

Features of AgHal Crystals Photolysis

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Introduction

Single crystals of silver halide represent a convenient modeling system for detailed research of metallic silver localization. Such localization appears on the surface of the crystal after exposure. The change of ionic equilibrium in liquid solutions leads to the modification of AgBr and AgCl microcrystals surface. This change is revealed through the modification of specific surface, through the concentration of low-coordinated Br⁻ ions on the surface, and through the change in ionic conductivity. Because the photolysis is happening on the surface, there is an interest for research of allocation and distribution of photolytic silver features on crystal surfaces after their modification in liquid solutions with active photographic substances. It is possible to obtain information about the process not only in dependence from equilibrium form of the crystal but also to investigate the photolysis details near surface localities containing typical quadrangular, triangular, and rhombic excrescences and holes. This possibility appears because the surface of a single crystal has a very developed micro-structure containing micro elements limited by planes with different Millers indexes.

Experiments

Crystals AgHal sized 0.2 – 0.5 cm were grown in the glass crystallizator by re-crystallization of microcrystallitic powder in liquid solution of ammonia hydroxide. It was done through slow evaporation of ammonia under room temperature. Crystals of AgBr, AgCl, AgBr(Cl) in cubo-octaeder form with most developed cubic sides and crystals of AgBr, AgBr(Cl) in rhomb-dodecaeder form with {110} habit (Fig. 1) were obtained.

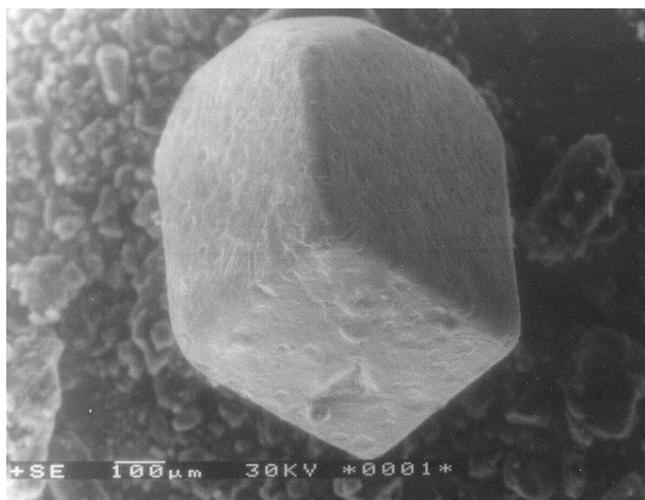


Figure 1 The single AgBr(Cl) crystal in the form of rhombododecaedr.

Various crystals were received depending on concentration of crystal-forming ions. Crystals surfaces were modified in liquid solutions of KBr with pBr = 1 and pBr = 3. This corresponds to the conditions of emulsion micro-crystals synthesis in the form of octaeders and cubes. Crystals were held in solutions for two hours. Crystals were exposed to mercury lamp after modification. Changes in the surface structure, changes in the character of localization, and the distribution of photolytic silver after exposition were studied by SEM and TEM methods using electron microscopes TESLA-BS340 and MK-125. The method of carbon replicas was used for the transmission electron microscopy.

Results

According to the thermodynamic theory of Gibbs, the crystal in equilibrium with its own solution must have the form corresponding to the minimum total surface energy under the constant volume [1] i.e.:

$$\sum_i G_i S_i = \min, \quad V = \text{const.}$$

The form of crystals after crystallization from the solution of ammonia hydroxide depends on many parameters such as over-concentration of crystal-forming ions, ammonia pH, formation of silver-ammonia complexes, the existence of impurities, the temperature, and the speed of molecular diffusion. The layer near growing crystal limited on one side by the surface of the growing crystal and on the other side by the over-concentrated solution is forming. In comparison with the inner parts of surface protruding parts are in a better position for nourishing. Therefore, gradients of over-concentration are appearing along the crystal side. Correspondingly, the appearance of elements limited by sides with various Miller indexes, including indexes of higher order, observed on the sides matching the equilibrium form of the crystal under the given conditions of growth. Consequently, under careful examination, the sides of the equilibrium form of the crystal are irregular, with their own microstructure. The use of such crystals for research of photolysis allows us to obtain the information about distribution of metallic silver on the sides. This distribution depends not only on the crystal form (i.e. cube, octaeder, rhombododecaeder) and content (i.e. AgBr, AgCl, AgBr(Cl)), but it also depends on the existence of micro-elements which are appearing on the surface as the result of growth, hunting, and modification.

Initially, crystals with rather smooth surface were used in the experiment. The surface changed after holding the crystals in KBr solution under pBr = 1, pBr = 3. This corresponds to the conditions of synthesis of emulsion microcrystals. Terraces and of correct quadrangular and hombic forms (Fig. 2), hills, holes, shapeless formations of various sizes appear on surface depending on the form and content of the crystal and also depending on pBr-modifying solutions. For example, the surface of AgBr rhombodo-

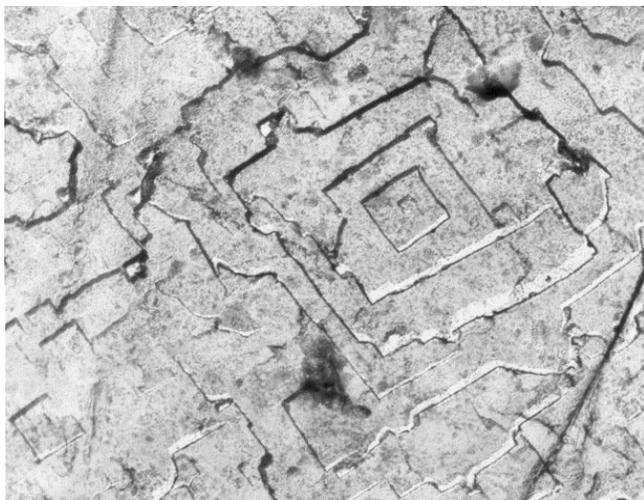


Figure 2 The surface of AgBr(Cl) single crystal after the modification in the KBr solution with $pBr = 1$ during 2 hours (X 8200).

decaeder is well developed. We have observed shapeless formations that are increasing in size in accordance to the greater pBr value. On the surface of AgBr(Cl) rhombododecaeders four-cornered terraces and rhombic holes appear. Crystals of cubooctaeders forms have various structure of the surface depending on their AgBr, AgCl or AgBr(Cl) content. This structure changes in the process of modification. The surface of AgCl crystals is more regular and less subjectable to change during modification than the surface of AgBr crystals.

Various pictures of protolithic silver particles formation on the sides (100), (111), (110) were observed when crystals with different content and habit were exposed. For example, on sides (111) AgBr crystals were discovered big unevenly distributed congregations of Ag particles. There are fewer of those particles on cubic sides (100). Analogues picture can be observed on the surface of AgCl cubooctaeder (Fig.3). The larger number of proto-

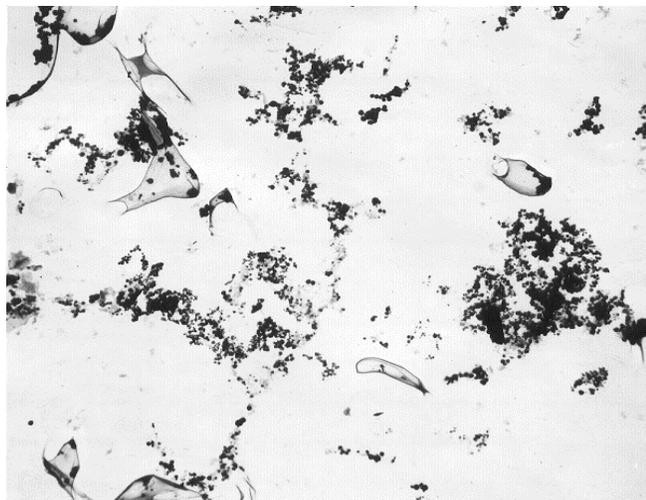


Figure 3 Microphotograph of the protolithic silver allocation on the single AgCl surface after 2 hours exposure (X 5000).

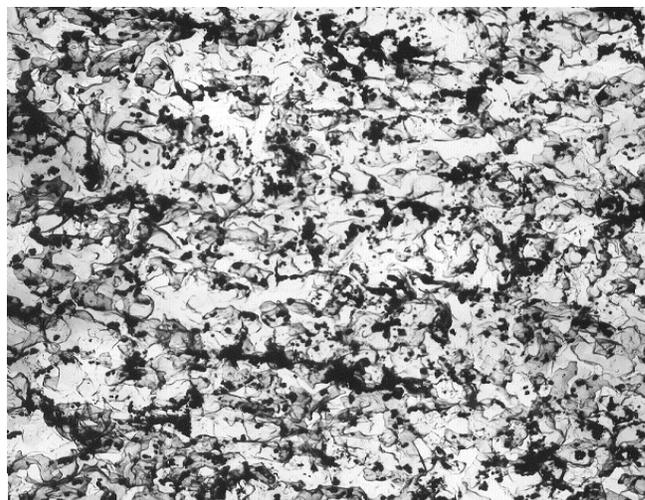


Figure 4 Microphotograph of the protolithic silver allocation on the single AgBr rhombododecaedr surface after 2 hours exposure (X 5000).

lithic silver particles appeared after the exposure of AgBr rhombododecaeders. These particles evenly cover all surface of the crystal (Fig. 4). A similar picture of Ag-particles distribution was discovered on (110) sides and on the surface of mixed type crystals. The difference is only in size of Ag-particles. These particles are much smaller on the surface of AgBr(Cl) crystals. Perhaps it could be explained by the fact that the surface of such crystals consists primarily of silver chloride. AgCl has a lower conductivity in comparison with AgBr.

Therefore, the structure of crystal surface is determined by conditions of their growth and modification. The number and the distribution of protolithic Ag-particles forming after exposure on the surface change depending on habit and content of crystals. The effectiveness of Ag-particles allocation on crystal sides of equilibrium form declines according to the sequence (110), (111), (100). This allows to make a conclusion about the changes in between-knots Ag-ions concentration and low-coordinated Br⁻ ions and Cl⁻ ions concentration in the near-surface layer. Predominant formation of discrete Ag particles or their congregations observed in the case of the developed surface and under the presence of dislocation protrusions and blocks boundaries. The particles and congregations are concentrated in the areas of these defects. It is necessary to stress that the formation of microcrystallites systems during the modification has a similar nature. This formation can take place in emulsion microcrystals. The effectiveness of latent image formation can depend from the habit and size of emulsion microcrystals if centres of sensitivity form on their surface.

Acknowledgement

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Reference

1. Kozlova, O. *Growth and morphology of crystals* // Moscow, 1980, 350 p.