



**AFRL-RX-WP-TP-2008-4322**

**ELECTRON CHANNELING: A PROBLEM FOR X-RAY  
MICROANALYSIS IN MATERIALS SCIENCE (PREPRINT)**

F. Meisenkothen, R. Wheeler, M.D. Uchic, R.D. Kerns, and F.J. Scheltens

UES, Inc.

**MAY 2008**

**Approved for public release; distribution unlimited.**

*See additional restrictions described on inside pages*

**STINFO COPY**

**AIR FORCE RESEARCH LABORATORY  
MATERIALS AND MANUFACTURING DIRECTORATE  
WRIGHT-PATTERSON AIR FORCE BASE, OH 45433-7750  
AIR FORCE MATERIEL COMMAND  
UNITED STATES AIR FORCE**

| REPORT DOCUMENTATION PAGE                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |                             |                                            |                                    | Form Approved<br>OMB No. 0704-0188                                                                                                                                                                                                                               |                                                                                                                    |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------|--------------------------------------------|------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------|
| <p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. <b>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</b></p>                                                                                                                                                              |                             |                                            |                                    |                                                                                                                                                                                                                                                                  |                                                                                                                    |
| 1. REPORT DATE (DD-MM-YY)<br>May 2008                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                             | 2. REPORT TYPE<br>Journal Article Preprint |                                    | 3. DATES COVERED (From - To)                                                                                                                                                                                                                                     |                                                                                                                    |
| 4. TITLE AND SUBTITLE<br>ELECTRON CHANNELING: A PROBLEM FOR X-RAY MICROANALYSIS IN MATERIALS SCIENCE (PREPRINT)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                             |                                            |                                    | 5a. CONTRACT NUMBER<br>F33615-03-C-5206                                                                                                                                                                                                                          |                                                                                                                    |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                             |                                            |                                    | 5b. GRANT NUMBER                                                                                                                                                                                                                                                 |                                                                                                                    |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                             |                                            |                                    | 5c. PROGRAM ELEMENT NUMBER<br>62102F                                                                                                                                                                                                                             |                                                                                                                    |
| 6. AUTHOR(S)<br>F. Meisenkothen, R. Wheeler, R.D. Kerns, and F.J. Scheltens (UES, Inc.)<br>M.D. Uchic (AFRL/RXLMP)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                             |                                            |                                    | 5d. PROJECT NUMBER<br>4347                                                                                                                                                                                                                                       |                                                                                                                    |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                             |                                            |                                    | 5e. TASK NUMBER<br>13                                                                                                                                                                                                                                            |                                                                                                                    |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                             |                                            |                                    | 5f. WORK UNIT NUMBER<br>43471301                                                                                                                                                                                                                                 |                                                                                                                    |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)<br>UES, Inc.<br>4401 Dayton-Xenia Road<br>Dayton OH 45432-1894                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |                             |                                            |                                    | 8. PERFORMING ORGANIZATION REPORT NUMBER<br>Metals Branch (AFRL/RXLMP)<br>Metals, Ceramics, and NDE Division<br>Materials and Manufacturing Directorate<br>Wright-Patterson Air Force Base, OH 45433-7750<br>Air Force Materiel Command, United States Air Force |                                                                                                                    |
| 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)<br>Air Force Research Laboratory<br>Materials and Manufacturing Directorate<br>Wright-Patterson Air Force Base, OH 45433-7750<br>Air Force Materiel Command<br>United States Air Force                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                             |                                            |                                    | 10. SPONSORING/MONITORING AGENCY ACRONYM(S)<br>AFRL/RXLMP                                                                                                                                                                                                        |                                                                                                                    |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                             |                                            |                                    | 11. SPONSORING/MONITORING AGENCY REPORT NUMBER(S)<br>AFRL-RX-WP-TP-2008-4322                                                                                                                                                                                     |                                                                                                                    |
| 12. DISTRIBUTION/AVAILABILITY STATEMENT<br>Approved for public release; distribution unlimited.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                             |                                            |                                    |                                                                                                                                                                                                                                                                  |                                                                                                                    |
| 13. SUPPLEMENTARY NOTES<br>Journal article submitted to <i>Microscopy and Microanalysis</i> . PAO Case Number: WPAFB 08-3283; Clearance Date: 14 May 2008. The U.S. Government is joint author of this work and has the right to use, modify, reproduce, release, perform, display, or disclose the work. Paper contains color.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                             |                                            |                                    |                                                                                                                                                                                                                                                                  |                                                                                                                    |
| 14. ABSTRACT<br>Electron channeling effects, within the scanning electron microscope, are expected to create measurable signal intensity variations in all product signals that result from the scattering of the electron beam within a crystalline specimen. Of particular interest to the x-ray microanalyst, are any variations that occur within the characteristic x-ray signal that are not directly related to a specimen composition variation. Thus many researcher have worked to document the effect of crystallographic orientation on the local x-ray yield produced by a specimen. However, the vast majority of these studies were carried out in regards to thin foil specimens examine in transmission. Only a few x-ray microanalysis studies specifically addressed these effects in bulk specimen materials, and the analyses were generally carried out 35 to 40 years ago, at common scanning electron microscope, microanalysis overvoltage (>1.5). At these overvoltage levels, the anomalous transmission effect is generally very weak (typically <5% difference between intensity maxima and minima). |                             |                                            |                                    |                                                                                                                                                                                                                                                                  |                                                                                                                    |
| 15. SUBJECT TERMS<br>X-ray microanalysis, materials science, electron channeling, electron microscope, crystalline specimen, quantitative electron probe microanalysis, overvoltage                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                             |                                            |                                    |                                                                                                                                                                                                                                                                  |                                                                                                                    |
| 16. SECURITY CLASSIFICATION OF:                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                             |                                            | 17. LIMITATION OF ABSTRACT:<br>SAR | 18. NUMBER OF PAGES<br>22                                                                                                                                                                                                                                        | 19a. NAME OF RESPONSIBLE PERSON (Monitor)<br>David W. Mahaffey<br>19b. TELEPHONE NUMBER (Include Area Code)<br>N/A |
| a. REPORT<br>Unclassified                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | b. ABSTRACT<br>Unclassified | c. THIS PAGE<br>Unclassified               |                                    |                                                                                                                                                                                                                                                                  |                                                                                                                    |

# **Electron Channeling: A Problem for X-ray MicroAnalysis in Materials Science**

F. Meisenkothen<sup>1</sup>, R. Wheeler<sup>1</sup>, M.D. Uchic<sup>2</sup>, R.D. Kerns<sup>1</sup>, F.J. Scheltens<sup>1</sup>

<sup>1</sup>Air Force Research Laboratory | A.F.R.L., Microstructural Characterization Facility | M.C.F., operated by UES, Inc., at Wright Patterson Air Force Base | WPAFB, OH 45433.

<sup>2</sup>Air Force Research Laboratory | A.F.R.L., Materials and Manufacturing Directorate, Metals Development Group, Wright Patterson Air Force Base | WPAFB, OH 45433.

## **Abstract**

Electron channeling effects, within the scanning electron microscope, are expected to create measurable signal intensity variations in all product signals that result from the scattering of the electron beam within a crystalline specimen. Of particular interest to the x-ray microanalyst, are any variations that occur within the characteristic x-ray signal that are not directly related to a specimen composition variation. Thus many researchers have worked to document the effect of crystallographic orientation on the local x-ray yield produced by a specimen. However, the vast majority of these studies were carried out in regards to thin foil specimens examined in transmission. Only a few x-ray microanalysis studies specifically addressed these effects in bulk specimen materials, and the analyses were generally carried out 35-40 years ago, at common scanning electron microscope, microanalysis overvoltage ( $>1.5$ ). At these overvoltage levels, the anomalous transmission effect is generally very weak (typically  $<5\%$  difference between intensity maxima and minima). As a result, the effect of electron channeling on the generated characteristic x-ray signal intensity has traditionally been overlooked in the field of quantitative electron probe microanalysis (EPMA). The present work will demonstrate that electron channeling can produce a significant effect in the x-ray microanalysis of engineering structural materials, especially at low overvoltage.

## **Introduction**

P. P. Ewald was the first to predict the anomalous transmission of X-rays through crystalline materials. In December of 1917, while discussing his theories of diffraction, Ewald made the observation that “in the case of absorption of X-rays . . . under some circumstances diffracted X-rays will not suffer any weakening in an absorbing crystal [1].” The statement was describing what would come to be known as the “Borrmann Effect”, after G. Borrmann provided empirical data, in 1941, to support the conclusion that the x-ray absorption coefficient is greatly reduced at the Bragg condition [1,2]. By 1949, von Laue was able to use the dynamical theory of X-ray diffraction to show that the magnitude of Borrmann’s results were what was to be expected [1,2,3]. Campbell, working around the same time as Laue, provided additional empirical evidence to show that the X-ray penetration of a crystal is greatly increased at the Bragg condition [4], and that imperfections in the crystal structure could reduce the magnitude of the effect.

In his 1951 thesis, Castaing laid the foundation for the field of electron probe, quantitative, X-ray microanalysis. As an aside in this work, Castaing reported the observation of X-ray Kossel patterns that were created by the X-rays that were excited within his specimen as a result of the electron beam interaction with a crystal [5]. However, he noted that under his instrument operating conditions ( $< 40$  keV), there was a low probability of observing such phenomena during quantitative X-ray microanalysis. Further, the error in measured concentration that is expected to result from this effect would be about 1% and is therefore considered negligible [5].

In 1962, P. B. Hirsch, et al noted that fast electrons traveling through thin metal foils demonstrated an anomalous transmission effect that is similar to that observed in X-ray diffraction [6]. Hirsch, et al then calculated that the production efficiency of X-rays in thin film specimens also should be dependent upon the direction of the incident beam relative to the crystallographic orientation of the specimen – i.e. the X-ray production rate is a function of the deviation from the exact Bragg condition. The team further speculated that the orientation dependence of the X-ray production efficiency might also be present in bulk specimens. Based on the theory of Hirsch, et al, P. Duncumb realized that regions within the specimen that exhibit enhanced inelastic scattering, should generate increased characteristic X-ray signals [7]. Duncumb demonstrated that the X-ray emission did indeed vary across bend contours found in single crystal, gold films that were imaged in a scanning transmission electron microscope [7]. His experiments were the first to show such a dependence, thereby validating the theory of Hirsch, et al. The work also demonstrated an increased electron backscatter yield coincident with the specimen regions that produced the increased X-ray emission. In 1966, C.R. Hall conducted an experimental study into the variation of X-ray production with orientation [8]. The study showed that the magnitude of the anomalous x-ray production is significant in thin foil specimens like those found in transmission electron microscopy. However, the difference or variation between the maximum and minimum X-ray intensities was shown to decrease as specimen thickness increases. Therefore, Hall concluded that the impact of the orientation dependence of the x-ray generation process on x-ray microanalysis of homogeneous, crystalline, bulk specimens would be small. He added the caveat, that for some special circumstances there may be a significant effect (e.g. non-homogeneous, crystalline specimens having small near surface precipitates that are favorably oriented with respect to the electron beam). Hall's theory assumed that different Bloch waves could be treated independently in creating x-rays. The work of Cherns and Howie showed that the behavior of anomalous X-ray production would be more correctly modeled by considering interference effects between Bloch waves [9]. By considering these interference effects, the x-ray production behavior of very thin crystals could be more accurately represented. As in Hall's experiments [8], Cherns and Howie found that the anomalous x-ray production effect could generate up to a 350% increase in the x-rays generated by a thin crystal. Further, it was concluded that the anomalous x-ray production effect is more pronounced in axial channeling situations than in planar channeling situations.

In 1967, a new phenomenon was being reported by D. G. Coates - electron channeling patterns had been observed in low magnification images of large single crystal specimens within the scanning electron microscope [10]. Coates saw a possible connection between his electron channeling patterns and the aforementioned works of Hirsch, et al and Duncumb [6,7,10]. He

realized that the contrast that he was observing in the electron backscatter signal was likely due to the dependence of the electron backscatter yield on the orientation deviation from exact Bragg conditions. Coates even went so far as to speculate that similar channeling patterns would be produced by the X-ray emission signal of his specimen. However, he did not demonstrate the X-ray effect. The work of Booker, et al, later in the same year, showed that the effect that Coates had observed could be explained in terms of the works of Hirsch and of Duncumb mentioned earlier [6,7,11]. Like Duncumb, Booker and Shaw had studied bend contours in gold foils – another phenomenon that is related to the anomalous transmission of electrons and inelastic scattering [12]. The contrast of the bend contours present in these thin foils was found to decrease as the foil thickness increased [11]. So, it came as quite a surprise that these anomalous absorption effects that Coates had observed were visible at all in a bulk specimen [11]. By comparing their results with those of Hall [8], Booker, et al were able to surmise that though the variation in the x-ray signal that could be expected from Coates' electron channeling patterns would be less than 3 %, it would be measurable [11]. Neither the work of Coates nor Booker, et al produced a quantitative dynamical theory to explain the contrast band that they had observed in their electron channeling patterns. In 1970, this task of modeling the dynamical diffraction contrast was undertaken by Hirsch and Humphreys [13], and in 1972 Spencer followed with the theoretical work to describe the crystallographic orientation dependence of x-ray production in bulk crystalline specimens [14]. Spencer reports that for medium atomic weight materials, and typical microanalysis overvoltages, the orientation dependence of the x-ray signal should be weak - on the order of 1 %. However, the magnitude of the variation of the x-ray signal (i.e. the signal difference between maxima and minima) should increase significantly as the overvoltage decreases. In this work, Spencer provided no empirical evidence to support his calculations, other than to cite the work of Bramman and Yates [15]. Bramman and Yates reported a 1.5 % variation in x-ray intensity with changes in crystallographic orientation for a typical microanalysis overvoltage (i.e. 25 keV), on nickel, uranium dioxide, and 316 stainless steel specimens.

The effects of crystallographic orientation dependence on characteristic x-ray generation are not included within the current generation of quantitative x-ray microanalysis matrix correction schemes (e.g. Z.A.F. and Phi Rho Z). As mentioned earlier, the reason for this is that the channeling effect is usually small at normal microanalysis overvoltages. Also, the presence of the near a surface plastic deformation layer that is produced by the conventional specimen preparation processes (e.g. grinding and polishing) will act to further reduce the observed variation within the x-ray signal. However with the advent of low damage surface preparation procedures (e.g. large area ion milling by Focused Ion Beam or Precision Etching and Coating Systems), it becomes more likely that the analyst will encounter specimens that have very little residual surface deformation to mask the effects of electron channeling. Ironically, the problem may be further compounded by the tremendous improvements in x-ray detection systems, that have made it possible to collect hundreds of thousands (or even millions) of counts per second during x-ray mapping runs. Typically, the weak nature of the orientation dependent component of the x-ray signal means that it can only be reliably observed if large numbers of x-ray counts are collected. Alternatively, the overall signal can be reduced by lowering the analysis overvoltage, and thereby making the orientation dependent portion of the signal more pronounced (total signal decreases, but the measured signal variation increases). The present work provides additional experimental evidence in support of Spencer's claim that the variation in the x-ray signal of bulk,

crystalline specimens will become more pronounced in low overvoltage analyses [14]. However, it is precisely at these low overvoltages where the analyst can expect the best spatial resolution in x-ray images and other microanalyses.

## Theory

Electrons can be thought of as having both a wave nature and a particle nature. While the particle model is intuitively easy to understand, it does not adequately describe the behavior of the electrons within a crystalline material for the electron energies that are typical of the scanning electron microscope (SEM). For electron energies in the kilo-electron volt range, the electron interaction with the crystal is best described by the wave nature of the electron - the incident beam electron flux through the crystal can be described mathematically by the superposition of a number of standing waves, called Bloch waves. A brief, qualitative discussion of the theory behind electron channeling patterns will follow. Readers interested in a more rigorous explanation of the electron channeling (anomalous transmission) phenomenon and Bloch waves are referred to the following sources [6,8, 9,13,14, 17 - 20].

Each Bloch wave is a plane wave that travels through the crystal, has the same periodicity as the crystal lattice, and has a wavefront parallel to the crystal surface. The square of the amplitude of a Bloch wave, at any point, represents the probability of finding an electron at that location. For crystals oriented near to the Bragg condition, such that only one diffracted beam is excited (2-beam condition), the current traveling through the specimen can be represented by the interaction of two Bloch waves – the Type I and the Type II. The Bloch wave designations, and the sign conventions used in designating the deviation from the exact Bragg condition, change from author to author. Here, the Type I Bloch wave will have its intensity maxima aligned with the atom centers that make up the lattice planes. Therefore, the electrons described principally by the Type I Bloch wave, have a high probability of being found in close proximity to the atomic nuclei, and therefore have the highest probability of being scattered. The electrons described principally by the Type II Bloch wave are weakly scattered, because these electrons have a high probability of being found far from the atomic nuclei. The beam intensity is a constant. Therefore, the beam electrons have to be distributed between the two Bloch waves. The distribution of the beam electrons is determined by the deviation from the Bragg condition (the deviation from the Bragg condition is commonly referred to as the excitation error, or the deviation parameter,  $s$ ). When the angle of incidence of the electron beam is equivalent to the Bragg angle (i.e.  $\theta$ ) for a particular set of lattice planes, each type of Bloch wave receives an equal share of beam electrons. When the incident beam is aligned at an angle that is slightly less than the Bragg angle, the Type I Bloch wave is preferentially excited (i.e. more electrons are distributed to the Type I Bloch wave). For an incident beam angle that is slightly larger than the Bragg angle, the electron distribution will favor the Type II Bloch wave, and thus anomalous transmission.

We can now explain the contrast that is observed in the electron channeling pattern. Imagine that a 2-dimensional, single crystal is positioned under an electron beam, such that a single set of lattice planes (Bragg planes) are oriented perpendicular to the crystal surface. The electron beam is initially parallel to the Bragg planes, and normal to the crystal surface (Figure 1). As the beam

is rastered to the left or to the right of the starting position, the angle that the beam makes with the lattice planes will change, thereby altering the deviation parameter. For example, as the beam moves left of the starting position, the angle between the beam and the Bragg planes will initially be less than the Bragg angle. As the beam continues to move to the left, the angle between the beam and the Bragg planes will continue to increase, passing through the exact Bragg condition along the way. An electron backscatter image (BEI) collected as the beam rasters left and right across the crystal surface, will show an intensity variation that is directly related to the deviation parameter. The resulting intensity profile is an electron channeling pattern. The profile will be brightest in the center, as the beam scans through those deviations from the Bragg angle that favor electron distributions to Bloch wave I (orientations favoring scattering). The profile will darken as the beam moves through the exact Bragg condition. The rest of the profile, where the beam orientation favors electron distributions to Bloch wave II, will appear dark (orientations favoring anomalous transmission). The width of the bright band on the profile will be equal to twice the Bragg angle for the diffracting planes (Bragg planes). A similar effect should be detectable for all electron generated signals coming from the specimen, including the characteristic x-ray signal. In practice, channeling patterns, generated in the fashion that was just described, are quite large. The analyst will only be able to observe the pattern on large single crystals imaged at low magnifications. However, while the channeling pattern will not be visible in small individual crystals, these individual grains will exhibit contrast variations that are orientation dependent as a result of the channeling effect. The grain contrast will produce measurable signal variations at SEM magnifications. Instrument parameters and specimen surface condition also play a significant role determining the magnitude of the signal variations that are observed as a result of the channeling effects (e.g. beam current, beam energy, beam divergence, energy filtering, etc.) [19-23].

Thus the concern for x-ray microanalysis is that there is an assumption that the constituent elemental concentrations, within a specimen, are directly proportional to the measured intensity ratio (k-value). Any changes in the measured intensity ratio that result from electron channeling effects will produce an error of equal magnitude in the measured concentration ratio. The measured concentration being calculated from,

$$\frac{C_i}{C_o} = [Z_i A_i F_i] \frac{I_i}{I_o}$$

where C is the weight fraction of the element of interest, Z is the atomic number correction, A is the absorption correction, F is the fluorescence correction, and I is the measured intensity for the element of interest. The subscript “i” denotes the element of interest in the unknown. The subscript “o” denotes the element of interest in the known standard [24]. Further, the expressions used to define the Z, A, and F correction terms are functions of alloy composition. If the measured intensity ratio is incorrect, the ZAF correction will be incorrect as well.

## Experimental Procedures

Three different bulk specimen materials were selected for the present study: GaAs, TaC, and CP-Ni. The GaAs specimen was a [100] oriented single crystal, measuring about 3.3mm x 4.5 mm.

The GaAs crystal was used in the “as purchased” condition. Nothing is known about the surface preparation procedure except that the surface finish that was provided makes the material suitable for use as a substrate for thin film depositions. The GaAs used for the analysis, was a piece that had fractured from a larger wafer. Since GaAs is a semiconductor, no electrically conductive surface coating was required. The piece was mounted to a SEM pin stub using conductive silver paint. TaC is an electrically conductive, structural, ceramic material. The TaC specimen was polycrystalline, and contained a distribution of grains sizes that spanned a dimensional range from tens of microns to a couple of millimeters. The TaC specimen was mounted in an electrically conductive, hot compression metallographic mounting material and then polished through a schedule of successively finer diamond abrasives. The commercially pure (CP), Ni specimen was from the 200 series, and as such, contains small amounts of Cu, Fe, and Mn. The CP-Ni specimen was cut from a larger, rolled plate. The CP-Ni specimen was mounted in non-conductive, diallyl phthalate, glass filled, metallographic, hot compression mounting material, and then ground / polished through successively finer grit abrasives until reaching a 0.05 micron finish in colloidal silica. The colloidal silica is a basic attack polish, and possesses a pH of about 9. The non-conductive nature of the diallyl phthalate mount meant that the mounting material had to be coated with a conductive silver paint prior to analysis. The polycrystalline nature of the TaC and CP-Ni specimens made it possible to sample many different crystallographic orientations within a given SEM field of view, while evaluating the effect on x-ray production.

A field emission, Leica 360 SEM, with a Voyager EDS system was used for SEM electron backscatter imaging and x-ray imaging of the GaAs specimen (@15kV). The same instrument was used to conduct incremental tilting experiments on the CP-Ni specimen (@15kV) to verify electron channeling related, grain contrast was present within the specimen. A FEI, field emission, Sirion SEM was used for imaging the TaC specimen under similar incremental stage tilts (@10kV). The OIM data for the CP-Ni specimen was collected on a FEI, field emission, XL-30 SEM instrument coupled with an EDAX/TSL OIM analysis system (@20kV). In all cases, a 4-Pi image acquisition system was used to provide total control over digital image resolution, and dwell time. The x-ray microanalysis work on the TaC and CP-Ni specimens was done on a Cameca SX-100, EPMA instrument with five WDS spectrometers. Given that the human eye is sensitive to slight variations in contrast, x-ray imaging (a.k.a. mapping) of crystalline specimens becomes an efficient way to demonstrate the orientation dependence of the characteristic x-ray signal. The technique collects many measurements (pixels) within each specimen grain, and then displays the pixels as an image that contains contrast variations detectable to the eye. The raw x-ray counts (not the normalized greyscale level), for the group of pixels associated with a given grain, can then be averaged, to quantify the intensity variations that result from the orientation dependence of the characteristic x-ray signal. In an effort to improve the signal to noise ratio in the x-ray images, it was desirable to sum the signals from multiple spectrometers, thereby increasing the total number of x-ray counts per image pixel, for a given acquisition time. The low overvoltage, x-ray images that will be presented for the  $\text{TaL}\alpha$  (@10.5keV) and the  $\text{NiK}\alpha$  (@9keV) both represent the sum simultaneous signal acquired by three WDS spectrometers - WDS 1 (LIF), WDS 3 (LLIF), and WDS 5 (LLIF)). The standard overvoltage, x-ray image acquired for  $\text{NiK}\alpha$  (@15keV) is the sum of two spectrometers – WDS 3 (LLIF) and WDS 5 (LLIF). Electron backscatter images were collected in the EPMA instrument, just prior to the acquisition of the x-ray images, so that the electron channeling contrast observed in the electron image could be

directly related to the x-ray image intensities. In each analysis, the grains exhibiting the greatest electron backscatter contrast were the ones that were selected for x-ray analysis. All of the x-ray images presented in this work display raw x-ray counts, with the exception of GaAs x-ray images, which are background subtracted images.

## Results and Discussion

### GaAs (Overvoltage $\approx 12.5$ , @ 15 keV)

Reminiscent of the work done by Coates in 1967 [10], a [100] oriented, bulk, single crystal of GaAs, measuring about 3 mm x 4 mm, was used for imaging an electron channeling pattern. The resulting electron backscatter image, shown in Figure 1A, was collected with 15 keV electrons. A low magnification (around 30 x) was required to capture this image; therefore, the image in Figure 1A displays the full extents of the crystal – the image boundaries are essentially the crystal boundaries. Figure 1B shows the x-ray image that results from taking the sum total of nearly all of the x-ray photons that were collected by the EDS detector. Note that the contrast in the x-ray image follows the contrast that was displayed by the electron backscatter image. Due to the energy resolution of the EDS detector ( $\approx 140$  eV MnK $\alpha$ ), the GaL $\alpha$  peak will lie on overlap with the AsL $\alpha$  peak. As a result, the integrated intensity under the combined GaAsL $\alpha$  peak was used for x-ray mapping to quantify the orientation dependent effects on the characteristic x-ray signal. Figure 1C is a background subtracted, GaAsL $\alpha$  x-ray image. Two red circles have been drawn on Figure 1C to indicate the two analysis regions used for quantification of the orientation effect. A x-ray line profile through these two regions, and into the neighboring regions of the image, reveals a 3% difference in the number of characteristic x-ray counts detected. The effect is significant (the overvoltage in this case is about 12.5), for a technique that is often cited as having an accuracy of 1-2 %. It is important to note that the measured regions in no way establish an upper bound to the types of orientation dependent variations that we might expect for medium atomic weight materials analyzed at a high overvoltage. It is entirely possible that a larger variation can be observed for another pair of orientations.

### TaC (Overvoltage = 1.06, @ 10.5 keV)

The TaC material is a very hard, structural ceramic that is used in the manufacture of rocket nozzles. Even though the specimen was prepared by conventional metallographic preparations – i.e. no attack polish or electropolish – it is expected that little or no plastic deformation will remain resident near the specimen surface to foul the electron channeling process. Further, since the material is electrically conductive, no conductive surface coating need be applied prior to electron beam imaging or EPMA. As such, the polycrystalline material should display electron channeling related grain contrast. Figure 3 shows a series of images that were acquired for the TaC, bulk, polycrystalline specimen. An electron backscatter imaging experiment was performed at incremental specimen tilt angles to verify that the observed grain contrast was in fact due to electron channeling effects. The specimen was imaged as the stage was tilted to 20 degrees, at 5 degree increments (@10 kV). Figures 3A – Figure 3C show a sampling of the images that were collected. Note that the grain contrast changes significantly as the specimen is tilted, thereby indicating that the contrast is based on electron channeling. The TaL $\alpha$  x-ray image that corre-

sponds to Figure 3A (0 degrees tilt) is shown in Figure 3D. The lightest grain (white grain on the right side of the image) and the darkest grain (black twin near the bottom, center of the image) were selected as regions of interest for the analysis. The average x-ray count within the darkest grain was 385 counts, while the lightest grain yielded an average of 450 counts – an incredible 17 % difference in characteristic x-ray yield ! The average x-ray count difference between the grains having the mid-grey intensities and the lightest (or darkest) grains is about 7%. Since the exact crystallographic orientations were not known during this experiment, it is again conceivable that even larger variations might be encountered for favorably oriented crystals.

The problem becomes even more interesting if we consider that the analyst gets his best spatial resolution at low overvoltage. The lower the overvoltage, the more closely the characteristic x-ray signal is generated to the electron beam and to the specimen surface. So, the qualitative or quantitative analysis of dimensionally small phases requires low overvoltage work. Now back to the problem with TaC. TaC can have small amounts of TaC<sub>2</sub> distributed throughout the bulk. TaC<sub>2</sub> has a Ta weight fraction of 0.88, while the Ta weight fraction in TaC is 0.94. At low overvoltage, one has to wonder if it would even be possible for EPMA to be able to distinguish between these two phases, given that the TaC, TaL $\alpha$  x-ray signal can easily vary by 8-17 %, as a result of electron channeling differences between different crystal orientations.

#### CP-Ni (Overvoltage = 1.8, @ 15 keV & Overvoltage = 1.08, @ 9keV)

The results from the CP-Ni specimen are provided in Figure 4-Figure 6. As with the TaC specimen, tilting experiments show that the grain contrast will vary significantly with slight changes in specimen orientation, as would be expected for channeling induced contrast (Figure 4A and Figure 4B). Figure 4C shows the results from the analysis that was carried out under the conventional EPMA overvoltage condition (overvoltage of 1.8, @ 15keV). The NiK $\alpha$  x-ray map, shown in Figure 4C, contains a 2.5 % difference in the characteristic x-ray count between the lightest and the darkest grain. The average number of x-ray counts for the darkest grain is 4163, while the lightest grain had an average of 4270 counts. Hall had suggested that the x-ray production from any one grain will differ from the average production rate, if the grain in question is oriented such that it lies within twice the Bragg angle of the diffracting planes [8]. For a face centered cubic material, assuming that only the {111}, {200}, and {220} Bragg planes produce a noticeable effect, there is a 25 % chance that a crystal will be oriented in such a way so as to affect the x-ray production rate [8]. Booker, et al had calculated that  $2\theta_B$  commonly lies in the range of 1 - 5 degrees for 20 keV electrons [11]. The CP-Ni analysis provided here, was done at 15 kV. Therefore, to estimate the angular range within which we can expect grains to differ from the average x-ray production rate, we can calculate  $\theta_B$  for the {111} ( $\theta_B = 1.4$  degrees), {200} ( $\theta_B = 1.6$  degrees), and {220} ( $\theta_B = 2.3$  degrees) Ni planes. Thus as a very rough guideline, we would expect that the lightest and the darkest grains observed within the field of view of should fall  $\pm \theta_B$  from the respective set of diffracting planes. The OIM data, provided in Figure 4D, shows four grains with the greatest difference in x-ray production rate relative to the surrounding average grains. Grain 1 is oriented along the [-2 -23 24] direction, which lies within 1 degree of the (111) plane. Grain 2 is oriented along the [4 1 6] direction, which lies on the (-2 -4 2) plane. Grain 3 is oriented along the [-2 0 7] direction, which lies on the (0 2 0) plane. Grain 4 is oriented along the [17 -17 19] direction, which lies on the (2 2 0) plane. With the possible exception

of Grain 2, the four grains fall within the  $2\theta$  range that Hall had specified. Though these orientation effects are weak at this overvoltage, it is<sup>B</sup> clear that there is a measurable channeling effect on the characteristic x-ray generation process, and the grain contrast is also clearly visible in the electron backscatter image. It is worth mentioning that the authors have observed results of the same magnitude in Cu and Inconel 600, though the data has been omitted here ( $< 5\%$  variation in x-ray production, @ 15 keV).

Since the electron wavelength is a function of the accelerating voltage used, the same grains that had exhibited a significant x-ray production rate difference at 15 kV, will generally not be the grains that exhibit the greatest x-ray production rate difference at 9 kV. A quick search of the CP-Ni specimen yielded the analysis region shown in Figure 5. Here a low overvoltage of 1.08 was used (9 keV). The average number of NiK $\alpha$  x-ray counts for the darkest grain is 1361 counts, while the lightest grain yielded an average of 1715 counts – a 26 % greater yield ! Note how the effect of the low overvoltage is to lower the overall x-ray signal, while the increasing the magnitude of the signal variation. Micro-analyses run at this overvoltage would certainly not yield the correct results that should indicate that this sample is nearly pure Ni. Repositioning the specimen stage to a random location shows that there are significant contrast variations to be found in just about any part of the specimen surface (Figure 6). Here the signal variation between lightest and darkest grains is about 20 %. In both Figure 5 and Figure 6, the mid-grey grains have count rates that are about half way between the reported extrema – i.e. for Figure 5 and Figure 6, the lightest (and darkest) grains show a count rate difference of about 10-12 % from the mid-greys.

The combined results from the GaAs, TaC, and CP-Ni indicate that the characteristic x-ray production rate will vary with crystallographic orientation and analysis overvoltage. The magnitude of the observed variations are expected to be small, on the order of a few percent, for analyses done at normal and high overvoltage. However, the orientation effect on the x-ray production process becomes greater for low overvoltage analyses, where variations of up to 25 % have been observed. No special specimen surface preparations are necessary to observe this effect, so long as the Bilby layer (region of residual plastically deformed material near the specimen surface) thickness is minimized. The specimen preparation procedures used here are conventional metallographic preparation procedures that are commonly employed in metallographic laboratories for the preparation of structural materials specimens.

## Conclusions

- 1) Electron channeling can have a significant impact on the accuracy of qualitative and quantitative x-ray microanalyses by EPMA.
- 2) Electron channeling effects can produce direct quantitative x-ray microanalysis analysis errors on the order of 1-25 %.
- 3) The magnitude of the observed variation in the x-ray production process increases as the overvoltage of the analysis decreases.
- 4) The present study has been concerned with common aerospace structural materials; however, there is no reason to expect that the results should be any different for other crystalline materials.

- 5) Electron channeling effects on x-ray microanalysis will be encountered more frequently as low damage, surface preparation procedures and more efficient x-ray detection systems become commonplace.

### **Special Thanks**

Thanks go to Mahalingam Krishnamurthy of AFRL/RXPSO, the teaching staff of the Lehigh Microscopy School "Quantitative X-ray Microanalysis" course and the members of the East Coast Cameca EPMA Users Group, for helpful discussions on the technical issues involved in this work. Gratitude is due to Robert Lewis and Kevin Shiveley of the AFRL/MCF metallography facility for the specimen preparations that made this work possible. The authors would also like to thank Jared Shank, of UES, Inc., for his help in editing this paper.

### **Bibliography**

- [1] Ewald, P. P., "A Review of My Paper on Crystal Optics 1912 to 1968," *Acta Crystallographica*, A35, 1979, p.p. 1-9.
- [2] Hirsch, P. B., "The Reflexion and Transmission of X-rays in Perfect Absorbing Crystals," *Acta Crystallographica*, 5, 1952, pp. 176-181.
- [3] von Laue, M., "Die Absorption der Rontgenstrahlen in Kristallen im Interferenzfall," *Acta Crystallographica*, 2, 1949, pp. 106-113.
- [4] Campbell, H. N., "X-ray Absorption in a Crystal Set at the Bragg Angle," *Journal of Applied Physics*, 22, 1951, pp. 1139-1142.
- [5] Castaing, R., "Application of Electron Probes to Local Chemical and Crystallographic Analyses," Thesis, University of Paris, 1951, pp. 103-109.
- [6] Hirsch, P. B., Howie, A., and Whelan, M. J., "On the Production of X-rays in Thin Metal Foils," *Philosophical Magazine*, 7, 1962, pp.2095-2100.
- [7] Duncumb, P., "Enhanced X-ray Emission from Extinction Contours in a Single-Crystal Gold Film," *Philosophical Magazine*, 7, 1962, pp.2102-2105.
- [8] Hall, C. R., "On the Production of Characteristic X-rays in Thin Metal Crystals," *Proceedings of the Royal Society of London*, A295, 1966, pp. 140-163.
- [9] Cherns, D. and Howie, A., "Characteristic X-ray Production in Thin Films," *Zeitschrift fur Naturforschung*, A28, 1973, pp. 565-571.
- [10] Coates, D. G., "Kikuchi-like Reflection Patterns Obtained with the Scanning Electron Microscope," *Philosophical Magazine*, 16, 1967, pp. 1179-1184.

- [11] Booker, G. R., Shaw, A. M. B., Whelan, M. J., Hirsch, P. B., “Some Comments on the Interpretation of the ‘Kikuchi-like Reflection Patterns’ observed by Scanning Electron Microscopy,” *Philosophical Magazine*, 16, 1967, pp. 1185-1191.
- [12] Howie, A., “Inelastic Scattering of Electrons and Anomalous Absorption Effects,” *Proceedings from the Fifth International Congress for Electron Microscopy*; Philadelphia, 1962, Academic Press, NY, pp. AA-9.
- [13] Hirsch, P. B. and Humphreys, C. J., “The Dynamical Theory of Scanning Electron Microscope Channelling Patterns,” *Scanning Electron Microscopy*; *Proceedings of the Third Annual Scanning Electron Microscope Symposium*, Chicago, 1970, IIT Research Institute, IL, pp. 451-455.
- [14] Spencer, J. P., “The Crystallographic Orientation Dependence of X-ray Production from Bulk Crystals: A Theoretical Assessment,” *Electron Microscopy*; *Proceedings of the Fifth European Congress on Electron Microscopy*, University of Manchester, 1972, The Institute of Physics, London, pp. 478-479.
- [15] Bramman, J. I. And Yates, G., “Specimen Surface Preparation Errors in Quantitative Electron-Probe Microanalysis,” *Journal of Applied Crystallography*, 2, 1969, pp. 18-24.
- [16] Miyake, S., Hayakawa, K., Miida, R., “XXXXXXXXXX,” *Acta Crystallographica*, A24, 1968, pp. 182-???
- [17] Humphreys, C. J., “The Scattering of Fast Electrons by Crystals,” *Reports on Progress in Physics*, 42, 1979, pp. 122-1826-1887.
- [18] Hashimoto, H., Howie, A., Whelan, M. J., “Anomalous Electron Absorption Effects in Metal Foils: Theory and Comparison with Experiment,” *Proceedings of the Royal Society*, 269, 1962, pp. 80-103.
- [19] Joy, D. C., Newbury, D. E., Davidson, D. L., “Electron Channeling Patterns in the Scanning Electron Microscope,” *Journal of Applied Physics*, Vol. 53, 8, August 1982, pp. R81-R122.
- [20] Newbury, D. E., Joy, D. C., Echlin, P., Fiori, C. E., Goldstein, J.I, *Advanced Scanning Electron Microscopy and X-ray Microanalysis*, Plenum Press, NY, 1986, pp. 87-142.
- [21] Morin, P., Pitaval, M., Besnard, D., Fontaine, G., “Electron Channelling Imaging in Scanning Electron Microscopy,” *Philosophical Magazine*, A40, 1979, pp. 511-524.
- [22] Schulson, E. M. and van Essen, C. G., “Optimum Conditions for Generating Channelling Patterns in the Scanning Electron Microscope,” *Journal of Scientific Instruments (Journal of Physics)*, 2, 1969, pp. 247-251.

[23] Joy, D. C., Booker, G. R., “ United States Patent # 3786271, 1974.

[24] Goldstein, J. I., Newbury, D. E., Echlin, P., Joy, D. C., Romig, A. D., Lyman, C. E., Fiori, C., Lifshin, E., Scanning Electron Microscopy and X-Ray Microanalysis, Plenum Press, NY, 1992, pp. 401.

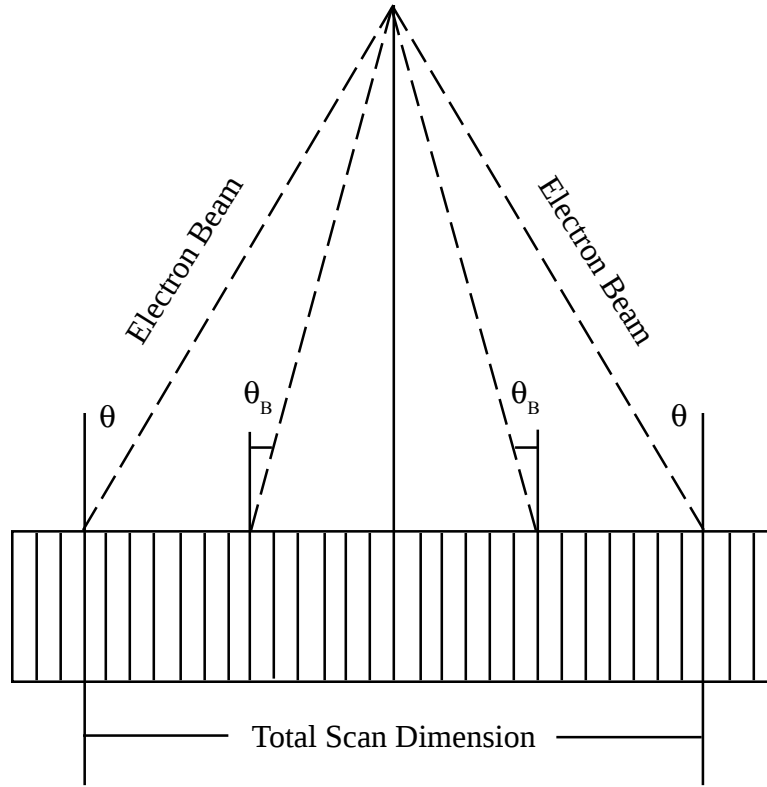


Figure 1: A 2-dimensional crystal positioned under a rastering electron beam (similar to [19]). The electron backscatter signal intensity changes as a function of the angular deviation from the exact Bragg condition. The backscatter intensity is bright for  $\theta < \theta_B$ . The intensity will darken as the beam scans through  $\theta = \theta_B$ , passing through a minimum when  $\theta$  is just slightly larger than  $\theta_B$ . The backscatter intensity will remain dark for  $\theta > \theta_B$ , but not as dark as the minimum.

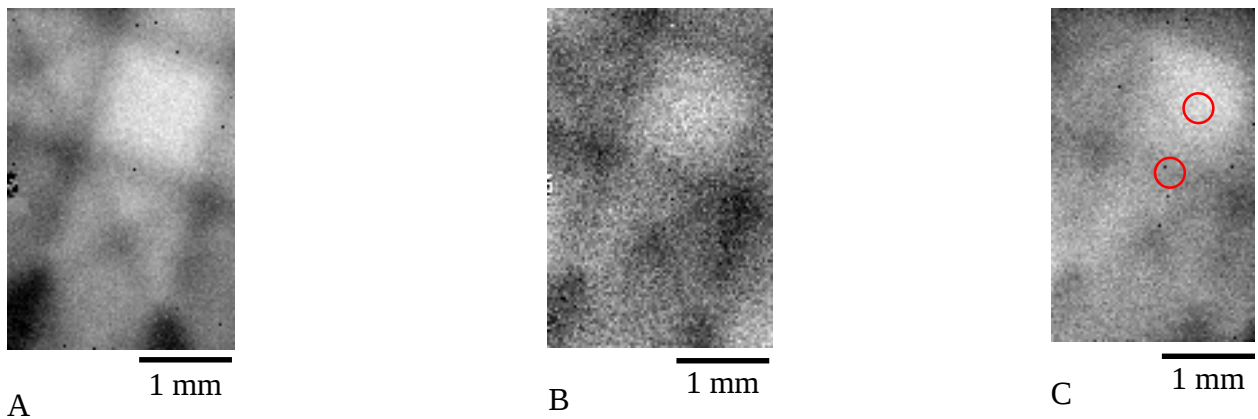


Figure 2: GaAs, [100] oriented single crystal, electron channeling pattern, 15 keV. A) Backscatter electron image. B) EDS x-ray image (total x-rays entering the detector). C) EDS x-ray image (total GaL $\alpha$  and AsL $\alpha$  entering the detector). The difference in total L $\alpha$  x-ray yield between the two circled regions indicated on the channeling pattern is about 3 % (overvoltage is approximately 12.5 @ 15 keV).

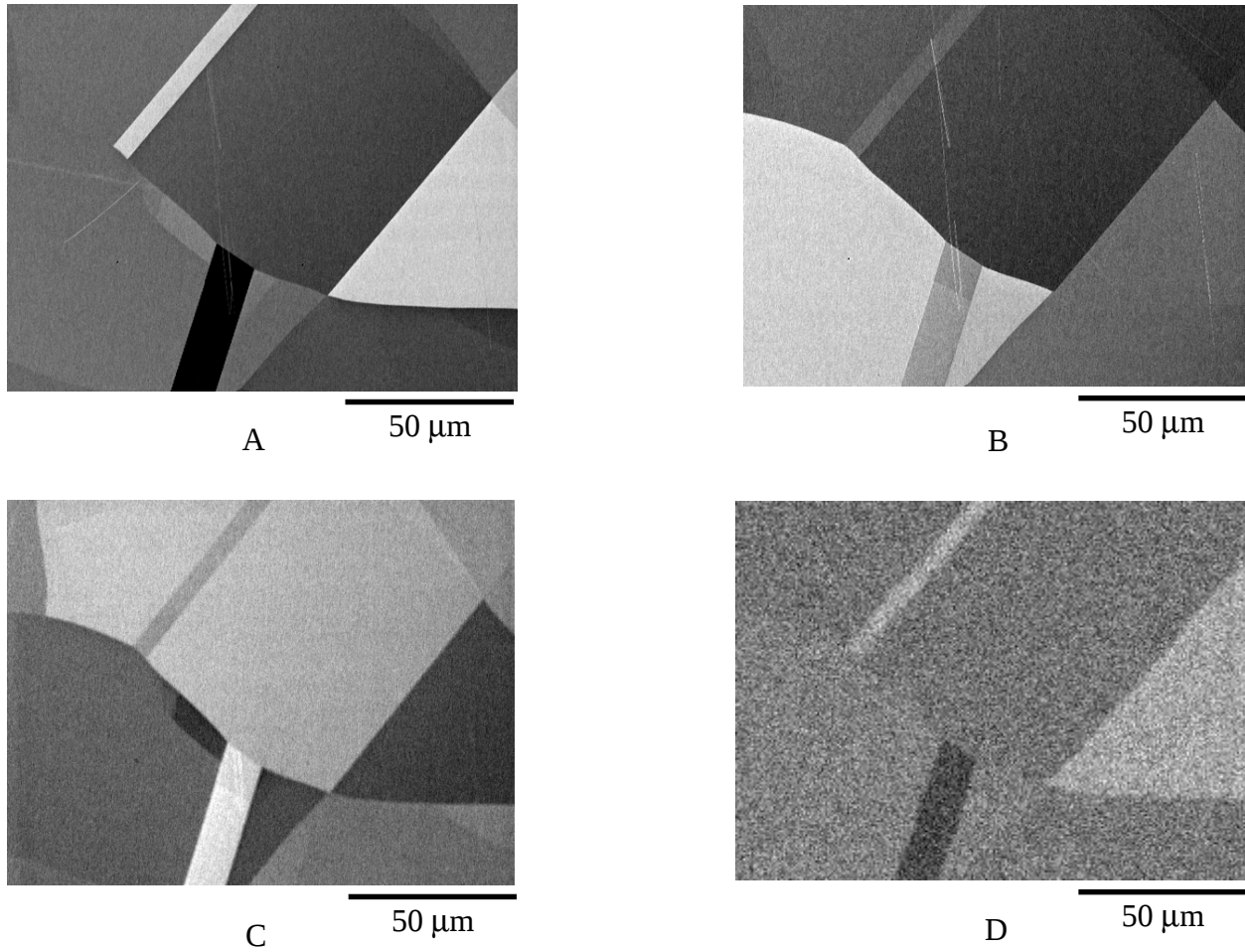


Figure 3: TaC, polished by conventional metallographic stepped grinding / polishing schedule. Overvoltage is 1.06 (10.5 keV). A) Backscatter electron image @ 0 deg. tilt. B) Backscatter image @ 5 deg. tilt. The significant contrast changes that result from small specimen inclination changes is one way to verify that the contrast results from electron channeling effects. C) Backscatter image @ 20 deg. tilt. D) TaL $\alpha$  WDS x-ray image, corresponding to image A. The average number of x-ray counts for the darkest contrast is 385 while the lightest contrast regions yielded an average of 450 counts (17 % greater x-ray yield).

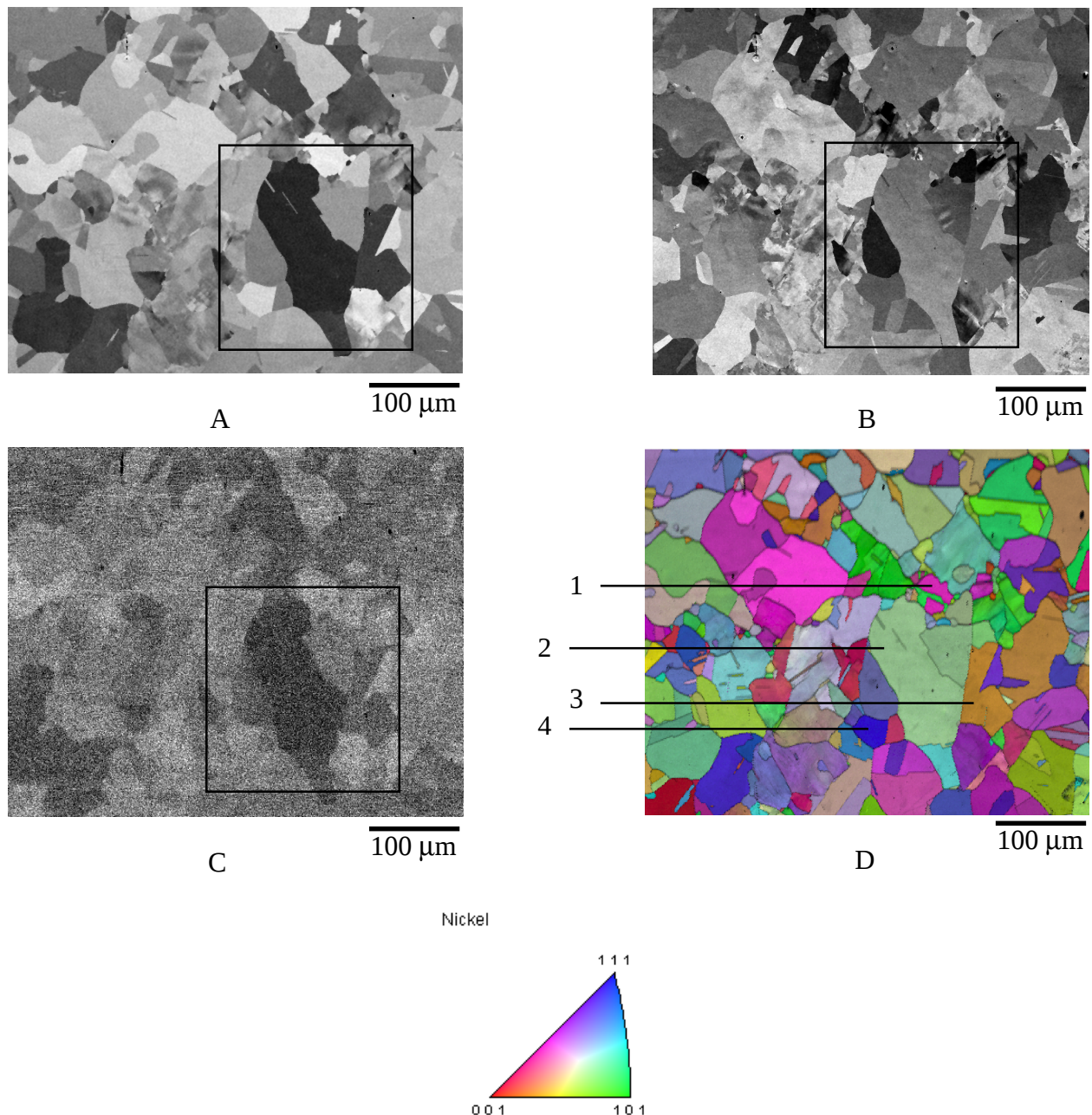
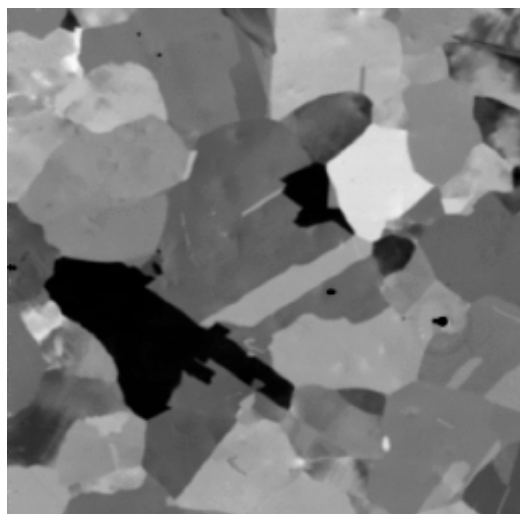
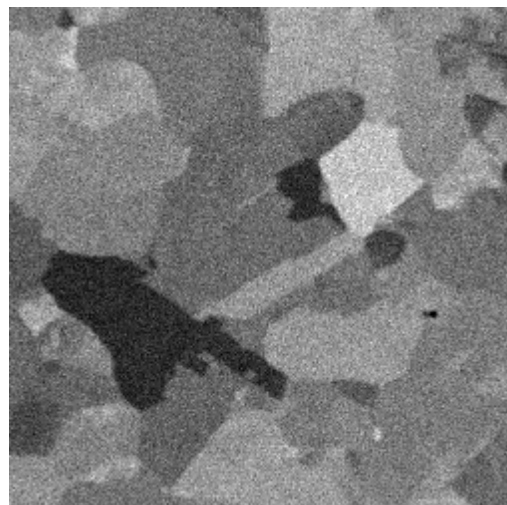


Figure 4: CP-Ni specimen, final polish colloidal silica. A) Backscatter electron image @ 0 deg. tilt. B) Backscatter electron image @ 5 deg. tilt. The significant contrast changes that result from small specimen inclination changes is one way to verify that the contrast results from electron channeling effects. C) NiK $\alpha$  WDS x-ray image, corresponding to image A. Overvoltage is 1.8 (15 keV). The average number of x-ray counts for the darkest contrast is 4163 while the lightest contrast regions yielded an average of 4270 counts (2.5 % greater x-ray yield). D) OIM inverse pole figure data showing crystallographic orientation information. Four of the grains showing the greatest backscatter contrast were selected for further analysis. Each of these grains lies within the angular range that Hall [8] had expected would yield a x-ray production rate that differs from the average production rate.



A

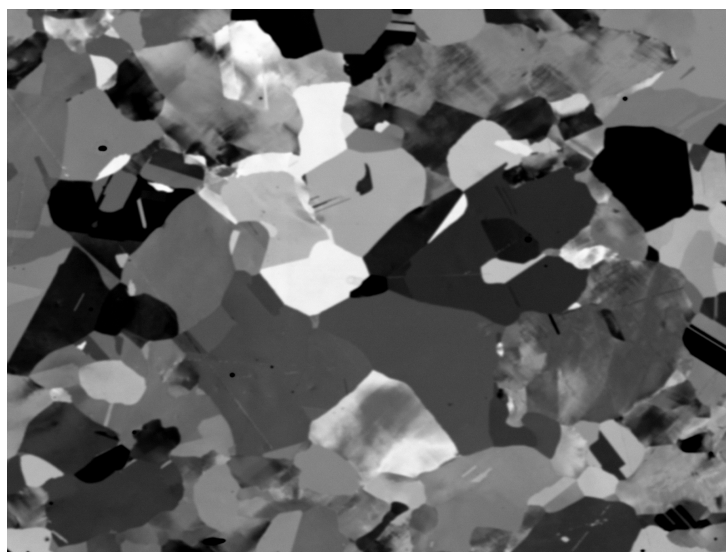
100 μm



B

100 μm

Figure 5: CP-Ni, final polish colloidal silica. Overvoltage is 1.08 (9 keV). A) Backscatter electron image. B) NiK $\alpha$  WDS x-ray image. The average number of x-ray counts for the darkest contrast is 1361, while the lightest contrast regions yielded an average of 1715 counts (26 % greater x-ray yield).



100 μm

Figure 6: CP-Ni, final polish colloidal silica. Backscatter electron image at 9 keV showing the large variations in grain contrast that result from electron channeling. The measured difference in the NiK $\alpha$  x-ray yield between the lightest and darkest contrast regions is in excess of 20 %.