APPLICATIONS OF X-RAY MICRODIFFRACTION IN THE IMAGING INDUSTRY

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ABSTRACT

Characterization of materials used in the digital imaging industry has been performed using micro X-ray diffraction (microXRD) techniques. Case studies are described that demonstrate the use of microXRD for identification of phases, texture, and microstructure morphology of components used in imaging applications.

INTRODUCTION

Digital imaging is comprised of capture, storage and display of an image. Whether it is a digital camera, secure disk (SD) card, ink jet printer, or liquid crystal display, the growth of this industry has required the development of new materials. Critical to this development are analytical techniques capable of characterizing composition and microstructure. X-ray diffraction is one of the most important tools available for analyzing solids, with microdiffraction being a critical component for the success of emerging technologies and in some instances the only technique capable of providing the answer to a materials analysis question. The original microdiffractometers were X-ray diffraction (XRD) cameras. Laue, Debye-Scherrer, precession, and Statton cameras, shown in Figure 1, are examples of early instrumentation that were used for micro diffraction analysis.

Figure 1. MicroXRD cameras a) Laue, b) Debye-Scherrer, c) precession, d) Statton.

Though their popularity has diminished with the availability of modern X-ray diffractometers, these cameras still function as useful instruments for X-ray diffraction analysis. Improvements in
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X-ray sources, optics, and detectors have resulted in microdiffraction systems that are capable of analyzing very small samples or regions on a sample qualitatively and quantitatively and in a timely manner. With a microdiffractometer, the sample size is typically a few millimeters down to 50 microns in diameter. It is possible to analyze samples down to 10 microns in diameter when comprised of high Z elements. Analysis techniques include confirmation of crystallinity, phase identification, texture, and residual stress. The microdiffractometer used in this study is shown in Figure 2.

![Microdiffractometer](image1.png)

Figure 2. Eastman Kodak microdiffractometer.

Typically, the detector used for microXRD analysis is two-dimensional. X-ray photographic film [1], image plates [2], and multiwire detectors [3] are the principle detectors of choice depending on the application and results required for analysis. Examples of diffraction data obtained using these detectors are demonstrated in Figure 3.

![Diffraction Patterns](image2.png)

Figure 3. Two-dimensional XRD patterns (a) Film – back reflection Laue pattern of beryl single crystal, (b) image plate – transmission Laue pattern of polyethylene-2,6-naphthalate film, (c) multiwire – grazing incidence pattern of silver behenate in polyvinyl alcohol.

Film will provide the best resolution of all detectors but data collection and chemical processing times are long. Image plate detectors based on photostimulable BaBrF:Eu^{2+} are an order of magnitude faster than film and on a flexible support allowing for use anywhere film is used, but require the use of a laser scanning system for data readout. Multiwire detectors offer real time viewing of data collection allowing for immediate assessment of sample alignment and diffraction pattern quality, but will have lower resolution and intensity dynamic range than image plate detectors. For applications described in this study, the multiwire detector was utilized.
In addition to microXRD, other analytical techniques that are complimentary in the characterization of small samples include microFTIR, microRaman, scanning electron microscopy and transmission electron microscopy.

EXPERIMENTAL

All microXRD data were collected using a microdiffractometer comprised of a Rigaku copper rotating anode X-ray source, and a Bruker goniometer consisting of Goebel mirrors aligned for CuKa radiation, XYZ sample stage, video alignment camera, and GADDS two-dimensional (2D) multiwire detector. The operating power for the X-ray source was 30kV, 60mA. The final X-ray beam size was controlled with collimators and ranged from 50 – 300 microns in diameter depending on the sample size. Data collection times ranged from 60 seconds to 10 minutes depending on the material composition, sample size, and sample crystallinity. Samples were evaluated as received and mounted on an appropriate sample holder for data collection. Data analysis was performed using software from Bruker (GADDS and EVA) or MDI (Jade). Some 2D diffraction patterns are converted to one-dimensional (1D) intensity versus 2-theta diffraction patterns for phase identification analysis.

RESULTS AND DISCUSSION

Motion Picture Imager
Movies shown in theaters have begun the transformation from film to digital projection. The imager chip used for projecting the movie onto a movie screen will become very hot during use. The substrate (Figure 4) used to hold the imager must be thermally stable and have an expansion coefficient matched to the imager to insure the projected image on the screen remains in focus.

Figure 4. Motion picture imager assembly, backside. Location of microXRD analysis marked by *. Location of imager on the front side of the substrate marked by the rectangular box.

A group of imager assemblies was found to produce unacceptable image quality. The cause was attributed to either the imager chips or the substrates provided by an external supplier. A request was made to determine the phase composition of these substrates without exposing the imager to an X-ray beam. Micro X-ray fluorescence determined that silicon was present in the substrate. The microXRD pattern collected from the substrate (Figure 5) shows diffraction rings that are spotty indicating very large crystalline grains in the substrate.
Combining XRF and the 1D XRD pattern results, a search of the Powder Diffraction File (PDF) [4] allowed for confirmation of silicon and silicon carbide as phases present in the substrate. With this information it was determined that the composition of the imager substrate was not correct resulting in a thermal expansion coefficient that was not matched with the imager. This mismatch explained the defocusing of the projected image. Because of the small size of the X-ray beam during the collection of microXRD data, the imager devices had not been exposed to a direct X-ray beam. The imagers were preserved and could be removed from the defective substrates to be used on other imager assemblies.

**CRT Cathode**

Digital print services utilize high intensity light sources for printing photographic pictures. These light sources use cathode ray tubes (CRT) containing cathode assemblies (Figure 6) that are expected to be in service for greater than 20,000 (20K) hours. Early failure (<2K hours) of some CRTs prompted an investigation as to the cause. The supplier of these cathodes indicated that the electron-generating portion was comprised of tungsten (W) and the surrounding cup was comprised of tantalum (Ta), and that nothing had changed in the manufacture process of CRTs.

Figure 5. MicroXRD data from the backside of the imager substrate. Inset is the original 2D pattern; X-Y plot is a result of integration of the 2D pattern and conversion to a traditional 1D XRD pattern.

Figure 6. CRT cathode. Image on the left is the W region, image on the right is the Ta cup.
MicroXRD patterns (Figure 7) were collected in the W region for a new cathode, a cathode operated for 26K hours and still working, and a cathode that failed after 1K hours of operation.

Figure 7. MicroXRD two-dimensional (inset) and corresponding 1D diffraction patterns for (a) new cathode, (b) working cathode 26K hours of operation, (c) failed cathode 1K hours of operation, collected in the respective W regions.

Phase identification determined that two phases were present in the W region of the new cathode, tungsten and osmium (Os) (W and Os confirmed by micro XRF). The supplier did not indicate the presence of osmium. The absence of complete knowledge of the composition of components is often a problem when dealing with external suppliers. Note that in the 2D microXRD pattern of Figure 7a the diffraction rings due to W are spotty (large grain) whereas the rings due to Os are continuous (small grain). This microstructure observation would not be possible using a conventional point detector for XRD data collection. For the used cathodes, both showed the presence of two phases. Tungsten is present at reduced intensity, and Os is absent. In both of these samples the additional phase could be indexed based on a hexagonal unit cell with lattice constants of $a = 2.755 \, \text{Å}$ and $c = 4.416 \, \text{Å}$. A match for any W or Os phases or alloys with this unit cell was made for a $\text{Os}_{(1-x)}\text{W}_x$ phase with a Mg structure type, using Pearson’s Handbook.
At this point, there was no obvious answer to explain why one cathode was working after 26K hours and the other failed after 1K hours.

The next step was to analyze the Ta cup region. Analysis of the new and 26K hour cathodes revealed the presence of Ta metal. No other phases were detected. When the failed cathode was analyzed, several additional diffraction rings in addition to Ta metal were observed (Figure 8).

![MicroXRD two-dimensional and corresponding 1D diffraction patterns for (a) working cathode 26K hours of operation, (b) failed cathode 1K hours of operation, both collected in the respective Ta cup regions.](image)

Phase identification for the failed cathode sampled revealed that Ta$_2$O$_5$ was present. Tantalum is an excellent gettering element for oxygen and the presence of Ta$_2$O$_5$ explains why the cathode failed prematurely. With these findings, the manufacturer of the CRTs concluded that a new type of seal (original discussion indicated no manufacturing changes!) being used was not working properly and oxygen was being allowed to enter the CRT. Replacement of the defective seals solved the problem and service lifetimes returned to the expected 20K+ hours.

**Plastic Camera Gear**

Gears in digital and film cameras can be made of plastic to help reduce weight and cost. Typically, these gears are made using an injection molding process, followed by a cooling period.
before the finished gear is removed from the mold. In one site manufacturing plastic gears, the
gear teeth were found to be distorted rendering the gear unusable. A visual comparison of a good
versus a bad gear can be found in Figure 9.

![Figure 9. Section of camera plastic gear (a) good, undistorted teeth and (b) bad, distorted teeth.](image)

MicroFTIR confirmed that the polymer in both samples was polymethylene oxide (PMO). XRD
analysis was requested to determine if there were crystallinity differences between the two
samples. The use of a conventional diffractometer would not allow characterization in only the
region of the gear teeth, as the X-ray beam would be as large as the entire gear. MicroXRD is
well suited for this analysis since the X-ray beam can be collimated to irradiate a single tooth.
Two-dimensional diffraction patterns for both samples are shown in Figure 10.

![Figure 10. MicroXRD two-dimensional XRD patterns for (a) good gear tooth and (b) bad gear
tooth.](image)

Both diffraction patterns in Figure 10 show the (100) and (200) PMO diffraction rings. In Figure
10a, the rings are uniform in intensity indicating a random orientation of crystallites. In Figure
10b, the rings are not uniform in intensity, indicating that texture (preferred orientation) of the
crystallites is present. The preferred orientation is an indication that the bad gear tooth was
pulled during processing at a temperature below the melting point of PMO. A review of the
manufacturing procedure revealed that a change in the process had been instituted recently. The hold time between injection molding and release from the mold was shortened, with the intention of increasing the number of gears produced in a production cycle. With the reduced hold time, the PMO was at a higher temperature during the release step and the gear teeth were sticking to the mold and being stretched when being removed. A return to the original hold time for cooling after injection molding eliminated the distortion of the gear teeth.

**Clay-PEO Nanocomposite**

Clay-polymer nanocomposite materials have received significant attention from the industrial community because of their wide range of novel physical properties [6]. Clay has been identified as an inexpensive, transparent, environmentally benign nanoparticulate material with unique, electrical, mechanical, optical, and rheological properties, which are of interest in the imaging industry, including applications in ink jet receiver media [7]. X-ray diffraction patterns of clay films show basal plane (00L) diffraction peaks. The interplanar distance between (001) planes is defined as the basal plane spacing. This spacing can be used as a measure to determine the extent (or absence) of polymer insertion into the clay layers as a function of composition.

Free standing films of NaClOisite clay and polyethylene oxide (PEO)/NaClOisite clay (80/20 wt/wt) were provided for XRD analysis. These films were initially analyzed on a Rigaku D2000 Bragg-Brentano diffractometer equipped with a copper rotating anode, diffracted beam graphite monochromator tuned to CuKα radiation, and a scintillation point detector. Data were collected using reflection mode geometry. The resulting diffraction patterns are shown in Figure 11.

![Figure 11. Bragg-Brentano diffractometer patterns for (a) NaClOisite and (b) PEO/NaClOisite 80/20 wt/wt. Both scans collected in reflection mode geometry.](image)

The diffraction pattern of the NaClOisite film has a basal plane (001) diffraction peak at ~7.1° 2-theta corresponding to a d₀₀₁ = 12.5 Å. The PEO/NaClOisite film in Figure 11b shows the (001) peak has shifted to lower angle giving a dₐ₀₀₁ = 26.0 Å. It is also noteworthy that multiple orders of (00L) diffraction peaks are observed in Figure 11b indicating that the lattice of the PEO/NaClOisite nanocomposite is more ordered than neat NaClOisite. The results in Figure 11 confirm that NaClOisite has been intercalated by PEO. However, with the PEO/NaClOisite ratio at 80/20, there is excess PEO that would be expected to be crystalline. A differential scanning calorimetry (DSC) scan of the 80/20 PEO/NaClOisite sample showed a melt peak at 61 °C, indicating crystalline PEO was present in the sample. A diffractometer scan of a neat PEO film
shows two prominent diffraction peaks at ~19 and 23° 2-theta (Figure 12). These diffraction peaks were not observed in Figure 11b.

Figure 12. Bragg Brentano diffractometer pattern for PEO, reflection mode geometry.

To investigate the absence of a PEO diffraction pattern in Figure 11b, the PEO/NaCloisite film was analyzed on the microdiffractometer. A sample was mounted with the sample edge perpendicular to the X-ray beam to approximate the reflection mode geometry of the Bragg-Brentano diffractometer, and mounted with the film plane perpendicular to the X-ray beam for transmission mode geometry. The 2D diffraction patterns are shown in Figure 13.

Figure 13. MicroXRD two-dimensional XRD patterns for a 80/20 PEO/NaCloisite film (a) reflection mode geometry (b) transmission mode geometry. The white rectangles approximate the equivalent region that would be scanned with a point detector on a Bragg-Brentano diffractometer

In Figure 13a there are diffraction arcs in the equatorial and meridinal positions. In Figure 13b there are two prominent diffraction rings. The equatorial arcs in Figure 13a are due to the
NaCloisite clay intercalated with PEO. The meridinal arcs in Figure 13a and diffraction rings in Figure 13b are due to PEO. The white rectangular box on Figure 13a shows the region of the diffraction pattern that a scintillation detector would detect. The point detector will never be in the correct position to see the PEO meridian arcs, which explains why PEO was not observed in the diffraction pattern of Figure 12b. Had a transmission diffraction pattern been collected using the Bragg-Brentano diffractometer, the PEO diffraction peaks would have been observed as indicated by the white rectangle on FIGURE 13b. In addition to addressing the presence of PEO, the 2D diffraction patterns allow one to define the microstructure of the PEO/NaCloisite nanocomposite. The equatorial arcs indicate that NaCloisite platelets lie parallel to the film plane. The PEO meridinal arcs in Figure 13a and PEO rings in Figure 13b are an indication that crystalline PEO planes are perpendicular to the film plane but are cylindrically symmetrical within the film plane. This microstructure is illustrated in Figure 14.

![Figure 14. Microstructure model of NaCloisite intercalated with PEO.](image)

Though the original request was to determine if PEO interacted with NaCloisite clay, the use of a microdiffractometer with a 2D detector allowed for a more complete understanding of the nanocomposite. With this enhanced knowledge the composition can be modified to obtain desired physical properties.

**SUMMARY**

MicroXRD has been described as an important analytical tool for characterizing materials used in digital imaging. Combining a small diameter X-ray beam with a two-dimensional detector, materials analysis including phase identification, preferred orientation, production concerns, and new materials development has been successfully demonstrated.
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