

Stability and Developability of Silver and Gold Latent-Image Centres

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Introduction

The basis of classical photographic process in silver halide emulsions consists of photochemical nucleation and subsequent electrochemical growth of the silver clusters to metallic silver phase. However, the problem of the nature and size of the silver clusters capable to initiate the development of emulsion grains remains not enough clear.

The present report is devoted to an analysis of the process of silver centres growth in silver bromide microcrystals and other substrates based on the concepts of the thermodynamics of a new phase formation and growth taking into account results obtained by means of electron microscope studies. Furthermore the peculiarities of activity and stability of clusters formed by a metal nobler than silver are discussed too.

Thermodynamic Aspects of the Problem

The problem of stability and developability of metal clusters can be treated on the basis of the Gibbs-Volmer theory of nucleation of a new phase.¹ The analysis is based on the dependence of the Gibbs free energy of particle formation on their size:

$$\Delta G_i = 4\pi r_i^2 \sigma - 4\pi r_i^3 / 3v kT \cdot \ln(c/c_\infty) \quad (1)$$

where r_i is the radius of the particle, σ is its free specific surface energy (surface tension), c/c_∞ is the present supersaturation in the system, and v is the volume per silver atom. The first term of equation (1) represents the contribution of the free energy necessary for the formation of a boundary surface of the particle of the new phase. The second term denotes the free energy which is being liberated owing to bulk increase of the particle under the action of capillary pressure existing inside any particle or drop of small radius. Equation (1) reaches its maximum at critical radius $r_i = r_c$. At this point the increase in free energy becomes equal to zero, the system becomes a quasi-equilibrium one, and Gibbs-Thomson equation becomes valid:

$$\Delta\mu = kT \cdot \ln(c/c_\infty) = 2\sigma v/r = e(E_{\text{Me}(+)/\text{Me}} - E_{\text{redox}}) \quad (2)$$

where $\Delta\mu$ is the increase in chemical potential of metal in the process of formation of supersaturation c/c_∞ , $2\sigma/r$ is the capillary pressure inside the drop, $E_{\text{Me}(+)/\text{Me}}$ is the electrode potential of the system in thermodynamic equilibrium, E_{redox} is the redox potential of the buffer solution or the developer.

It is essential to draw attention to the fact that critical size is achieved under conditions of maximum and not minimum value of free energy. A nucleus of critical size is a most unstable object and is first to disappear from the complete size distribution of particles. This process is spontaneous and is accompanied by a decrease in free energy of the system as a whole. The initial system is of quasi-equilibrium nature only owing to the fact that in buffer or in developer solution corresponding to equation (2) the probability of growth of a metal cluster, i.e. initiation of the development precisely equals the probability of its oxidation.

The above peculiarities of equations (1) and (2) of classical theory suggest that the nucleus of critical size represent a particle of the new phase of minimal dimensions, thus possessing a volume and boundary surface.

On the Sub—and the Full Centres of Latent Image

From the viewpoint of the theory of nucleation and growth of a new phase, the sub- and the full latent image centres (LICs) cannot be ascribed any strictly defined fixed sizes. The sub- and full LICs arising during the exposure are separated, depending of their size, only at the development stage, and this is determined by the developer potential. For silver particles the position of the boundary between sub- and full LICs must be determined by the critical size of the nuclei, r_c , in the developer with the potential ΔE , according to the equation (2). Figure 1 shows the dependence of the quasi-equilibrium value of the silver particle potential on its radius, calculated from the equation (2). Particles for which $r < r_c$ are oxidized in the developer and make up the latent image sub-centres while those with $r > r_c$ are capable of spontaneous growth owing to the reduction of silver halide

microcrystals and are classified as full LICs. As shown in [2], the probability of the growth or decay of particles close to the critical size changes abruptly from 0 to 1. Therefore, for every specific developer, subdivision into sub- and full LICs can be estimated with sufficient strictness.

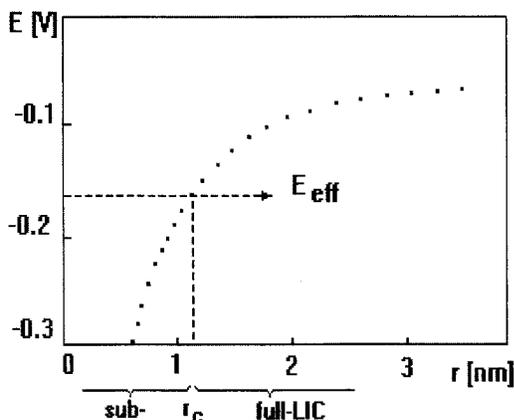


Figure 1. (Quasi-equilibrium potential of silver particles (E) vs their size (r). E_g is the effective value of developer redox potential; sub- the region of sub-centres; full-LIC—the region of full latent image centres.

Let us consider activity and stability of nuclei formed by metals of higher nobility (for example gold) than the metal deposited in the course of photographic development (silver). Activity of such particles will be high only if their size approaches critical value for development centres. However, subcritical-size clusters of nobler metal will not oxidize in the developer, unlike particles of less noble metal. The reason for higher stability of noble metal particles lies in the circumstance that the equilibrium value of the potential of the massive electrode is considerably more positive than in case of a less noble metal. The diagram in figure 2 shows that in one and the same developer a higher super-

voltage is produced far more noble metal than for a less noble one.

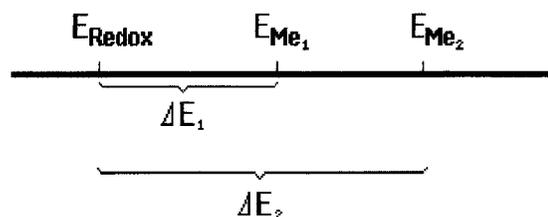


Figure 2. Scheme of supervoltage in redox-buffer solution for two different metals

For a noble metal the critical size at which their oxidation becomes possible, is much smaller than in the case of common development centres. The above considerations lead to the following peculiarities of nuclei formed by metals nobler than the metal deposited in the course of development. The nuclei are characterized by the existence of two critical sizes. Their activity is achieved jumpwise on attainment of critical size of the development centre. Oxidation of clusters is possible at sizes smaller than the critical ones in the case of nobler metals. Particles of intermediate size cannot initiate a development process and are capable of growth only through coalescence.

Acknowledgment

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References

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