A New Technique to Study Partial Grain Development

Donald L. Black, Thomas B. Brust and Stephen C. Stoker
Eastman Kodak Company, Imaging Research and Advanced Development
Rochester, New York, USA

Abstract

A technique is described that allows a detailed analysis of the developed grain fraction and the amount of developed silver per grain in a polydisperse emulsion. The technique uses analytical electron microscopy and microanalysis techniques to analyze individual microcrystals. Results from two different size emulsions are used to compare with the measured photographic response.

Introduction

As the demand for high-speed films increases, more interest is focused on factors that influence photographic imaging efficiency. Although it is known that intrinsic speed depends on grain size, inefficiencies occur as the grain size of the silver halide microcrystal increases. To understand the inefficiencies, one must consider all the events in the imaging chain that include light absorption, latent image formation, detection, amplification, and dye formation.

Earlier, House et al.[1] used a monodisperse AgBr octahedral emulsion to study the inefficiencies in light absorption and development that occur when the emulsion grain size is increased. They found that reduced light absorption and amplification are two of the key factors contributing to the inefficiencies. One of these factors, amplification, is dependent on the amount of silver that is produced during the development process. Because this was a monodisperse, single halide phase system, bulk analysis techniques could be used to study this process. In many current color negative photographic systems polydisperse AgBrI emulsion grains are used. These mixed halides, which usually have lower developability than pure AgBr, and their polydispersity provide additional complications that require more complex analysis techniques when studying the development part of the imaging chain. This paper describes a microscopic technique that has been used to gain a more detailed understanding of the detection and amplification process that occurs in the development of some AgBrI emulsion grains.

Methodology

The technique involves using the unique capabilities of analytical electron microscopy (AEM), which were described at an earlier conference,[2] to generate quantitative chemical and structural information from very small, well-defined regions of specimens. The compositional information is obtained using the technique of x-ray microanalysis. For a thin sample in the electron microscope, the intensity (I) of the emitted x-rays for an element is proportional to its concentration (C) and the sample thickness.[3] Since the thickness of the analyzed volume is difficult to determine, Cliff and Lorimer[4] showed that by proportioning the intensity values for two elements, the thickness value could be eliminated and the equation simplified to

$$I_A/I_B = k_{AB}C_A/C_B.$$

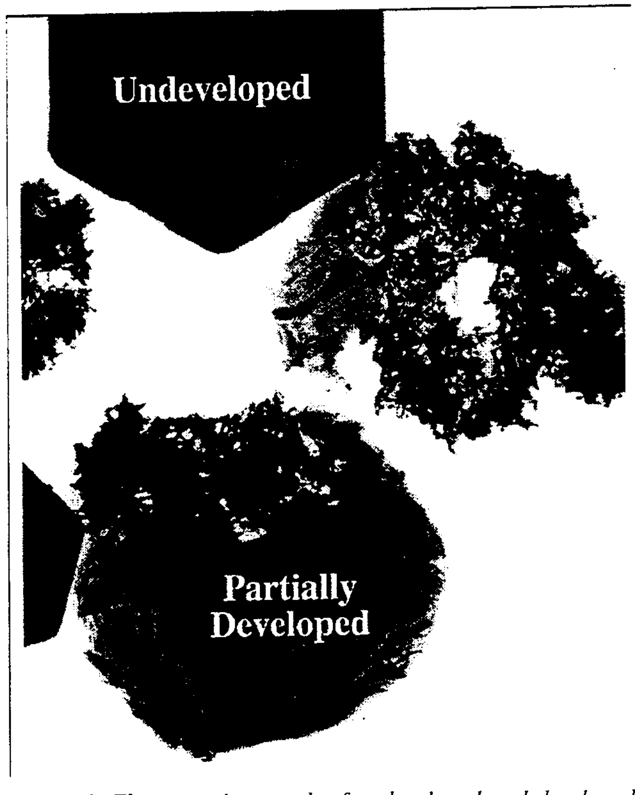

Figure 1. Electron micrograph of undeveloped and developed microcryatals of an AgBrI emulsion.

Using the appropriate standards, the constant k_{AB} can be determined for any combination of elements. The relative concentration of elements in an analyzed volume can be determined by first measuring the intensity ratios of the elements of interest, subtracting the background continuum, and finally, calculating the concentration ratios using the simplified equation. For thicker samples such as three-dimensional grains, an absorption and fluorescence correction may be needed.

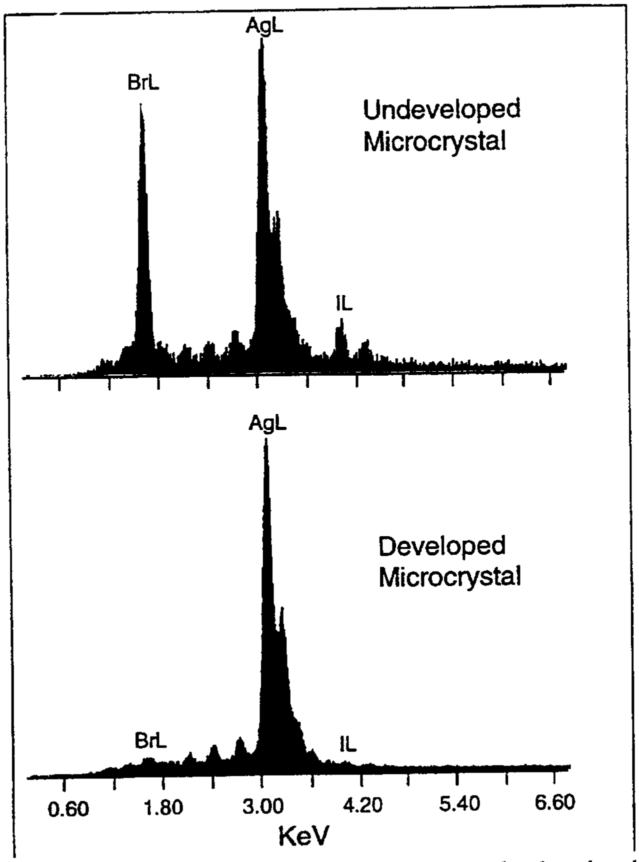

Figure 2. X-ray microanalysis spectra of an undeveloped and developed AgBrI microcrystal.

A typical micrograph of an undeveloped and developed grain is shown in Figure 1 and representative spectra in Figure 2. The filamentary nature of the developed silver clearly distinguishes it from the undeveloped silver halide. Since the diameter of the electron beam and where it is focused determine the portion of the sample being analyzed, the intergrain (grain-to-grain) composition of individual grains in an emulsion sample can be determined by focusing the electron beam to a diameter that irradiates only a single grain. Using the concentration ratios, the percentage of developed silver in an individual grain can be determined by subtracting the molar halide concentration from the silver concentration. This process is repeated for many developed grains and the average value is evaluated by comparison to the bulk value.

The average percentage of developed silver per grain and the fraction of developed grains can be used to understand the photographic response curve. These techniques are illustrated using two AgBrI emulsions with average grain sizes of 2.5 and 7.0 microns. The emulsions were coated in magenta dye-forming single-layer coatings, exposed and processed in C-41, excluding the bleach and fix parts of the process. Both the silver and silver halide remain in the coating. After removal of the grains from the coated film, they were dispersed in an aqueous suspension and collected on a carbon-support film on a microscope grid that was analyzed in an analytical electron microscope.

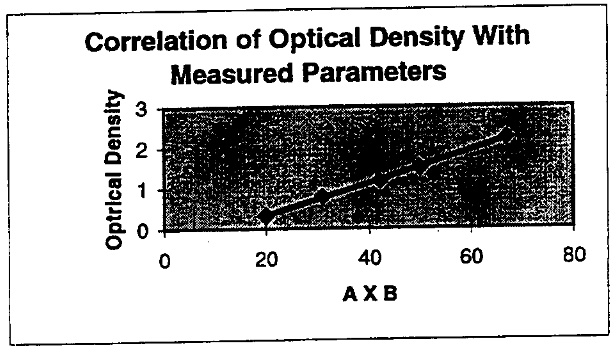

Figure 3. Correlation of the optical density from the photographic response curve with the product of the average percentage of developed Ag/Grain (A) and the developed grain fraction (B).

Results and Discussion

Micrographs and elemental compositional data for a representative population of emulsion microcrystals in both samples were collected and analyzed to determine the fraction of developed grains and the average percentage of developed silver per grain. The data for three different exposures are summarized in Table I. Although increases in the developed grain fraction are observed for the higher exposures, larger increases are observed for the smaller grain size. Changes are also observed for the average percentage of developed silver per grain. The smaller grain size emulsion shows more development per grain than the larger size emulsion at each exposure. As the exposure is increased, an increase in the percentage of developed silver per grain is observed for the larger size emulsion, but little increase is observed for the smaller size one. To determine if these parameters correlate with the photographic

Table I. Optical Density and Development Parameters for Two AgBrI Emulsions

Sample ID		Exposure	Optical Density	Ave% Dev. Ag/Grain (A)	Dev. Grain Fraction (B)	AxB
A	2.5 microns	Toe	0.34	65	0.31	20
B	7.0 microns	Toe	0.32	25	0.79	20
A	2.5 microns	Mid-scale	1.18	58	0.73	42
B	7.0 microns	Mid-scale	0.8	32	0.97	31
A	2.5 microns	Dmax	2.22	71	0.94	67
B	7.0 microns	Dmax	1.5	50	1	50

response curve, a model using the product of the average percentage of developed silver per grain, (A), and the developed grain fraction, (B), was plotted vs. the optical density from the response curve. The plot, Figure 3, shows a linear correlation is observed. This type of analysis will prove useful in helping us define the development properties of a polydisperse mixed halide emulsion system that will have the greatest impact on photographic efficiency.

References

1. G. L. House, J. T. Kofron, and R. J. Newmiller, Proceedings of SPSE International East-West Symposium II, 1988, p. B10.
2. D. L. Black and J. A. Timmons, Proceedings of IS&T International East-West Symposium III, 1992, p. A-21.
3. J. I. Goldstein, in ìIntroduction to Analytical Electron Microscopyî, Plenum, New York (1983).
4. G. Cliff and G. W. Lorimer, J. Microsc. 103, 203 (1975).