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Imaging of Surfaces and Defects of Crystals

Progress Report

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Abstract

Application of the novel techniques developed in this laboratory and especially those resulting from our modifications of the scanning transmission electron microscope, have allowed considerable progress with studies on the oxidation of chromium and chromium-iron alloys and on the surface structure of magnesium oxide and related materials. Microdiffraction from regions 10-20Å in diameter has allowed clarification of the nature and epitaxial relationships of the very thin oxide layers formed when chromium films are heated. The new observations include the existence of a uniform thin layer of a previously undetected spinel-structure phase. Deductions have been made on the factors influencing growth of the oxide layers. Also it has been shown by use of STEM imaging, microdiffraction and ELS that the oxide film formed on thin chromium films in air at room temperature is amorphous and about 5Å thick.

The development of techniques for the study of surfaces by reflection diffraction imaging have allowed the visualization of growth steps only 2-5Å high on the surfaces of MgO smoke particles and a combination of ELS, imaging and diffraction methods has permitted the detection of excited surface states of the first few atomic layers on crystal surfaces

The observation of a new type of interference fringe in defocussed images of small crystals promises to provide extremely sensitive methods for study of the variations of potential at crystal surfaces. Remodelling of the medium-energy electron diffraction and microscopy system should allow greatly improved performance for surface studies.

1. General

The period since our previous report has, in some respects been one of consolidation in that work then reported as being in its initial stages has been carried to a satisfying state of completeness and techniques then suggested as possible have been proven and used to obtain interesting results. On the other hand we have, in this period, generated new ideas for techniques and methods which could greatly expand our capabilities for further attacks on the problems of the structures and defects of surfaces and the progress of surface reactions.

Post-doctoral research associate Fumio Watari, in collaboration with the Principal Investigator, has carried through the study of the oxidation of thin films of chromium to the stage that the modes of formation newly detected spinel oxide phase and the previously known rhombohedral oxide phase have been established in detail. The epitaxial relationships of these phases to the chromium have been determined. Deductions have been possible concerning the rate determining factors for the growth of oxide films. All this is entirely new information, made possible only by the use of the special microdiffraction techniques available with the unique array of attachments added to our scanning transmission electron microscopy (STEM) instrument.

The combination of STEM, microdiffraction and electron energy loss spectroscopy (ELS) has enabled Watari to gain important new insights on the subject of the protective oxide layer formed at room temperature on chromium and on chromium-iron alloys.

The use of the STEM instrument for exploitation of our previously explored ideas on the imaging of surfaces using reflection diffracted beams was envisaged in the previous report. Since then this idea has

been shown by the Principal Investigator to be not only feasible, but very useful in the study of the surface structures of small magnesium oxide and other crystals. From this work has sprung the further new concept of combining the imaging of surfaces by reflected diffracted beams with the studies of surface energy states and the microanalysis of surface layers by use of ELS in the STEM.

An incidental observation by the Principal Investigator of a new type of interference fringe effect in STEM images of surfaces has lead to a collaborative program of investigation with visiting scientist Peter S. Turner (on leave from Griffith University, Queensland, Australia for the period December 1979 to May 1980) in which the phenomenon was explored and established and possible applications as a very sensitive means for detecting small modifications of surface structure were proposed.

Student and research assistant Gary Hembree completed his Ph.D. program in the summer of 1979 with an excellent thesis on the theory and technique of medium energy electron diffraction and imaging and applications to the study of surface structure. He now holds a research fellowship with the National Bureau of Standards in Washington.

Student Cuneyt Elibol took over from Gary Hembree the task of remodeling the REMEDIE system for the study of surfaces using medium energy electrons and now has a much more powerful system ready for operation. Student Paul Fields has been engaged with theoretical problems basic to the understanding of much of our work on the imaging of crystals and their surfaces with inelastically scattered electrons.

The Principal Investigator has carried out most of the testing and exploration of new ideas on the STEM instrument and also the design, testing and standardizing the use of the new attachments added to it.

He has contributed to the interpretation of the diffraction and imaging data for all aspects of the program and has provided overall surveillance and guidance. He has spent at least 20 percent of his time on the project during the Academic Year plus one full month during the summer of 1979.

2. Further development of the STEM instrument

As outlined in our previous report, we have greatly enhanced the usefulness of our STEM instrument for studies of crystal surfaces and surface reactions by the addition of an optical system. This enables us to see and record microdiffraction patterns with an efficiency enhanced by a factor of 10^4 relative to the conventional means. For example, we have recorded microdiffraction patterns from specimen areas 10-15Å in diameter in 1/30 secs (one video-tape frame) whereas with the scanning recording system previously available a pattern of equivalent quality (signal-to-noise ratio) from 20-30Å diameter regions has commonly required 50-100 secs. Also we are able to obtain up to three different image signals (bright field, dark-field from diffraction spots, dark field from diffuse scattering etc) simultaneously and can also obtain images from areas of arbitrary shape and size chosen from the diffraction pattern.

These techniques, currently available only in this laboratory, have proved invaluable for the investigations of surface structure and reactions which form the basis for this program. The further developments of these techniques during the last year have allowed the full capabilities of the optical system to be exploited. In particular, the fluorescent screen, fibre optic plate and image intensifier which form the input to the system have been replaced by units specially built for us by Westinghouse using P47 phosphors in place of the standard P20.

This has reduced the time constant of the imaging system so that images can be produced in 10 secs or less instead of the previous (very inconvenient) minimum of 200 secs. It has also allowed us to couple the optical system to the fast digital data recording and processing system which has been built here with support from an NSF grant and which allows much more accurate and versatile data collection and image processing.

Circuitry has been completed and installed for all four photomultiplier detectors on the optical system, allowing the full versatility of the system to be explored. Images of good quality and of resolution 4-5Å have been obtained by its use in a manner much more convenient than by the use of the standard STEM methods. Fringe patterns corresponding to lattice plane spacings of 1.5Å or less have been seen and a wide variety of new coherent interference phenomena have been observed (see Appendix 2).

The reflection stub, useful for the reflection-diffraction imaging (as well as conventional SEM) of bulk crystal specimens, has been installed, tested and found capable of giving reflection images of crystal surfaces with a lateral resolution of about 20Å.

Experiments are now in hand on means whereby small bulk specimens (e.g. crystals having dimensions of the order of 1mm) may be held in the standard high resolution tilting stage of the STEM instrument so that surface reflection imaging from their surfaces may be achieved with the much better resolution of 5-10Å. Some success has been achieved by the use of folding grids to form a cage for the specimen.

An outstanding deficiency of our STEM system for applications to surface structure and surface reactions is the lack of any means for heating or cleaning the surfaces in situ. The manufacturers offer no heating cartridge. If they did it would presumably cost considerably

more than the \$23,000 now charged for the non-heating specimen tilting cartridge. The vacuum in the STEM instrument is sufficient (10^{-9} torr or better) to allow clean surfaces to be produced and maintained. We need means for heating the specimen to 1000°C or more and for ion etching of the surface. It is the provision of these capabilities in an ultra-high vacuum microscope which has allowed the group at the Tokyo Institute of Technology (Osakabe et al, 1980, see Appendix 3) to obtain extraordinary pictures of the surface structures and superlattice formation on clean silicon surfaces. We have therefore designed and initiated construction in the ASU Dept. of Physics workshops of

- (1) a heating tilting stage, using conductive heating, to provide temperatures up to about 800°C (and down to liquid nitrogen temperatures).
- (2) a device for the heating of either transmission or reflection specimens by means of a laser beam, directed from outside of the microscope.
- (3) means for ion etching of a specimen held in the microscope airlock.

3. Studies on the oxidation of chromium and chromium-iron alloys

A rather lengthy paper submitted for publication on this subject is included here as Appendix 1. The length, and the large amount of data presented, reflect the very thorough and complete nature of the study carried out largely by Fumio Watari. To this it is necessary to add just a few remarks to place the report in a proper perspective.

- (1) This is the only investigation (apart from other projects in this laboratory) which has used microdiffraction from areas of $20\text{\AA}$

diameter or less as a consistently applied research tool. Other people have demonstrated the possibility of obtaining patterns from 20-30Å areas but the inconvenience of the technique was such as to discourage its consistent use. It is the use of our optical system which has made the routine application of microdiffraction from regions 10-15Å diameter feasible.

(2) Studies on the initial stages of oxidation of chromium have been started by several research groups but dropped because the problems seemed too intractable (as indeed they are without the application of microdiffraction).

(3) It has been stated that a spinel-phase chromium oxide cannot exist because tetrahedral coordination of chromium with oxygen is unknown. This may well be so for bulk phases, but there is considerable evidence to suggest that special conditions (including charge imbalance) may operate to stabilize special structures in thin surface films 5-10Å thick.

Further work on chromium oxidation has been directed towards the elucidation of the structure of the very thin, presumably amorphous, oxide layers formed on chromium at room temperature and responsible for its corrosion-resistant properties.

Such layers are too thin to contribute appreciably to the diffraction patterns or images from the relatively thick (200Å or more) chromium films used for the high temperature oxidation studies reported in Appendix 1. Hence very thin chromium films were formed by vacuum evaporation. Comparison of the ratios of zero-loss to plasmon loss peaks in ELS spectra with those for thicker films of known thickness established that these films were about 30Å thick.

The oxygen K-loss and chromium L-loss peaks in the ELS spectrum were measured to determine quantitatively the relative amounts of oxygen and chromium present in the films as formed and after further oxidation by heating. In this way it has been established that the oxide layer on the thin chromium films is a surface layer about $5\text{\AA}$ thick when formed at room temperature.

Diffraction patterns, even from regions $10\text{--}15\text{\AA}$ diameter, showed only three very diffuse haloes, indicating a structure (of the Cr and the oxide) which is very close to being truly amorphous. The haloes correspond to spacings of about $3.5\text{\AA}$, $2.5\text{\AA}$ and $1.4\text{\AA}$. The outer two of these haloes could be given by near-amorphous chromium or by either a spinel or a rhombohedral oxide. The inner halo seems more likely to come from a spinel-type structure but this requires further analysis.

For comparison, similar thin films have been prepared from chromium-iron alloys and from pure iron, with results which are almost identical except for the apparent absence of the inner halo of the diffraction pattern.

Hence the further capabilities of the STEM instrument of allowing microanalysis by ELS, in conjunction with the microdiffraction and imaging, are proving valuable for the further stages in the studies in this area of great scientific and technological interest.

4. The Surface Structure of MgO Crystals

The method of imaging of surfaces using diffracted beams in transmission electron microscopes was explored in this laboratory previously (Nielsen and Cowley, 1975) and proved useful for the study of oxidation of surfaces of crystals. Use of this technique in a conventional TEM is severely limited by the poor vacuum which does not permit application to clean surfaces. As outlined in the Appendix 3 (invited paper for Presidential Symposium, Microbeam Analysis Society meeting, August 1980) we have

now applied this method in our HB-5 STEM instrument in which the vacuum is better by a factor of 10^4 or so. Since we do not as yet have specimen heating or cleaning facilities in the STEM, we have used specimens which are clean when prepared; in particular the small crystals of MgO smoke formed by burning magnesium in air. These crystals are usually no more than $1\mu\text{m}$ in dimensions. Even so images have been obtained by reflection from the crystal faces (fig. 2 of Appendix 3).

The detail of these images has been shown to be given mostly by surface steps and evidence has been found that the height of these steps is usually in the range of 2 to $10\text{\AA}$ in favorable cases.

Preliminary experiments have been made on the extension of these observations to include studies of MgO crystal faces on which small amounts of gold or nickel have been evaporated. Also NiO crystals, which can be induced to grow in the shape of small cubes in the presence of a silicon impurity, have been examined. The samples available have been found to have rather rough faces and better preparations are being sought.

An additional technique for the study of crystals surfaces has been evolved by combining the capabilities of the STEM for microanalysis by ELS with its capabilities for imaging and microdiffraction patterns. The diffraction patterns from the MgO crystal faces usually show doubled reflections, one component coming from the surface reflection and one coming from electrons transmitted through a crystal edge. These reflections may be separately selected and guided through the energy analyzer (Appendix 3).

For electron beams diffracted from flat crystal surfaces the penetration of the electrons into the surface may be no more than about $10\text{\AA}$. The ELS spectrum from the surface reflected beam should therefore be a very

sensitive probe of the energy loss processes of very thin surface layers. It is to be expected that energy losses in the range of 0 to 20eV could reveal surface states such as are known to exist from theoretical work and some other experimental techniques. Also variations of composition at the surface, due to surface segregation, surface reactions or impurities, could be detected by the examination of the inner shell energy loss peaks in the range of 100 to 1000eV. Other techniques for obtaining such information (Auger spectroscopy, ESCA etc) usually require the use of large specimens and have very limited spatial resolution. The ELS technique in the STEM can be applied to very small crystals and can in addition be combined with imaging having $10\text{\AA}$ spatial resolution and microdiffraction from areas of $10\text{\AA}$ diameter.

The results obtained so far on MgO (and NiO) show some indications of information on surface states. The ELS spectrum in figure 3 of Appendix 3 obtained from surface reflected electrons shows some enhancement of small peaks corresponding to energy losses of about 7 and 10eV, relative to the spectra from transmitted electrons.

In principle the emission of X-rays from atoms on crystal surfaces can be enhanced when the X-rays are generated by an incident beam diffracted from the crystal surface. Our attempts to demonstrate this effect have so far proved inconclusive. The samples used were MgO cubes on which layers of Ni a few $\text{\AA}$ thick had been evaporated. Images were obtained from the $\text{NiK}\alpha$ X-rays emitted and detected using the EDS attachment to the HB-5 STEM. The images showed clearly the concentration of Ni on the MgO surfaces with a noise-limited spatial resolution of about $20\text{\AA}$. However no clear indication of an enhancement of the X-ray emission was observed for the incident electron beam angles giving strong diffraction.

The exploration of these techniques of surface analysis is proceeding.

5. Interference Effects in Images of Small Crystals

Interference fringes of a type not previously reported have been observed using high resolution electron microscopy (both TEM and STEM) at the edges of images of cubic MgO crystals oriented so that one flat {100} face is almost parallel to the incident electron beam. Electrons which are incident at glancing angles on this face may be Bragg diffracted within the atomic planes close to the surface. They may emerge through the same face, in which case they are deviated by refraction at the surface. Alternatively they may emerge through the bottom face almost perpendicular to the beam direction and suffer no refraction bending. Thus two waves emerge from the crystal at slightly different angles. In out-of-focus images these waves will overlap and produce interference fringes. In the same way electrons which enter the crystal through the top face, almost perpendicular to the beam, may emerge through the parallel bottom face or else through the side face which is almost parallel to the beam. In the latter case the beam suffers a bending due to refraction. Again interference fringes are produced in out-of-focus images.

These refraction effects may occur either with or without Bragg reflection. Hence the interference fringes may be seen in both bright field and dark field images. They were first observed, with a periodicity of about $16\text{\AA}$, in STEM dark-field images and later have been examined in both bright field and dark field TEM.

The importance of these fringes may well arise from their dependence on the form of the change in potential at the crystal surface. For a simple discontinuity of potential, which represents the usual over-simplified picture, they will be sinusoidal. We anticipate that the form of the fringes may well reflect in a very sensitive way, the deviations from

this simple picture, including the effects of thin surface layers of foreign atoms.

In the course of this investigation an additional effect of interest was observed; namely the total internal reflection of electrons from a crystal surface. In a relatively thin crystal such as an MgO smoke particle of thickness about $1000\text{\AA}$, an electron beam may enter one crystal face and then approach another face at less than the critical angle of about 10^{-3} radians so that it is totally internally reflected, giving a striking enhancement of intensity at the exit face of the crystal. This has been clearly observed in both TEM and STEM.

The significance of this observation may well be that, as in the case of visible light, the total internal reflection is extremely sensitive to imperfections of the crystal surface or to the presence of any foreign matter (absorbed gases, deposited layers) on the crystal surface. Also the effect produces a channelling of electrons along the surface which may well stimulate X-ray emission or ELS losses from atoms which are concentrated near the surface. The thickness of the layer of channelled electrons along a flat surface is expected to be $5\text{-}10\text{\AA}$. Detailed calculations on these possibilities are planned.

This work on interference effects on MgO and other crystals was carried on in collaboration with Dr. Peter Turner, who has been extending his studies on the influence of chemical factors on surface structure while here. He has shown that the smoothness of MgO smoke crystal surfaces is strongly dependent on water vapour pressure (in the range of normal atmospheric humidities) and has investigated the form of the surface irregularities by use of high resolution TEM.

6. Remodelling of the REMEDIE System

Over the past few years the concept of the REMEDIE system (for Reflection Electron Microscopy and Electron Diffraction at Intermediate Energies) has been shown to be essentially sound. It has provided useful data on the diffraction and imaging of surfaces which is not accessible by other means as for example, in the studies on the oxidation of copper (Hembree, Cowley and Otooni, 1980). It has allowed evaluations of new imaging modes using reflected diffracted electrons of medium energy (1 to 15keV) and using diffraction channelling effects in SEM or near-grazing incidence.

This system has the important advantages over the use of the STEM or TEM systems for imaging and diffraction from surfaces in that (a) there is much less foreshortening of images (b) heating and surface treatment (e.g. ion bombardment) of surfaces is possible in high vacuum (10^{-9} torr) (c) the sensitivity of surface diffraction to surface morphology is less severe. However the system has suffered from: (1) a limited microscope resolution ($300\text{\AA}$), (2) lack of a convenient means for observing diffraction patterns (3) vacuum which is not sufficiently good to allow observation of very clean surfaces, (4) lack of versatility in the selection of diffraction spots for imaging and (5) the absence of an azimuthal rotation of the specimen.

All of these defects are being taken care of in a remodelled system which is almost ready for trial runs. The microscope resolution has been improved to about $100\text{\AA}$ by use of a rebuilt lens. The diffraction patterns will be observed by means of a channel-plate plus fluorescent screen assembly. The vacuum system has been rebuilt to eliminate gasket seals so that a pressure of better than 10^{-10} torr should be attainable. It will be possible to choose any diffraction spots to form a scanning image

by means of an optical system attached to the channel-plate, fluorescent screen display. A commercial specimen manipulator has been added to provide rotation about two axes as well as translations.

Use of this system will complement the work with the HB-5 STEM very nicely, providing sensitivity to surface structure comparable to that of LEED but with the important addition of imaging capabilities giving data on the non-uniformities of surface structures, the surface morphologies and the structures of highly localized features.

6. Publications based on the Grant Program

(1) Publications previously listed (last report) as in press but now published

(a) "The oxidation of copper studied by electron scattering techniques" G. G. Hembree, J. M. Cowley and M. A. Otooni, Oxidation of Metals 13, 331-351 (1979).

(b) "Electron channelling and microdiffraction from crystal surfaces" G. G. Hembree and J. M. Cowley in Scanning Electron Microscopy/1979 Vol. 1, Om Johari, Ed., SEM Inc., AMF O'Hare, Illinois. pp. 145-152.

(c) "Study of oxidation on the surface of chromium by STEM" Fumio Watari and J. M. Cowley, 37th Ann. Proc. Electron Microscopy Soc. Amer., G. W. Bailey Ed., Claitor's Publ. Co. Baton Rouge, LA. pp. 472-3.

(d) "A new technique for the production of thin single crystal films of copper" M. A. Otooni. J. Crystal Growth 46, 209-212 (1979).

(2) New and pending publications

(a) "The study of oxide formation on (001), (011), (111) and (113) surfaces of Cr thin films using STEM-Microdiffraction methods" Fumio Watari and J. M. Cowley. Submitted to Surface Science.

Removed

(b) "Optical processing of diffraction information in STEM" J. M. Cowley in Scanning Electron Microscopy/1980, Om Johari, Ed., SEM Inc., AMF O'Hare, Illinois. In press.

(c) "Surface imaging and analysis with reflection diffracted electrons" J. M. Cowley in Proc. 15th Annual Meeting Microbeam Analysis Soc. (1980) In press.

(d) "Reflection and refraction imaging of oxide surfaces in TEM and STEM" P. S. Turner and J. M. Cowley in Proc. 7th European Congress on Electron Microscopy (1980). In press.

(e) "Application of microdiffraction with a STEM instrument" J. M. Cowley and Fumio Watari, Proc. 7th European Congress on Electron Microscopy (1980). In press.

(f) "STEM and ELS observation of early oxide formation on the surface of Cr thin films" Fumio Watari and J. M. Cowley, Proc. 38th Annual Meeting Electron Microscopy Soc. Amer. (1980) In press.

(g) "STEM and CTEM observations of interference between Laue- and Bragg-diffracted electrons in images of polyhedral crystals" P. S. Turner and J. M. Cowley. In preparation.

(h) "Detection of protective oxide layers on Cr formed by exposure to air by STEM-ELS method" Fumio Watari. In preparation.