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I. G. STOYANOVA

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Abstract

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I. G. STOYANOVA

ELECTRON-MICROSCOPIC INVESTIGATION OF OBJECTS IN A GASEOUS MEDIUM

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One of the conditions for investigating objects in an electron microscope is the need to place them in a vacuum. At the same time, there are a number of objects and processes for whose investigation the presence of a gas is necessary. Therefore, from the time the first model of the electron microscope appeared, searches were undertaken for the possibility of electron-microscopic investigation of objects in air or gas ([1–7]). A closed gas chamber was developed into which an object could be placed without preliminary drying ([7]), and an open chamber that made it possible to observe objects in a gas atmosphere at a pressure of 10–20 mm Hg ([4–6]). Further increase of the pressure in the region of the object was accompanied by deterioration of the vacuum in the microscope column and disruption of image stability.

Since electron-microscopic investigation of objects in a gaseous medium requires increasing the pressure directly in the object zone by several orders of magnitude compared with the pressure in the microscope column, the elements of the chamber in which the objects are contained must have high mechanical strength in order to withstand a considerable pressure difference, must be sufficiently hermetic so as not to allow gas to pass from the chamber into the microscope column, and at the same time must be sufficiently thin in the region of action of the beam so as not to cause significant scattering of the electrons passing through the object.

The experiments we carried out made it possible to develop an open microchamber satisfying the requirements listed above ([9]). This chamber differs from existing ones in that the gas pressure in it can be varied from 0 to 700 mm Hg without disturbing the operating regime of the microscope, without interrupting the process of observing the image. The hermetic sealing of the chamber was provided by seals and protective films deposited on diaphragms bounding the object chamber on two sides. Collodion films coated with a thin carbon layer were used as protective films.

The gas pressure in the chamber was changed by connecting it to a cylinder containing the required gas. The gas pressure in the object zone was measured with a U-shaped mercury manometer; the pressure in the microscope was measured with an ionization manometer. Tests showed good tightness of the chamber:

when the pressure in it was changed up to 600–700 mm Hg, the vacuum in the microscope column decreased by no more than 5–10%.

The influence of gas and protective films on the quality of the electron-microscopic image. The presence of protective films and gas above the object leads to an increase in the total thickness of the layer through which the electrons forming the image pass and, consequently, to a deterioration of resolution due to chromatic error. Using the empirical formula expressing the relation between the thickness of the object and the chromatic error, showing,

that the resolvable distance cannot be less than 1/10 of the object thickness, we obtained, for our case, a resolving power of 50 Å (for the limiting regime).

As the thickness of the scattering layer increases, the number of electrons scattered through such large angles that most of them are stopped by the aperture diaphragm increases. This circumstance leads to a decrease in the brightness of the image. To restore the initial brightness it is necessary to increase the load on the object.

The investigations showed that two carbon-collodion films of the microchamber scatter up to 30% of the incident electrons beyond an aperture angle of $8 \cdot 10^{-3}$ radian at a voltage of 80 kV. Increasing the pressure in the gas chamber causes a decrease in image brightness by 70% at a gas-layer height of 0.1 mm and by 20% at 0.03 mm, at a pressure close to atmospheric. The decrease in brightness was accompanied by a considerable decrease in image contrast. To choose the optimum contrast conditions, the intensity distribution in the image[8] was found as a function of the objective aperture and the accelerating voltage by the photographic method, and from it the optimum objective aperture was determined. It proved to be $8 \cdot 10^{-3}$ radian. It was found, moreover, that the value of the minimum contrast depends little on the objective aperture up to an angle of $8 \cdot 10^{-3}$ radian and increases appreciably when it is increased above 10^{-2} radian. From the standpoint of sufficient image brightness, an objective aperture of $8 \cdot 10^{-3}$ radian may be considered satisfactory. Taking the limiting contrast of the image of a particle as 0.2, we find that in the gas microchamber a gold particle 3 Å in diameter and a particle of material of organic origin ~ 50 Å in diameter can be detected.

The resolution of the electron-microscopic image was determined from particles of colloidal gold deposited on one of the protective films. At pressures in the microchamber of 120–170 mm Hg, a resolution of 80 Å–100 Å was obtained, and at a pressure of 520 mm Hg, 120 Å (Fig. 1).

Observation in the electron microscope of the process of a chemical reaction. The results obtained indicate the possibility of carrying out electron-microscopic investigation of objects located in a gaseous medium, including observation of chemical reactions between gaseous and solid phases.

As an example we chose the reaction between silver and gaseous hydrogen sulfide in the presence of oxygen. The silver was deposited by evaporation in vacuum

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

on the film of one of the chamber diaphragms. The experiments were carried out with microchambers having good hermetic sealing.

Before the start of the reaction, the structure of the initial layer was checked by electron-microscopic and electron-diffraction methods. The appearance of the initial silver layer and its electron diffraction pattern are shown in Fig. 2a, a'. Introducing into the chamber a mixture of gaseous hydrogen sulfide ($p^{H_2S} = 30$ mm Hg) and oxygen ($p^{O_2} = 10$ mm Hg), we followed the change in the structure of the initial layer. In the observed region, two minutes after the gas was admitted, motion of the particles began (Fig. 2b, b'). The high rate at which migration occurred did not allow a sharp photograph to be obtained at that moment with an exposure of 1-2 sec. From the electron-diffraction pattern it was established that this moment corresponds to the beginning of the chemical reaction: here, along with

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Fig. 1. Colloidal gold in the microchamber; $V = 80$ kV. a—$p = 170$ mm Hg, b—$p = 520$ mm Hg.

Fig. 2. Electron-microscopic images (a, b, c, c_0, d) and electron diffraction patterns (a', b', c') of the structure of a silver layer during reaction with hydrogen sulfide and oxygen; $V = 80$ kV. a, a'—initial layer, b, b'—layer 2 min after the start of the reaction, c_0, c, c'—layer 3 and 4 min after the start of the reaction, d—adjacent to the irradiated region: I—farther from the irradiated region, II—bordering the irradiated region.

Fig. 1

Fig. 2

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with the silver lines, lines of Ag_2S appeared (Fig. 2 $'$). The complete transformation of silver into Ag_2S in the observed region ended after 3-4 min (Fig. 2 $_0$, , $'$).

Further observations showed that such a rapid transformation of Ag into Ag_2S occurred only in the region irradiated by electrons. In the neighboring regions, shielded from irradiation, the original structure was preserved (Fig. 2).

Control experiments in a tube, carried out under conditions identical to those in the gas microchamber, showed that the rapid (within 2-3 min) transformation of Ag into Ag_2S occurs at a temperature of 95-100°. At a temperature below 80°, no noticeable change in the structure of silver is observed over such a short time. Consequently, the beam exerts a thermal action on the object, accelerating the reaction.

In the electron-microscopic study of the reaction process, in a number of cases a decrease in the amount of substance in the irradiated region and an increase in the adjacent region were observed (Fig. 2). Apparently, this occurred as a result of a considerable temperature difference between the irradiated and nonirradiated regions.

In addition to the positive action of the electrons, which promoted a more rapid course of the reaction, their negative effect was also observed, manifested in the formation on the object of a film whose thickness increased in proportion to the time and intensity of irradiation. The appearance of the film led to a significant decrease in image contrast. In the case when the reaction proceeded faster than the process of film formation, it was possible to observe all stages of the reaction. Otherwise, the reaction stopped at one of the initial stages. In choosing the reaction regime, this circumstance must be taken into account.

Electron-microscopic observation of the reaction process between silver and hydrogen sulfide in the presence of oxygen made it possible to follow the process of the transformation of silver into silver sulfide and to discover, in doing so, that the layer of silver obtained by evaporation in vacuum consists of agglomerates that are not individual structural units but an aggregate of several structural units. It is not the entire agglomerate that enters into the reaction, but each structural unit separately, with subsequent coarsening due to coagulation of the particles during the transformation of silver into silver sulfide.

Thus, the method developed has shown the possibility of electron-microscopic investigation of objects in a gaseous medium with a resolution not less than 120 Å at a pressure close to atmospheric. Its application to the study of a chemical reaction makes it possible to follow in the electron microscope the reaction process between the gaseous and solid phases at various stages of the reaction.

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