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Cryo-Analytical Electron Microscopy in Imaging Science and Engineering of AgX Imaging Products and Their Micro- and Nanocomponents

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Contemporary AgX (X=Br, I, Cl) imaging materials comprise a large family of black-and-white and color negative, positive and instant films and papers, diagnostic X-ray films, micro- and printing films involved in various kinds of technologies. In spite of rapid advances in digital imaging, AgX imaging products are still superior in sensitivity and resolution. Nowadays, materials composed of 4-18 photosensitive layers and interlayers (10-20 μm thick, Fig. 1a) may comprise up to 100 various components (AgX emulsions, dispersions of color couplers, nanocolloids, latexes, chemical and spectral sensitizers, hardeners, plasticisers, stabilizers, antihalation dyes and antistatic agents, etc.) distributed in a gelatin matrix to provide specified sensitometric, structure-sharpness, and color parameters. Admixtures, inter- and intramolecular interactions in thin layers and at interfaces are of decisive importance for formation of the required functional characteristics. As photographic materials become increasingly sophisticated, their comprehensive structural characterization is more desirable. The optimal strategy for multilevel structural and analytical diagnosis of imaging systems by a combination of cryo-AEM techniques (Fig. 1b) emphasizes the importance of integrated research performance, instrumentation, preparation techniques, modeling of electron-beam interactions and related structural, electronic, optical and functional properties [1-3]. Although the replacement of AgX imaging by digital methods was already predicted in the early 80s, the world manufacturing of AgX films and papers is still growing and a peak is expected in 2007. However, in order to be successfully incorporated into electronic and hybrid information technologies for the 21st century, photographic materials should further improve their quantum efficiency, image quality, and environmental safety. In order to achieve these objectives, the key components should be intentionally modified with a focus primarily at the nanostructural level and the main stages of the photographic process should be further optimized. Due to the introduction of thin tabular AgX grains of mixed composition, incorporation of phase boundaries in AgX microcrystals (core-shell structures, Fig. 1d) and the controlled chemical and enhanced two-electron spectral sensitizations, the overall efficiency of the photographic process has been remarkably increased and the working grain volume has been decreased by factor of 10 during the last two decades. Since knowledge of the morphology, crystalline and defect structures and halide distributions is quite important from the point of view of improving the performance of AgX emulsions, it attracts continuous research interest. Direct investigations are only possible when the crystals are cryo-cooled because of their high propensity to decompose under probing irradiation. This papers overviews applications of cryo-energy-filtering TEM (EFTEM)/ electron spectroscopic diffraction (ESD)/ electron energy-loss spectroscopy (EELS) and cryo- (field-emission) scanning TEM (STEM)/energy-dispersive X-ray spectroscopy (EDXS)/parallel EELS and digital image analysis for the characterization of AgX imaging products and their micro- and nanocomponents and studies of chemical sensitization, latent image formation and development [2,3]. Chemical composition and size distribution characterization including combined STEM/EDXS/EFTEM mapping, line profiling and element distribution-size-thickness population analyses of Ag(Br,I) emulsion grains have been performed. A low-loss fine structure in EEL spectra of AgX between 4 and 26 eV attributed to excitons and plasmons superimposed with interband transitions has been evaluated by Kramers-Kronig analysis and *ab initio* calculations of the AgBr electronic band structure [4]. Contrast tuning under energy filtering and ESD (Fig 1c) were used to image the AgX crystal morphology and defect structure (clusters of interstitials and $\{11\bar{1}\}$ stacking faults) as well as exciton states and coupling of volume and surface excitations and the morphology of nano-sized droplets of color couplers [5].

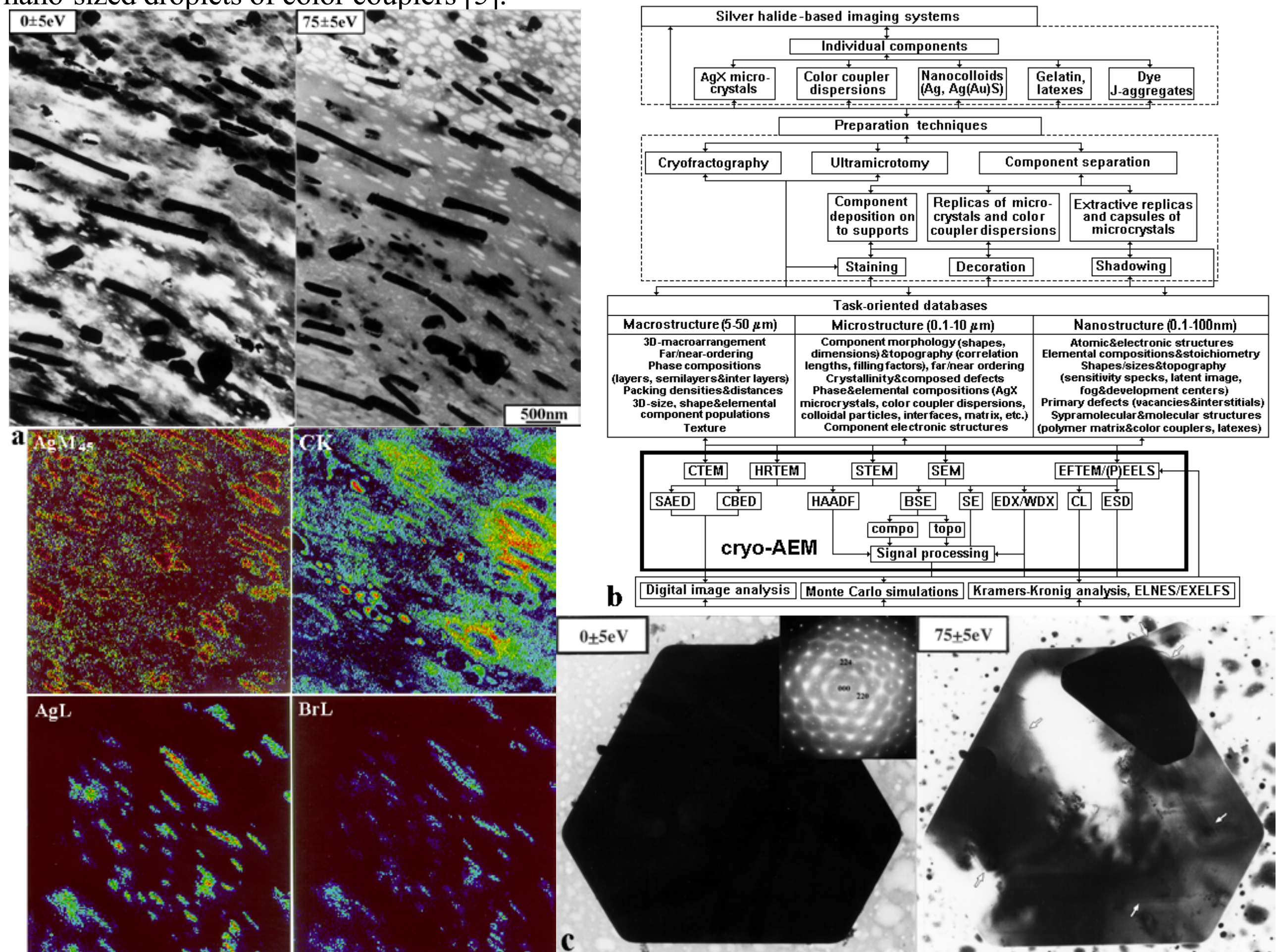

FIG. 1. (a) The color negative film Ektapress Gold-100, Series II, Eastman Kodak, ultrathin section of red-sensitive (top) and green-sensitive (bottom) layers, cryo-EFTEM at 0 and 75 eV indicating the contrast reversal for color couplers in the top layer and combined Ag $M_{4,5}$- and C K- (EFTEM, three-window) and AgL- and BrL-(STEM/EDXS) elemental maps acquired on the same layers (below). (b) Algorithm of combined structural and analytical characterization of AgX imaging systems by cryo-AEM. (c) Multistructured Ag(Br,I) tabular microcrystal, cryo-EFTEM at 0 and 75 eV. The 120 nm-thick crystal is dark against the background in the zero-loss mode. ZLESD, near [111] zone, (insert) exhibits extra reflections in between the main Bragg spots due to the presence of stacking faults (shown by arrows in the right image) and contours of diffuse intensity due to clustering of interstitials.

References

[1] V.P. Oleshko et al., Micron 31 (2000) 55. [2] V.P. Oleshko, in: Industrial Applications of Electron Microscopy. Eds. Z. R. Li, Marcel Dekker, N.Y. 2002, 51-112. [3] V.P. Oleshko, J.M. Howe, J. Phot. Sci. Technol. Japan 65 (2002) 332. [4] V.P. Oleshko et al., these proceedings (2003). [5] Current support by the Division of Materials Science & Engineering, Office of Science, US Department of Energy through Contract No DE-FG02-01ER45918 is gratefully acknowledged.

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