V. A. Trapeznikov. *Study of surface layers by the method of electron spectroscopy.* The smaller is the depth of the analyzed layer, the greater is the amount of information on the surface layers of the material, as compared with information on its bulk, that can be obtained by different methods. For the overwhelming majority of the methods used to study materials in the condensed state, the depth of the analyzed layer is so large that the relative fraction of the surface information on the composition, properties and processes occurring on the surface at a depth of one or several atomic layers, is negligibly small and it is unnoticeable in the total information obtained. The method of electronic spectroscopy in all its diverse forms (x-ray-electronic, photoelectronic, Auger spectroscopy, abbreviated as XES, PES, and AES) is the most informative method of all surface methods, of which there are already more than 50,[1] because for this method the depth of the analyzed layer is determined by the average mean-free path of electrons, which for different materials and energies of excited electrons is equal to a few or tens of angstroms, a magnitude comparable to the Debye screening radius—the main dimensional parameter of the surface. This problem is discussed in greater detail in a review of studies of the surface layers of materials in the condensed state.[2]

Surface effects in solids are manifested most strongly in samples and those parts of the samples where the largest deviations from the classical state with an ordered arrangement of atoms in the crystal lattice are observed in samples of macroscopic size. Such effects are very significant for the outer surfaces of bodies with a large specific surface area (powders, especially aerosol) and amorphous materials, in cracks, for internal interfaces: boundaries of grains and of blocks in a mosaic pattern, interphase boundaries, and layers between coatings and the main material.

The study of nickel aerosol powders by the XES method and based on the saturation magnetization[3] showed that the drop in the saturation magnetization for small particles of size ~ 100 Å is explained by their oxidation. The thin oxide layer on surfaces of such supersmall particles could not be observed by other methods. The temperature stability of the oxide is different in powders of different sizes. A procedure has been developed for determining the thickness of the oxidized layer, the depth of the analyzed layer, and the diameter of the particles from the ratio of the intensities of electron spectra from oxidized particle surfaces and from unoxidized nuclei. For example, the smallest size of particles is 70 Å, the depth of the analyzed layer is 20 Å, the thickness of the oxide layer on the surface of the particles is 10 Å, and the temperature at which the oxide vanishes when such particles are heated is 250°C, whereas for macroscopic samples the temperature of restoration and dissociation of such an oxide is much higher. An analogous result was obtained by an electron-diffraction study of the phase composition of the initial stages of a cobalt condensate from an amorphous state,[4] where the temperature of its restoration increases with the thickness of the oxide layer. Such a CoO layer 10 Å thick is restored at a temperature of 300°C, which is much lower than the temperature for the macroscopic sample.

Widespread use of XES in studies of the structure of thin surface layers of samples of hard amorphous metallic alloys (HAMA) enabled the observation of a number of interesting effects. Thus, in the case of the corrosion-resistant HAMA $FeCr_{10}C_7P_{13}$, obtained by quenching from the liquid state, an anomalously high surface content of carbon, forming here a C–C bond with mixed sp^2 and sp^3 hybridization of the valence electrons was observed.[5,6] Figure 1 gives an idea of the distribution of the alloy components over the depth from the surface, obtained under different vacuum conditions (10^{-6} and 10^{-9} Torr). The latter does not affect the result because of the passivation of the surface of the alloy. A direct study of the electronic spectra of the inner levels and of the valence band in the HAMA FeC_7P_{13} over a wide temperature range, including the transitions HAMA →crystalline metallic alloys→liquid metallic alloys, first demonstrated the identity of the spectra of the hard amorphous and liquid states of the alloy.[7] At the same time it turned out that the transition HAMA→crystalline metallic alloy ($FeCr_{10}C_7P_{13}$, FeC_7P_{13}) is accompanied by a different restructuring of the composition and nature of the bonds in the surface layers of the samples.[8] The idea that the composition of thin surface layers of the HAMA $FeX_{10}C_7P_{13}$ (X = Cr, MO), obtained by quenching of the liquid from different temperatures of overheating, remains constant was confirmed experimentally. The discovery of the concentration "inheritance" of the composition of surface layers of HAMA is of great significance. As it turned out, the carbon concentration on a freshly prepared (after ion-etching in a high vacuum) surface of the HAMA $FeX_{10}C_7P_{13}$ (X = Cr, MO) is on being restored heated to magnitudes which are characteristic of the initial surface (before etching) of the samples. Based on the measurements of the kinetics of the

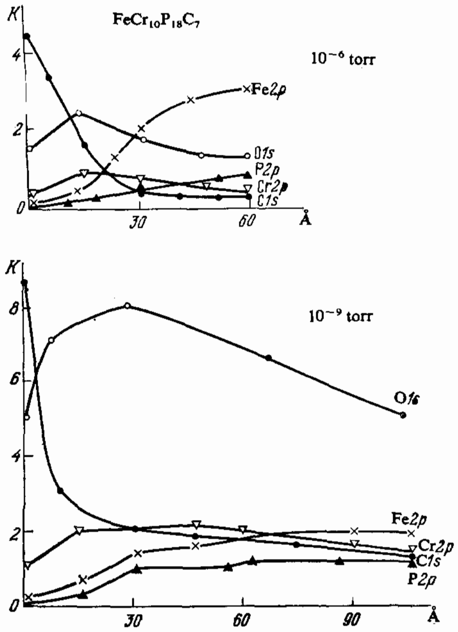

FIG. 1. Distribution of the concentration of components over the depth from the surface of amorphous samples, studied under different vacuum conditions.

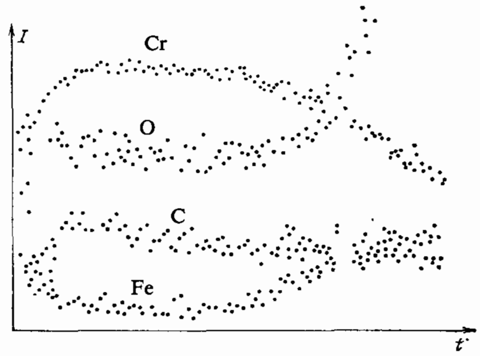

FIG. 2. Dependence of the intensity of the Auger spectra of chromium, iron, and impurities over the depth on the time of etching of an electrolytic chromium coating on steel.

surface accumulation of carbon in HAMA, a novel technique was developed for determining the diffusion characteristics of carbon in HAMA. As a result, a nearly linear temperature dependence was established for the coefficient of diffusion of carbon, indicating that the mechanism of diffusion of carbon in an iron-based HAMA is liquid-like.[9]

Cracks, which concentrate stresses, sharply lower the strength of materials. The elimination of cracks increases strength, as demonstrated by A. F. Ioffe in a well-known experiment with a crystal of rock salt by dissolving cracks on the surface of the sample in water. In Ref. 10 cracks on aluminum oxide were healed by deposition of copper. It was shown from the electronic spectra that the cracks are not healed completely by the deposit, as envisaged in Ref. 11, but only partially.

The transitional layer between the coating and the main material sometimes plays no less a role than the coating itself, since the coating chips off when it does not adhere strongly enough to the base. Chrome-plating of steel is widely used to increase the corrosion resistance and wearability of parts. An AES and XES analysis of electrolytic chrome coatings on steel parts which did not meet the requirements for chipping and wear showed that the damage appears due to weak adhesion as a result of the breakdown of the orientation-dimensional correspondence between the coating and the main material as a result of the appearance of oxygen in the transitional layer and formation of iron oxides (Fig. 2). It is evident in the figure that when the transitional layer is reached during ion etching, the curves of the intensity of the iron and oxygen spectra simultaneously begin to grow as the chromium intensity is reduced. The formation of oxides in the transitional layer accompanying electrolytic chrome-plating from an aqueous electrolyte is also confirmed by data obtained by scanning with an Auger probe over the surface of a section in the transitional layer with alternate setting of the energy analyzer of the apparatus for detection of iron and oxygen spectra—the position of the reflections from the two elements coincide. This result of the electron-spectral studies explains the different degree of breakdown of the strength of adhesion of the coating to the base on parts obtained in different factories and within a single factory depending on the time of year. The reason lies in the different concentration of free oxygen in the water obtained from different sources and used for making the electrolyte and the different saturation of the water with oxygen in the same source at different times during the year. It is difficult to improve substantially the adhesion of chromium on iron in electrolytic chrome-plating because of the large electronegativity of O_2, which, even with the careful cleaning of the surface of the part prior to chrome-plating, still causes the formation of Fe oxides in the transitional layer during the plating process. A more suitable method for depositing chromium on iron is vacuum sputtering and ion implantation, as a result of which the same method of analysis as used for the electrolytic coating shows that the oxygen concentration in the transitional layer does not increase together with the iron concentration (Fig. 3).

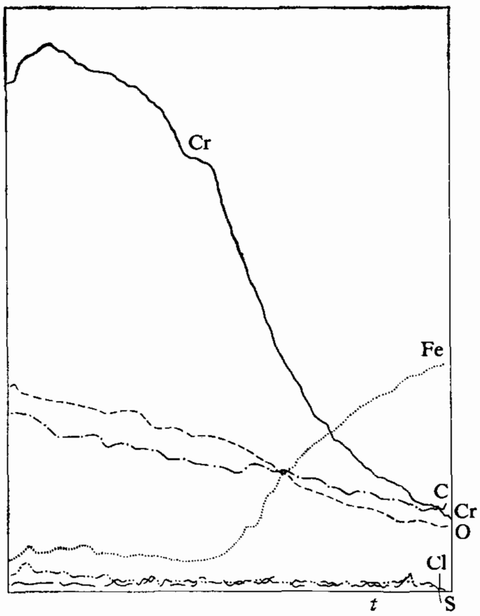

FIG. 3. Dependence of the intensity of Auger spectra of chromium, iron, and impurities over the depth on the time of etching of a chromium coating on steel obtained by vacuum sputtering with an ion beam.

Vacuum chrome-plating has one other important technological advantage over electrolytic plating: the chrome-plated parts can be forged without fear of destroying the coating, because such a coating is softer and correspondingly more plastic, which cannot be said of electrolytic chrome whose brittleness as a result of saturation with hydrogen is well known. Stamping of vacuum chrome-plated parts instead of parts without a coating followed by electrolytic chrome-plating has a number of other advantages: the part can be obtained an order of magnitude more quickly and waste due to variable thickness in different sections of the finished part is eliminated, making unnecessary 100% monitoring of the basic dimensions and replacing this operation by selective monitoring of the instrument.

Studies of grain boundaries, which are exposed when samples are fractured, by the method of electron spectroscopy and which have a ten-year history, are being further developed due to the possibilities opened up by the new techniques, for example, in the comparative study of the surfaces of fractures, obtained in the vacuum of a spectrometer and in air.[12] This is important in a number of respects. It is not always possible to obtain a fracture in a vacuum, where the exposed surface is not subjected to the action of the medium. In particular, this is important for determining the possibility of studying fractures in parts fractured during use in air. The conditions in the external medium can in a number of cases have a decisive effect on the mechanism of embrittlement. The results of studies of the surfaces of fractures obtained in a vacuum serve as a standard in this case. The study of the surface of fractures in 37XH3A steel in a state of temper brittleness revealed a phosphorus content at the grain boundaries exceeding the average content in the bulk by a factor of 600. A study of fractures obtained in vacuum and in air showed that the results of the quantitative analysis for the segregated phosphorus element are in good agreement, and the disagreement does not exceed the error in the quantitative analysis by the XES method. In the case of a fracture in air, however, information on the segregation of oxygen is lost. It is very important to obtain information on the state of the internal surfaces of the interface in a natural state, when they are located inside the material, without their being opened up in some manner. This can be done by using the Mössbauer method for studying the states of grain boundaries, using the diffusion of active isotopes in to the boundaries, which was demonstrated in Ref. 13 in a study of the state of cobalt atoms on copper boundaries.

The XES method plays an important role in the analysis of failures in microelectronics. In order to determine the reasons for the decrease in the welding strength, spectra obtained from locations of strong and weak contacts of Au in Ag were studied.[14] A weak bond was associated with the presence of sulfur and silver in the oxidized state at the location of the contact. Sulfur, present in the form of an impurity in the material of the contact, diffuses to the surface during welding and apparently facilitates the oxidation of silver. An examination of rejected multilayered microcircuit boards established the presence of copper and chromium atoms from lower-lying layers on the surface of the nickel coating. It was shown that these elements diffuse to depths of several tens of thousands of angstroms when the boards are heated to temperatures > 250 °C as a result of a breakdown in the coating technology. A high oxygen concentration (an oxygen barrier), appearing as a result of the decomposition of the substrate, was observed at the interface of a titanium coating on an organic substrate. This makes possible a constant oxidation of titanium and preserves the required adhesive and electrical properties of the coating.

The development of new and the improvement of existing methods play an important role in the present rapid development of the physics, chemistry, and mechanics of surfaces. This applies primarily to the most informative method of electron spectroscopy. The development of UVS with the use of intense (up to 10%) HeII emission (40.8 eV), in addition to the traditionally used HeI emission (21.2 eV)[15] makes possible the experimental study of the role of the ionization cross section for states by a direct method, for example, it elucidates the d and f symmetry by comparing with the sp symmetry, which is important in the study of transition metals; it permits studying over the entire depth the distribution of the states of wide valence bands (for graphite 24.5 eV) with a resolution which is two orders of magnitude higher than that obtained with the use of x-ray excitation in the XES method. Finally, this opens up the possibility of studying efficiently the action of hard ultraviolet and soft x-ray radiation on materials. The study of nonconducting materials, for example, polymers,[16] which give a high charging of samples, requires the development of methods for eliminating charging by placing a copper grid in front of the surface studied, feeding the surface with low-energy electrons, etc. A number of the techniques used in electronic magnetic spectrometers, with which a significant part of the studies presented in this report were performed, are described in Ref. 17.

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