***Proceedings of the 46th Annual Meeting of the Electron Microscopy Society of America,***
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G. W. Bailey, Ed., *Proceedings of the 46th Annual Meeting of the Electron Microscopy Society of America*

GEOMETRY AND FORMATION OF TWINS IN $YBa_2Cu_3O_{7-x}$

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Geometry and formation of twins in the orthorhombic $YBa_2Cu_3O_{7-x}$ phase are studied by transmission electron microscopy and modeling. Samples with bulk superconductivity at 90K are produced by heating the stoichiometric 1:2:3 proportions of metal oxides with a single heat treatment schedule involving a heating rate of 5°C/min to 950°C (1 hr) and 1°C/min cooling to room temperature. Powder mixtures were formed by colloidal mixing of oxide powders or by molecular mixing techniques.

Twinned domains with {110} twin boundaries, parallel to [001] of the orthorhombic lattice, usually form with both variants occurring in a single grain (Fig. 1). The twin boundary separation λ (Fig. 2) is dictated by energetic[1] and geometrical[2] requirements which are both related to $\Delta a = b - a$, where b and a are lattice parameters of the orthorhombic phase. Geometrical requirements lead to the estimate that the stable values of λ are integer values of the basic distance d. An estimate of d can be made by considering Figs. 3 and 4, where two parallel twin boundaries I/II and II/III eventually merge at a pointed tip (as in Fig. 2). Since orthorhombic regions I and III are coherent in a strain-free structure, the spacing cannot take continuously varying values. Referring to Fig. 3, the number of sections n which satisfies the required condition is given in $n\overline{EF} = \overline{AB}$ which, along the twin boundary, is the distance between two orthogonal Cu atoms in the orthorhombic lattice. Using this n, $d = n\overline{EC} = (ab)/(\sqrt{2}\Delta a)$. From the bulk values of $a = 3.826$ and $b = 3.891$ Å, Δa is 0.065, and, hence, d becomes 162 Å.

The measured values of λ of many twins (over 100) indicate that λ varies considerably as shown in the histogram charts in Fig. 5. The variation in d (hence in λ) can be related to microscopic variations in Δa due either to oxygen ordering or to the presence of strain in the lattice. Since the microscopic values of a and b are not available, Fig. 6 shows plots of d versus x (as in $YBa_2Cu_3O_{7-x}$) and versus $\Delta a/a$. As shown, both d and x change as bulk b and a and, hence, Δa varies. If this relation also holds microscopically, and based on the argument that T_c varies with oxygen ordering,[3,4] then it can be expected that variation in twin boundary spacing λ results in local variation in T_c. Both the local variations in $\Delta a/a$ measured by electron microdiffraction and anomalies observed in the superconducting properties of similar samples leading to superconducting glassy state[5] support this hypothesis.[6]

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6. This work was jointly sponsored by AFOSR and DARPA under Grant No. AFOSR-87-0114

Appendix - XV

"TEM Sample Preparation of Superconducting Oxides"

M. Sarikaya, B. L. Thiel, and J. P. Bradley

in ***Proceedings of the 46th Annual Meeting of the Electron Microscopy Society of America***, edited by G. W. Bailey (San Francisco Press, San Francisco, 1988), pp. 858-859.

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TEM SAMPLE PREPARATION OF SUPERCONDUCTING OXIDES

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The preparation and observation of high T_c superconducting TEM samples deserves a great deal of care since, as when characterizing any new material, mistreatment can bring about extrinsic features leading to erroneous conclusions. In dealing with materials such as these, where the structural origins of the electromagnetic properties are tantamount, this is especially true. The three most common practices of sample preparation are suspending crushed powder, ultramicrotomy, and ion-beam milling.[1] The illustrations will be made with $YBa_2Cu_3O_{7-x}$ samples.

The powder suspension technique requires grinding the material with a suitable mortar and pestle (e.g., agate) to a size which will allow electron transparency. Dispersing the particles in a suitable solvent such as water or acetone prevents aggregation. If the sample has large amounts of extraneous phases, the choice of medium is crucial as reactions will occur. Ni or Ti grids (50 to 75 mesh) with carbon films are used to fish out the suspended particles. The major drawback in this technique, in addition to mechanical deformation, is that even with careful grinding, only a small percentage of the particles are thin enough and highly tapered for electron transparency (Fig. 1). Furthermore, studying intergranular regions becomes nearly impossible.

In ultramicrotomy, fine particles, as prepared in the same manner as outlined above, are embedded in an epoxy matrix which has adequate conducting and stability properties under the electron beam. The resulting composite is then thin-sectioned with an ultramicrotome. A variety of inorganic particulate phases have been sectioned by this method.[2] The thin sections are briefly floated on water (or a glycol) prior to transfer from minuscus of liquid onto carbon coated grids. Ultramicrotomy provides uniformly thin (300-800 Å) crystals in multiple orientations (Fig. 2). Differential thinning on preferred crystallographic planes is not a problem here as it can be in ion etching.

Ion milling is the most involved procedure. Samples must first be hand thinned using stepped lapping discs down to 30 to 40 μm or by dimple grinder down to 10-20 μm. The samples are ion milled at 6 KV, 0.4 mA for five to ten hours at 22° tilt and then for another one to two hours at 18°. It is essential to use a cold stage (liquid nitrogen cooled) to avoid beam heating and the introduction of extrinsic defects (Fig. 3). Even so, ion milling time should be kept to a minimum. This method allows observation of large thin regions of the sample including grain boundaries which are more representative of the microstructure (Fig. 4).

Similar precautions must also be followed during TEM observations. A liquid nitrogen (or liquid helium) cooled specimen holder is preferred to reduce radiation damage due to beam heating. It is estimated that a beam with current of 20 microamps can produce a 500°C specimen temperature (Fig. 5). Higher voltages (300-400 kV) are desirable to reduce the radiation damage, however, too high a voltage (600-1000 kV) may introduce knock-on damage. By following the various procedures outlined here, it is possible to produce samples giving reliable information from a great variety of microstructural features.[3]

Appendix - XVI

"Characterization of Intergranular Cuprous Oxide in Polycrystalline $YBa_2Cu_3O_{7-x}$"

B. L. Thiel, C. Han, R. Kurosky, L. C. Hutter, I. A. Aksay, and M. Sarikaya

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CHARACTERIZATION OF INTERGRANULAR CUPROUS OXIDE IN POLYCRYSTALLINE $YBa_2Cu_3O_{7-x}$

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The identification of extraneous phases is important in understanding of high T_c superconducting oxides. The spectroscopic techniques commonly used in determining the origin of superconductivity (such as RAMAN, XPS, AES, and EXAFS) are surface-sensitive. Hence a grain boundary phase several nanometers thick could produce irrelevant spectroscopic results and cause erroneous conclusions.[1,2] The intergranular phases present a major technological consideration for practical applications. In this communication we report the identification of a Cu_2O grain boundary phase which forms during the sintering of $YBa_2Cu_3O_{7-x}$ (1 2:3 compound).

Samples are prepared using a mixture of Y_2O_3, CuO, and BaO_2 powders dispersed in ethanol for complete mixing. The pellets pressed at 20,000 psi are heated to 950°C at a rate of 5°C per min, held for 1 hr, and cooled at 1°C per min to room temperature. The samples show a T_c of 91K with a transition width of 2K. In order to prevent damage, a low temperature stage is used in milling to prepare thin foils which are then observed, using a liquid nitrogen holder, in a Philips 430T at 300 kV.

Fig. 1 presents spectra from the matrix (Fig. 1a) exhibiting Y, Ba, and Cu peaks in 1:2:3 ratios, and from the grain boundary phase (Fig. 1b), exhibiting a significant Cu peak and minute amounts of Ba and Y peaks in a 2:1 ratio. Microdiffraction patterns (Fig. 2a-c) taken from the same region (Fig. 2d) do not indicate the phase being pure Cu (fcc, a_o = 3.1468 Å), leaving two possibilities: cupric oxide, CuO (monoclinic, C2c, a_o = 4.653 Å, b_o = 3.410 Å, and c_o = 5.108 Å, β = 99°29'), and cuprite, Cu_2O (fcc, Pn3, a_o = 4.2696 Å). Analysis of the zone axis microdiffraction patterns shown in Fig. 2e indicates that patterns indeed correspond to Cu_2O.

The presence of Cu_2O in the microstructure is expected since phase diagrams at 950°C indicate a melt region centering around 1:2:3-CuO tie line.[3] The 1:2:3 phase has an oxygen deficient structure, and if there is insufficient oxygen over pressure, the equilibrium with 1:2:3 is set with the lower oxygen ratio Cu_2O state (Fig. 3) instead of CuO (Fig. 4).

Single phase polycrystalline is not easily produced.[1,2] Re-grinding and re-sintering have limited usefulness in incorporating Cu_2O into the 1:2:3 phase because of thermodynamical and kinetics requirements. Homogeneous mixing of powders, as well as rates of heating and, particularly, cooling, are most critical for successful densification. In the present system, by using the above heat treatment with or without post-oxygen annealing at 450°C, the amount of Cu_2O is reduced to 0.5 vol. %.[4,5]

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Appendix - XVII

"Aggregation and Packing of Nanosized Particles"

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Appendix C. Aggregation and Packing of Nanosized Particles

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Abstract

This work is a fundamental study on the interactions of nanometer-sized colloidal particles. Both direct imaging and scattering techniques are applied to monitor the structure of the aggregates. Transmission electron microscopy is used to study the agglomerate configuration and interfacial structures between the particles, and light scattering is used to yield in-situ information of the fractal structure of the aggregates. It is shown that the structure of the aggregates can be modified by the chemistry of the solution and the surface characteristics of the particles. It is found that the surfactants adsorbed onto the particles play a very important role on the restructuring of fractal aggregates. Ultrafine particles with reactive surfaces tend to form very strong agglomerates which are difficult to modify; but when some surfactants are present in the solution, compact structures can be obtained. A very dense packing of particles is possible when these surfactants act as good lubricants. The conclusions drawn from this

Appendix - XVIII

"Local Structural Variations in $YBa_2Cu_3O_{7-x}$ by Electron Microdiffraction"

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LOCAL STRUCTURAL VARIATIONS IN $YBa_2Cu_3O_{7-x}$ BY ELECTRON MICRODIFFRACTION

Mehmet Sarikaya

There is a growing interest in the effect of substructural features on the phase transformation characteristic, stability, and superconducting properties of $YBa_2Cu_3O_{7-x}$ which shows zero resistance at about 90 K.[1,2] Both in single crystal and polycrystal forms, twinning takes place where the twin boundary is {110} parallel to [001] orthorhombic direction.[3-5] Other planar defects such as stacking faults,[6] ninety-degree twins,[7] and nonstoichiometric oxygen domains[3] have also been observed but their real nature has so far not been determined.

The {110} twins form as a necessity to accommodate the transformation strains that develop as a result of the lattice parameter differences in the tetragonal and orthorhombic forms of $YBa_2Cu_3O_{7-x}$ phase.[4,5] It is known from the bulk measurements that due to oxygen ordering along [010] directions of the orthorhombic phase, b slightly expands and a contracts.[8] The largest difference between the bulk b and a corresponds to $\Delta a/a = 1.8\%$ and to T_c of 90K. The study presented in this paper describes the measurements of $\Delta a/a$ by microdiffraction in the TEM and relates the local variations in $\Delta a/a$ to oxygen ordering in the matrix. It further discusses the consequences of these structural vairations in terms of anomalies observed[3] in superconducting properties of these materials.

Experimental Procedures

Polycrystalline superconducting samples were prepared by a dry-powder processing technique in which Y_2O_3, BaO, and CuO were mixed in stoichiometric amounts to result in a 1:2:3 composition. After drying, the samples were heated (5 C/min) to 950 C, held there 1 h, and cooled (1 C/min) to room temperature. Samples exhibited T_c at 90 K with a transition width of about 2 K. The TEM samples were prepared by ion-beam (Ar) milling by use of liquid nitrogen holder to reduce damage to the structure. TEM studies were conducted with a Philips EM430T at 300 kV. The liquid nitrogen holder was used (with the measured sample temperature of 110 K) to eliminate the radiation damage. It has been found that low-temperature ion milling and TEM observation are essential to eliminate the beam damage in these materials.

The magnitudes of reciprocal lattice vectors a^* and b^* and the amount of splitting were measured directly on the microdiffraction patterns by a toolmaker's microscope with an accuracy of 2.5 um. A microdensitometer with a variable slit size was used to increase the resolution of the measurements, to distinguish the shape of the diffraction spots, and to delineate the existence of extra spots.

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Results and Discussion

The structures of the tetragonal and orthorhombic $YBa_2Cu_3O_{7-x}$ phase have been determined by neutron diffraction, which gives space groups of 4/mmm and Pmmm, respectively.[8] Although the orthorhombicity of the structure can readily be distinguished by the symmetry features developed within convergent beam patterns, slight changes in lattice parameter cannot be measured because of lack of necessary diffraction lines within the disks due to local changes in thickness, strain, and orientation. The convergent beam electron diffraction pattern given in Fig. 1 (taken from region P in Fig. 3) reveals a 2mm diffraction group in the [001] projection of the orthorhombic phase. For better sampling of the structure, microdiffraction is used, and all the variations in Δa are measured in [001] projection.

During a martensitic transformation, the amount of transformation strains dictates the degree of deformation in the product phase.[10] For example, if the transformation strains are accommodated by the formation of twins, as in high-carbon steels, then the twin spacing in the final phase is determined by the amount of strain (that is, by the amount of carbon) in the matrix. Analogously, higher strain (i.e., higher $\Delta a = b - a$) means narrower twin spacing in the orthorhombic $YBa_2Cu_3O_{7-x}$ on the basis of the analysis given below. In addition, bulk Δa is related to the oxygen content,[1,2] and hence varying values of twin spacing observed in the orthorhombic $YBa_2Cu_3O_{7-x}$ may be due to varying oxygen concentration, or ordering, across a single grain.[11]

The twin spacings can be determined from the energy[11] and the geometrical considerations.[5] In the former case, the minimization of total energy due to twins results in twin spacing λ, given by $\lambda = \sqrt{2}E_T/\mu(\Delta a/a)^{-1}$, where E_T is the twin boundary energy and μ is the shear modulus. Hence λ is inversely proportional to $(\Delta a/a)$.[11] The geometrical considerations require a basic distance $d = a/(\sqrt{2}\Delta a)$ for the twin spacing for the formation of strain-free matrix containing twins.[5] Here $\lambda = nd$, where n is an integer.

In order to check the inverse relationship between the twin spacing λ and $(\Delta a/a)$, micro-

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