THE PRODUCTION OF ULTRAFINE POWDERS OF FULLERITES BY THE SALTING OUT METHOD

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INTRODUCTION

Two main problems should be solved towards the mass use of fullerenes and fulleren-based materials. First, it is necessary to develop an effective technology for the fullerene containing soot production, and second, to develop technology for the cheap isolation and separation of a fullerene fraction. One of the fast and cheap methods for the fullerenes isolation from their solution is salting out. The work is devoted to the study on peculiarities of this method.

EXPERIMENTAL

The fullerenes containing soot has been produced by electric arc method [1]. Graphite cores have been evaporated in helium. The fullerenes separation from the soot has been performed in the Soxlet type continuous extractor. The samples topography has been studied using MBD-1 light microscope having a magnification of 1350 power. "Pentax-MZ-50" photographic camera has been used to photograph samples. X-ray patterns have been made by "DRON" type X-ray diffractometer using monochromatic CuK_α radiation.

Fullerenes solutions have been prepared by extraction of the fullerenes containing soot. Benzene and toluene have been used as extragents. The solutions containing 1.2-3.0 mass.% of fullerenes have been taken for experiments.

RESULTS AND DISCUSSION

a) Evaporation

During evaporation of solvents crystallization began at the gas-liquid-solid boundary. During crystallization from the toluene solution the crystals grow as vaporization of the solvent occurs from the triple boundary to the center. They have needlelike structure (Fig. 1, a). Under the same conditions other crystals grow at the triple boundary from the solution in benzene (Fig. 1, b).

The crystals growth in the drop volume has some peculiarities. Plenty of crystals precipitate from the solution in benzene, their size depends on growth time (Fig. 2, a). At sufficient stand the crystals gradually turn into a continuous film on the substrate surface (Fig. 3, a, b).

In the main the needlelike crystals precipitate in the volume from the solution in toluene. They can unite to form conglomerates (Fig. 2, b).

On the whole variety of geometrical forms of crystals growing from the solvents in hydrocarbons is determined by the solvent nature in particular surface tension and boiling point of the solvent.

If the first parameter is responsible for the crystals geometry, the second - for the growth rate. Experiments on changing surface tension for toluene and benzene shown that addition of gasoline into the toluene solution caused the crystals growth in the volume. The crystals are in the form of irregular hexa- and tetrahedral prisms (Fig. 2, b).

Addition of kerosene into the benzene solution does not allow nucleuses of a solid phase to precipitate at the triple boundary. Fragmentlike, transparent with a rink tint crystals are formed in the volume. They are not fixed on the substrate (glass). During evaporation of kerosene the dark-violet crystals precipitate in the solution. They are the same as those in crystallization from the solution in benzene without hydrocarbons addition (Fig. 1, b).

b) Salting out

In the experiments on salting out fullerenes from the solutions in benzene and toluene ethanol (C_2H_5OH) has been used. Two- and three atoms alkohols do not salt out fullerenes from hydrocarbons.

Addition of ethanol into the benzene solution causes separation of a precipitate in the form of highly dispersed powder (Fig. 4, a). Particles sizes vary from 1 to 10 μm. Sedimentation process lasts 5-6 hours. The 1-2 μm particles remain in the solvent volume in suspension.

After sedimentation of the precipitate in the solution the finest particles assemble in the chains like a highly cross-linked thermoreactive polymer, but they have a crystalline structure (Fig. 4, b, c).

During salting out fullerenes with ethanol from their solutions in toluene the precipitating crystals quickly unite in conglomerates (the huge "snow-flakes") that constantly pack (Fig. 4, d). For these samples X-ray

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analysis detects the crystalline structure with fcc lattice. Figure 5 shows the section in the diffractogram for samples studied. The peaks in the diffractogram correspond to 220 and 311 peaks for C_{60} fullerite [2]. Figure 5, b shows the same section in the diffractogram for the powder salted out from the solution in benzene. Considerable broadening in lines, and appearance of an intensive halo on the section studied evidence about a highly dispersed state of the sample.

Apparently upon addition of C_2H_5OH into the solution of C_{60} and C_{70} fullerenes mixture the C_{60} crystals are the first to precipitate, then after addition of extra ethanol the C_{60} precipitates.

Using the experimental results one can suggest the following technological chain for separation and isolation of fullerenes from their solutions in hydrocarbons:

1. Extraction

The fullerene containing soot is filled in with toluene. After filtering the soot and the fullerenes solution in toluene are produced.

$$(CB+F_S)+T=CB+(T+F_L)$$

2. Salting out

Ethanol is added into the fullerenes solution in toluene. The mixture of toluene and ethanol, and fullerenes in the solid state are produced.

$$(T+F_L)+E=F_S+(T+E)$$

3. Extraction

Water is added into the mixture of toluene and ethanol. The mixture is separated into two immiscibile fractions: toluene and the mixture of ethanol and water.

$$(T+E)+H_2O=T+(E+H_2O)$$

4. Rectification

At this stage ethanol and water are separated by rectification.

$$(E+H_2O)+Q=E+H_2O,$$

where **T** - toluene, $\mathbf{F_S}$ - fullerite, **E** - ethanol, **CB** - soot, $\mathbf{(T+F_L)}$ - fullerenes solution in toluene, **Q** - heat energy.

CONCLUSIONS

The possibility of using the method for salting out fullerenes with ethanol from their solutions in hydrocarbons has been shown in this work. Selection of fullerenes concentrations in the extract and amount of salter allows to carry out their fast and cheap isolation from the solution and perhaps separation in the fractions.

The fullerenes powders, produced by the method of salting out, have the high rate of dissolution in hydrocarbons, because they are superfine and ultrafine powders with very developed surface.

The proposed technological chain may be used for the fullerenes production on industrial scale.

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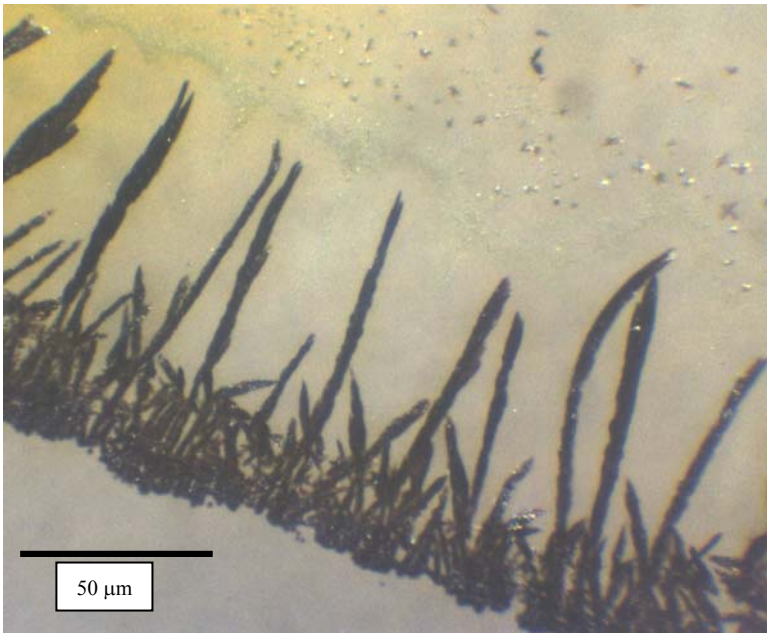

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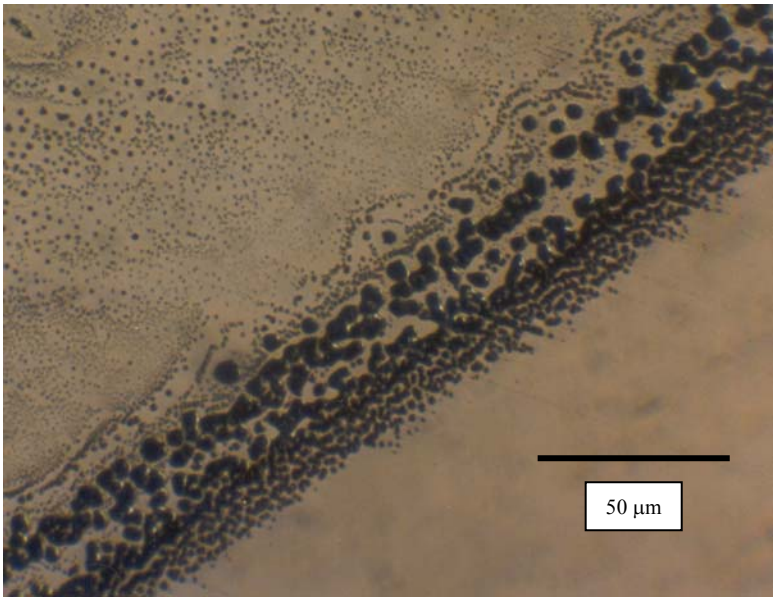

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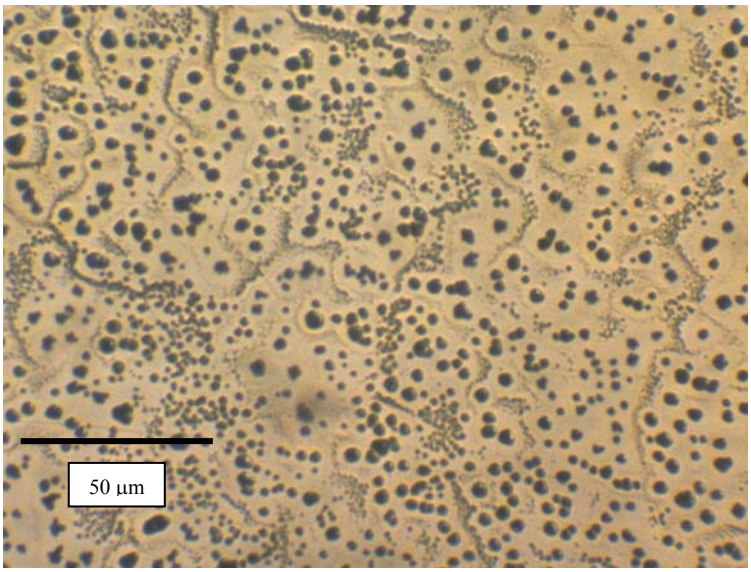
Fig. 1 / Рис. 1



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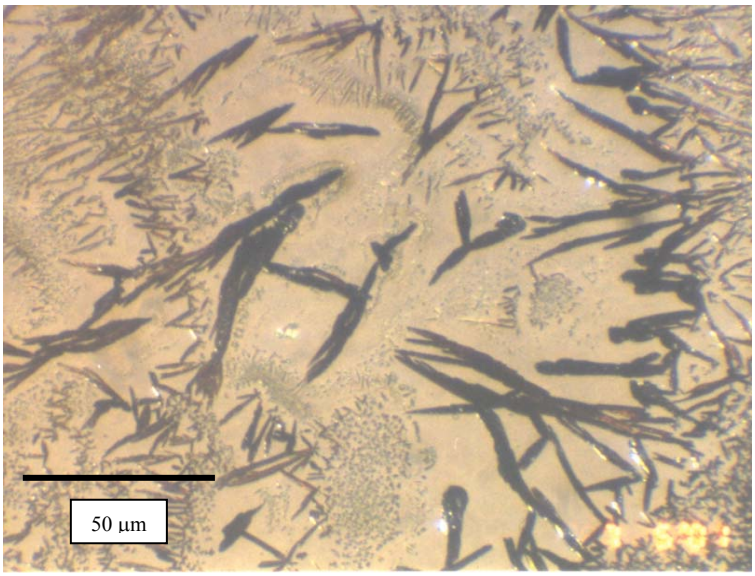

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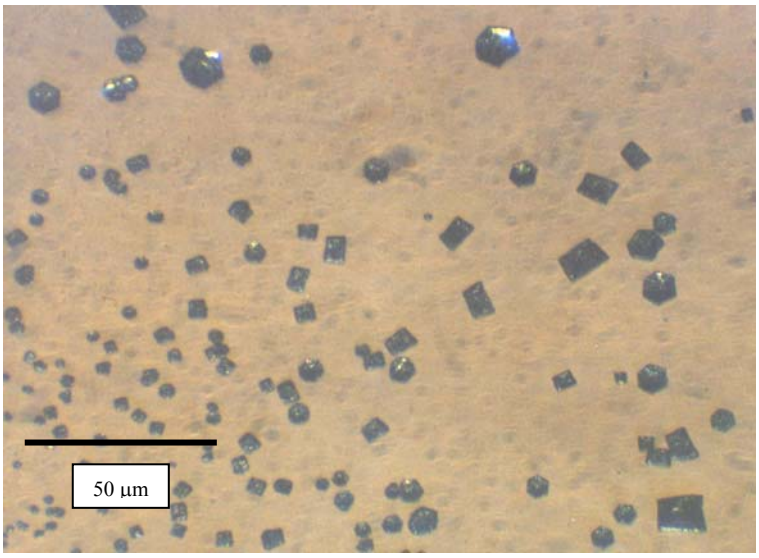

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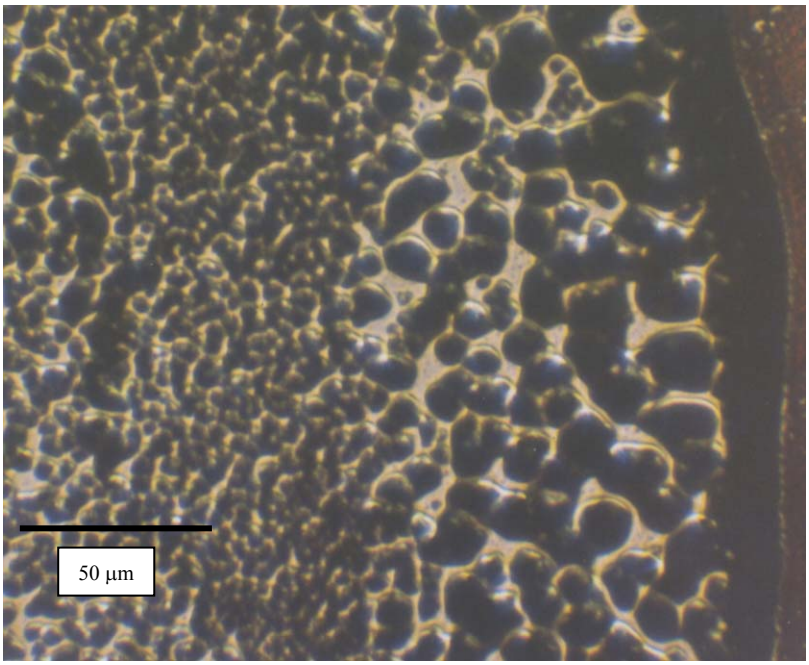
Fig.2 / Рис. 2



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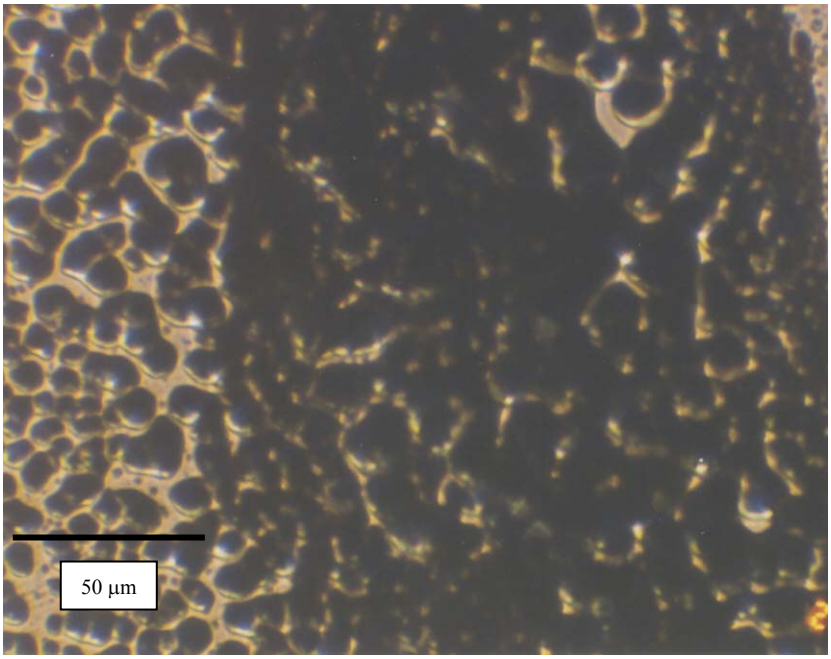

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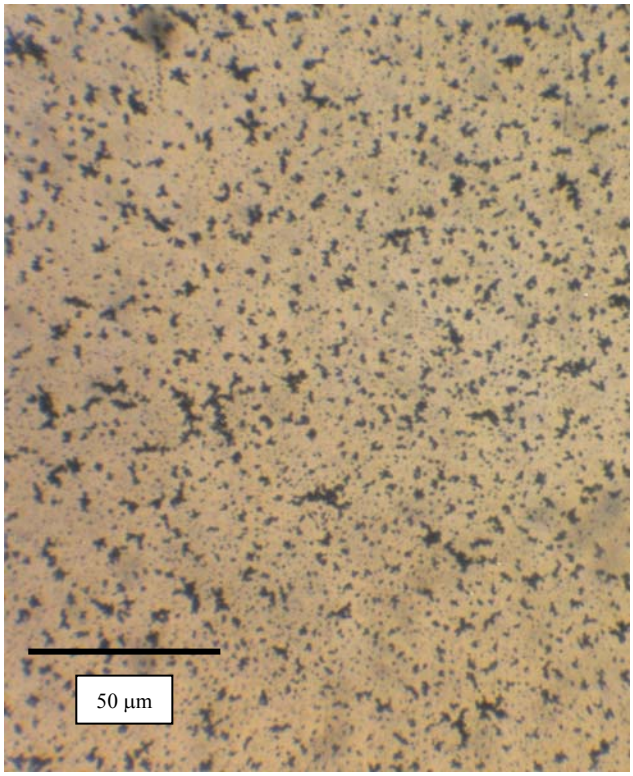

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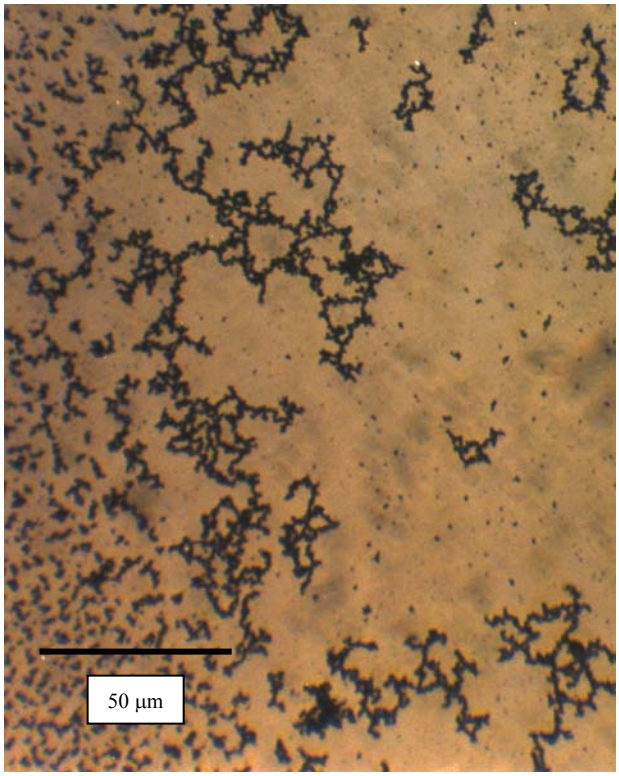

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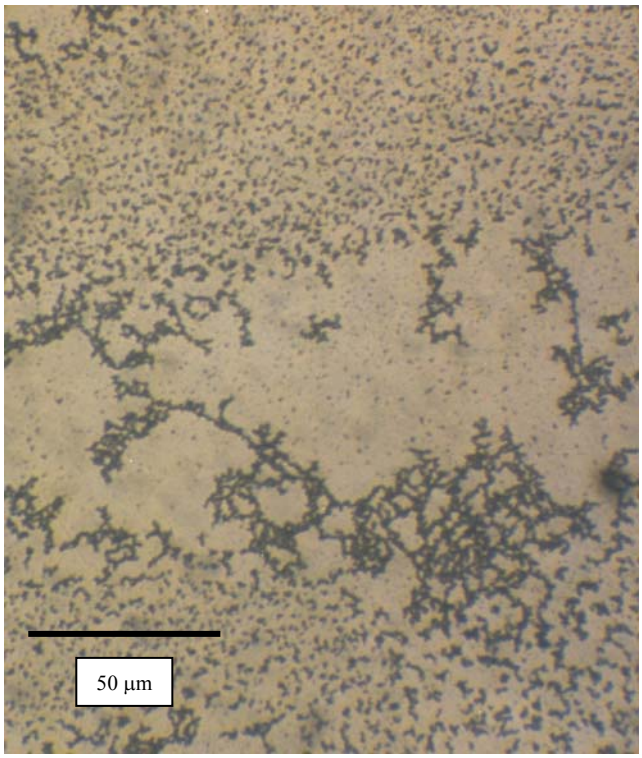

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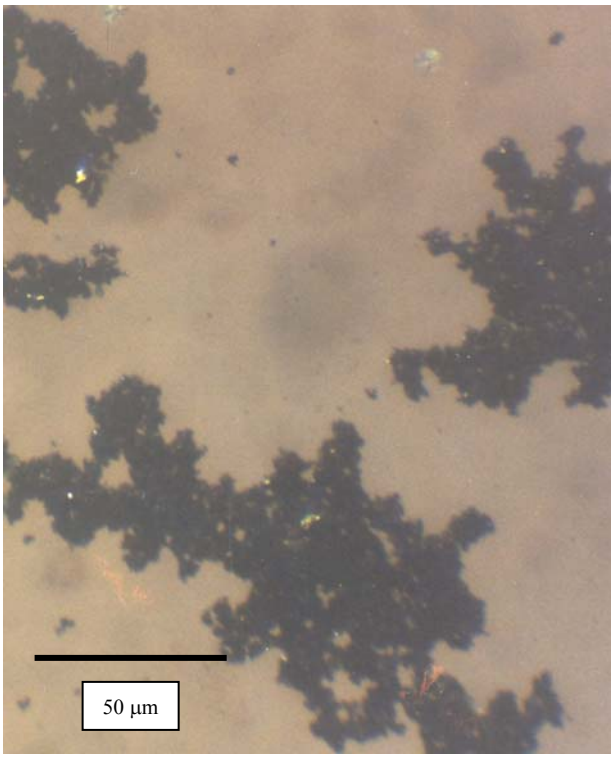

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Fig. 4 / Рис. 4

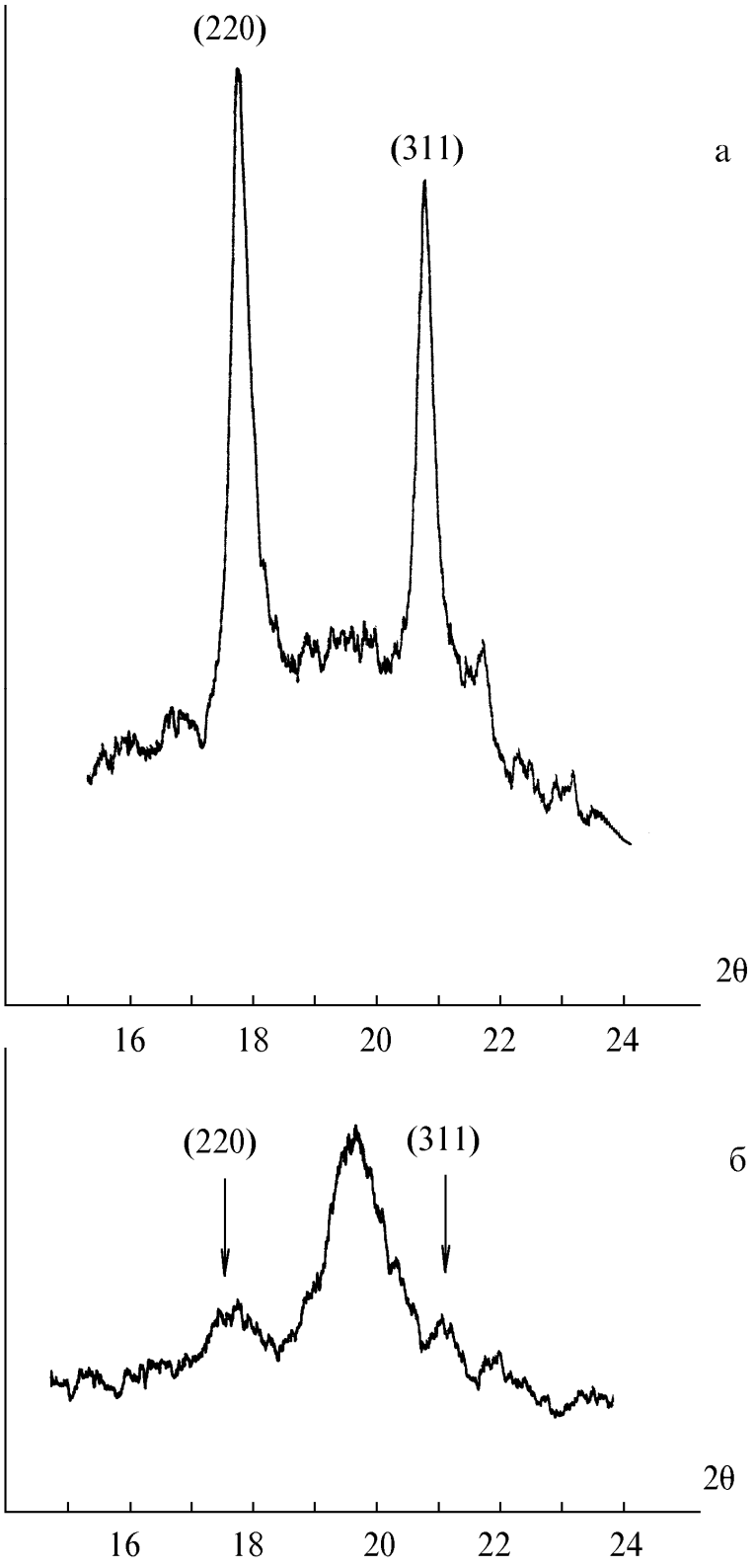

Fig. 5