ELECTROCHEMICAL BEHAVIOUR OF COMPOSITES A FULLERITE- MONOCRYSTAL OF COPPER

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Introduction

At present the significant number of theoretical and experimental works [1,2] about the problems of surface morphology and structure formation, physical and physical-chemical properties of fullerite films, their transformation at an irradiation depending on energy, doze and kind of bombardment ions are published. Protective properties of fullerite films at the stage of accumulation of experimental material are studied. It is shown [3], that on copper at presence of C_{60} under friction protective films are formed. The experimental results about electrochemical behaviour of fullerite films, which have been obtained in different ways, in carbon contained solvents, and the process restoration of fullerene at presence of different cations are presented in [4].

In the present work data about protective action of fullerite coatings on copper in the modeling corrosion environment (water solution of chloride-sodium) depending on orientation of substrate (monocrystal of copper) and on its change at an irradiation of covering by low energy ions of argon are presented.

Results and discussion

Fullerite films were obtained by thermal evaporation at 460 ºC of the mixture of fullerites, which contained 84% - C_{60} and 14% - C_{70} (the fullerites were synthesized in IPM NASU) on VUP-5M device at the pressure of $2\cdot10^{-5}$ Torr on heated up to 160 ºC copper monocrystals. Monocrystals were grown up by Bridgman- Stockburger method from copper (OSCh II-4) containing basic component 99,996%. Orientation of grown monocrystals was defined by X-ray, after that they were cut into samples by acid saw (height 0,007…0,008 mm) along crystalline planes (100), (110) and (111), respectively.

For irradiation fullerite-copper composites were placed in the vacuum chamber. The beam of accelerated ions was directed at the angle of 45º between beam and plane of substrate. The energy of ions was 3-4 keV, a doze of irradiation - 10^{18}-10^{19} ion·m^{-2}.

X-ray research of composites was carried out with the help of difractometer DRON-4M.

The electrochemical behaviour of fullerite-copper composites was studied using potentiodynamic method in 3-% water solution of sodium chloride which was carried out with help potentiostat P5827-M. The composite was placed to electrochemical cell with non divided electrode space. As the electrode of comparison chlorine-silver electrode was used, and as auxiliary electrode platinum wire was used. The surface of composite covered with isolating varnish, except working area (20 mm^2). The Stationary potential measured two hours after placing the sample into electrochemical cell. Cathode and electrochemical curves were measured by changing polarization potential gradually by 20 mV step with stability on each step for two minutes.

The dependence of electrochemical behaviour of fullerite coatings on substrate orientation was established (figures 1-3). For copper monocrystals we could observe anisotropy of thermodynamic instability, which was evaluated at value of stationary potential: (110)<(111)<(100). The corrosion velocity, which was evaluated from corrosion current, increased in the range (110)<(100)<(111). The fullerite coatings on the copper monocrystals have protection properties, which is proved by the presence of significant increase in stationary potential, for example for composite on (100) shift in positive side more than 200 mV, and almost 4 times decrease in corrosion current. The irradiation of their coatings by argon ions lead to significant decreasing of stationary potential and increasing of corrosion velocity of composites.

In addition, composites C_{60}\Cu(100) turned out to be most sensitive to irradiation, for which the stationary potential shifted from –175 mV to -910 mV, and the corrosion current increase almost in order of value. The minimum deterioration of anticorrosion properties is observed for composites C_{60}\Cu(111), for which the decreasing of potential was no more than 50 mV, and decrease in corrosion current was insignificant (30%).

The analysis of experimental data obtained showed the existence of anisotropy of electrochemical behaviour of fullerite coatings $U_{st}^{100} > U_{st}^{110} > U_{st}^{111}$; $j^{100} < j^{110} < j^{111}$. After irradiation by argon ions the anisotropy of stationary potential is preserved: $U_{st}^{111} > U_{st}^{110} > U_{st}^{100}$ and practically disappear for corrosion current; within the limits corrosion current is identical and equals to $2{,}2\cdot10^{-5}$ A/cm^2.

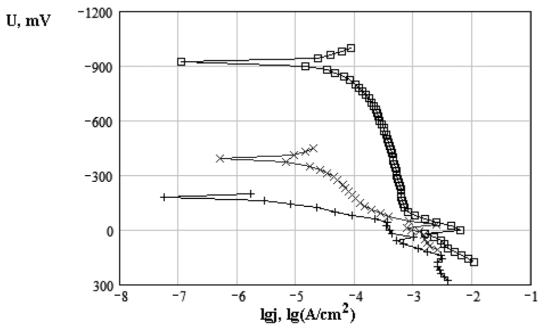

Fig.1. Polarization curves for monocrystal Cu(100) (x), for composite C_{60}/Cu(100) before (+) and after (−) irradiation by Ar^+ ions.

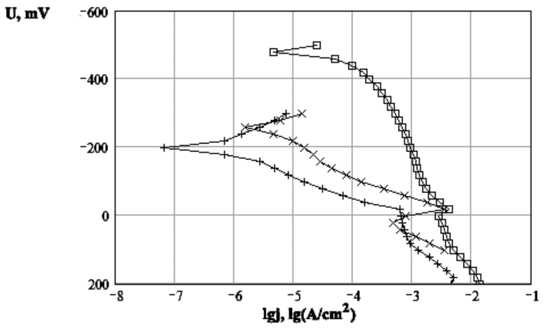

Fig.2. Polarization curves for monocrystal Cu(110) (x), for composite C_{60}/Cu(110) before (+) and after (−) irradiation by Ar^+ ions.

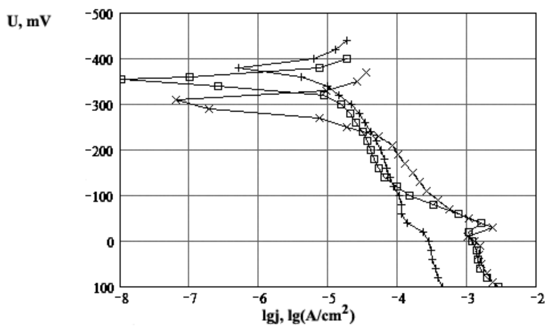

Fig.3. Polarization curves for monocrystal Cu(111) (x), for composite C_{60}/Cu(111) before (+) and after (−) irradiation by Ar^+ ions.

The polycrystalline fullerite films are being formed on the surface of copper monocrystals when fullerite deposition technology is used. For these films phase and polymorphous heterogeneity is typical. The phase heterogeneity evinces itself in the existence of C_{60} and C_{70} fullerites with dominating C_{60}. The polymorphous heterogeneity evinces in co-existence of the face centered cubic and hexagonal modifications. From intensity of diffraction maximums, it follows, that the hexagonal modification is predominant for substrate orientations (110) and (111). Disordering C_{60} structure resulting in the formation of dislocation implantation loops, as well as an increase in quantity of packing defects and vacancies occurs during irradiation by argon ions.

The splitting of X-ray maximums of cubic C_{60} and C_{70} modifications in fullerite coatings on the Cu(110) and Cu(111) is observed. It can mean the beginning of the transition to a lower symmetry structure.

Conclusions

Thus, the protective properties of films correlate with their heterogeneity and defects: the lower heterogeneity and quantity of defects are the higher the protective properties of fullerite films are.

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