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The influence of electron irradiation on the structure of nanosized metal particles

Abstract. In this article has been studied the structure of nano-sized copper powders, before and after irradiation with high-energy electrons in the dose range 1-10 Mrad, using the methods of electron microscopy, small-angle X-ray scattering and X-ray photography. This paper presents the results of studies of the structure of nanosized copper powders, obtained by electric explosion of conductors. New structural phases with different lattice types and parameters have been detected. The presence of the shell electronic structure is confirmed by the experimental studies of the dependence of properties of metal clusters on the number of atoms in the cluster. Passage of a voltage of about 40 kV through the chamber with a 0.03 m long, 3x10-4 m thick, piece of wire, which causes disruption of conduction electrons, and even electrons of the outer shells. The disruption of the outer shells of electrons leads to the Coulomb explosion and formation of nanoparticles, between the atoms of which multiple (covalent) bonds are formed. The size of nanopowders is determined by the supplied energy.
Keywords: nanopowders, electron microscopy, small-angle X-ray scattering, X-ray.

Introduction

It is known that fundamental properties of different materials change in their nanosized state. A rapid development of nanotechnology in the past two decades has contributed to an increase in the interest of researchers to the study of properties and characteristics of external influences on the structure and properties of materials at the nanometer level. This interest stems primarily from the possibility of using nanopowders in the field of advanced materials and technologies, brand new appliances and devices. Basic physical properties of metal nanoparticles differ significantly from the properties of metals in the normal bulk state and in many cases are unique. In these systems, interesting combinations of electrical, magnetic, thermal, superconducting, mechanical and other properties, not found in bulk materials, have been discovered [1].

At the present time, to explain specific features of physical properties of metal nanoparticles the so-called "jellium" model is used, which assumes that clusters of alkali and rare-earth metals have a shell electronic structure [2], [4] similar to the shell structure of atomic nuclei. The presence of the shell electronic structure is confirmed by the experimental studies of the dependence of properties of metal clusters on the number of atoms in the cluster.

This paper presents the results of studies of the structure of nanosized copper powders, obtained by electric explosion of conductors [3]. Using a scanning electron microscope Quanta 200i 3D, the sizes of copper particles, having a spherical shape of radii ranging from 30 nm to 300 microns (Fig. 1), were determined. The particle size distribution in the studied powders was determined by the method of small-angle X-ray scattering on the diffractometer Hecus S3-Micro. Fig. 2 shows the average particle size distribution. Stable clusters of particles of a definite size are formed as a result of action of the following factors:

a) Passage of a voltage of about 40kV through the chamber with a 0.03m long, 3×10^{-4}m thick, piece of wire, which causes disruption of conduction electrons, and even electrons of the outer shells. The disruption of the outer shells of electrons leads to the Coulomb explosion [5], [6] and formation of nanoparticles, between the atoms of which multiple (covalent) bonds are formed. The size of nanopowders is determined by the supplied energy.

b) The interaction of delocalized electrons and the nucleus of the nanoparticle causes formation of superatoms [2], [4], having a smaller radius than the radius of ordinary atoms, which leads to

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formation of new phases with smaller parameters of a unit cell.

c) Another factor is the structure that defines the stable shape and size of the cluster, i.e. determines the minimum and maximum density.

X-ray studies of copper powders were made on the diffractometer DRON-2M using CuKα radiation. The X-ray diffraction pattern of a copper monolith (Fig. 3) has clearly visible peaks corresponding to the reflections from the (111), (200), (220) and (311) planes of FCC copper structure with the lattice size smaller than that of nanopowders. The x-ray photograph also has a low diffraction peak at a small angle, which may correspond to defects in the crystal structure.

Fig. 4 presents the experimental X-ray diffraction data of non-irradiated copper powders, which show that peaks (111) and (200) have shoulders and an additional complex peak at small angles. The calculations showed that the peak observed at an angle 2 □ = 35.07 corresponds to the reflection from the plane (100). It is known that the peak of (100) plane can be observed only in the presence of a phase with a primitive cubic lattice, which is not observed in bulk copper crystals. The experiments were carried out in air, and, hence, the superatoms having the same properties as metal atoms were covered by an oxide layer.

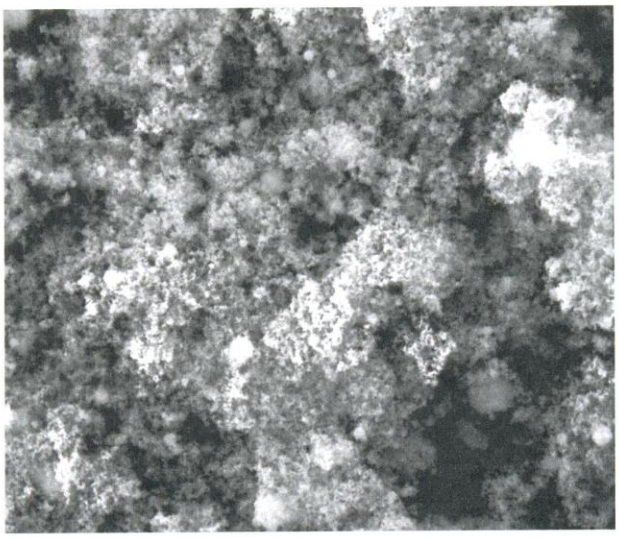

Figure 1 – A photograph of copper nanoparticles, obtained by electron microscopy

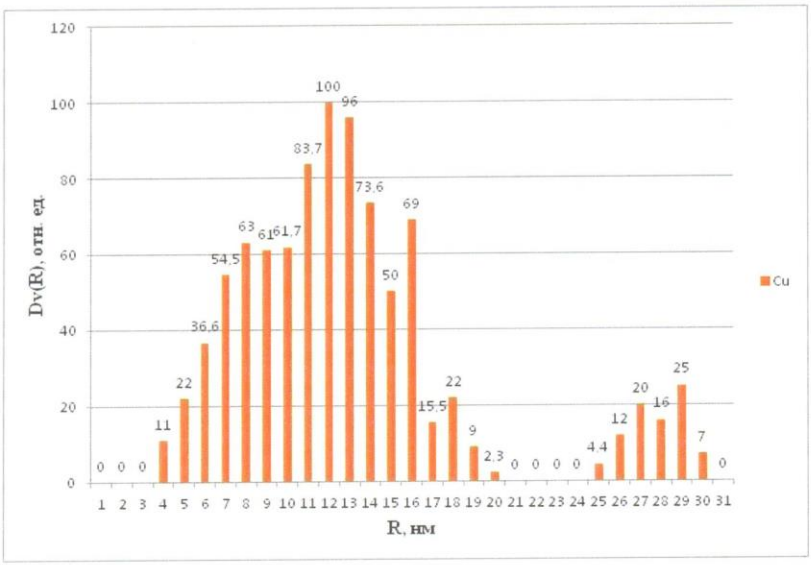

Figure 2 – The dependence of the volume function of the particle size distribution

The relatively low peaks, located between the peaks from (200) and (220) planes correspond to the reflections from copper oxides CuO and Cu_2O. These results indicate that the crystal structure of copper nanopowders is significantly different from that of the monolith. The splitting of the peaks can be attributed to the presence of clusters with different lattice parameters or the existence of several crystalline phases.

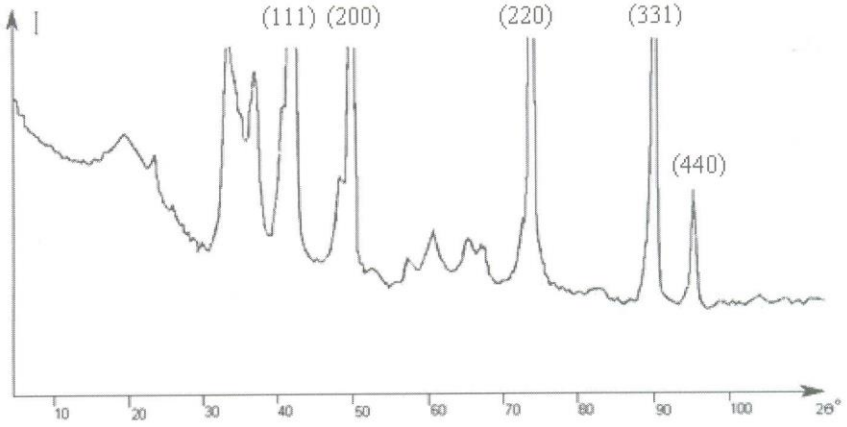

Figure 3 – A diffraction pattern of the copper monolith

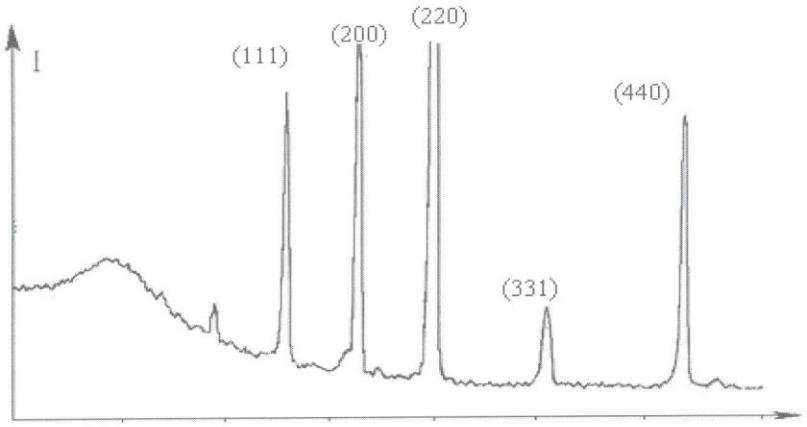

Figure 4 – Diffraction pattern of unirradiated copper nanopowder

The authors [3] suppose that structural changes in small particles are caused by the increase in their surface energy, which makes a considerable fraction of the volume energy. Therefore, in order to reduce the total energy of the system it may be advantageous to make such a deformation of the crystal, in which the decrease in the surface energy compensates the increase in the volume energy. In the simplest case, such a deformation is reduced to a change in the lattice constant of the crystal, which is often observed experimentally. For a more detailed study of specific features of the structure, the studied powders were irradiated by various doses of 2 Mev electrons. The irradiation was carried out in a vacuum chamber on the nano-electron accelerator ELU-4. Fig. 5 shows the diffraction pattern of the copper powder, irradiated by electrons to absorbed doses of 1 Mrad, which shows that peaks of (111) and (200) become narrower, and their splitting becomes more clearly seen.

The splitting of peaks, typical of the FCC copper structure, indicates the appearance of two new phases due to different radii of atoms, which, in turn, depend on the number of delocalized electrons. Reflections from the (100) plane may occur only in the presence of clusters with a primitive cubic lattice. In order to determine parameters of various phases, the radii of atoms in clusters were calculated, the results of calculations are presented in Table 1. The difference in the values of atomic radii is probably due to the fact that different clusters are formed by atoms with different numbers of delocalized valence electrons.

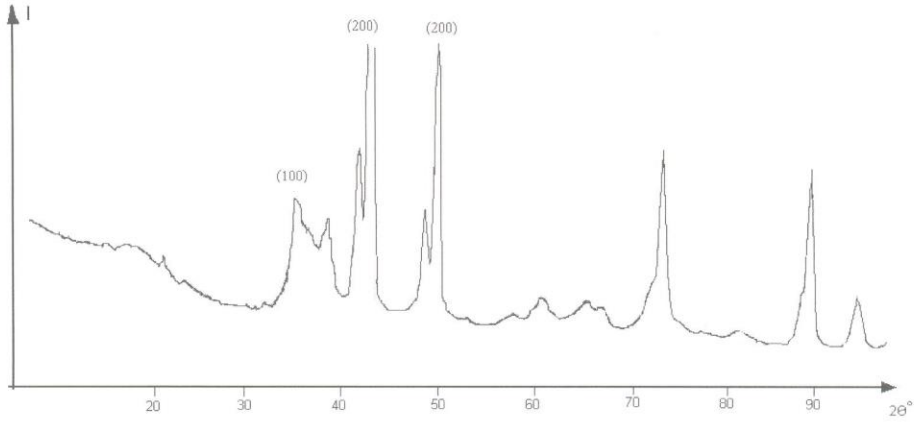

Figure 5 – Diffraction pattern of nanopowder copper irradiated to absorbed dose 1Mrd

Table 1 – Experimental parameters of Cu nanoparticles irradiated to a dose of 1 Mrad

Lattice type	*P*	F_1	F_2
Cluster radius, nm	8	12	16
Atomic radius, Å	1.2743	1.3158	1.2859
Lattice parameter, Å	2.5486	3.7218	3.6371
Residual electron shells of atoms	$3d^8$	$3d^{10}$	$3d^9$

A clear splitting of peaks shows that electron irradiation causes changes in the electron structure of atoms and clusters with quantitative redistribution of different structures. It increases the number of clusters with a strictly defined number of atoms corresponding to magic numbers. When a sample is irradiated with a dose of 5 Mrad (Fig. 6) the peak of the (100) plane increases, which shows that the electron irradiation causes an increase in the number of clusters with the coordination number 6 or a primitive cubic lattice among the powder particles. Fig. 7 shows the diffraction pattern of the copper powder, irradiated to a dose of 10 Mrad, which shows that splitting of (111) and (200) peaks vanishes, and the (100) peak becomes lower. Such intensive exposure to ionizing radiation leads to radiation fragmentation of nanoparticles, which, firstly, causes formation of particles of optimal size (magic number), and, secondly, agglomeration of nanoparticles.

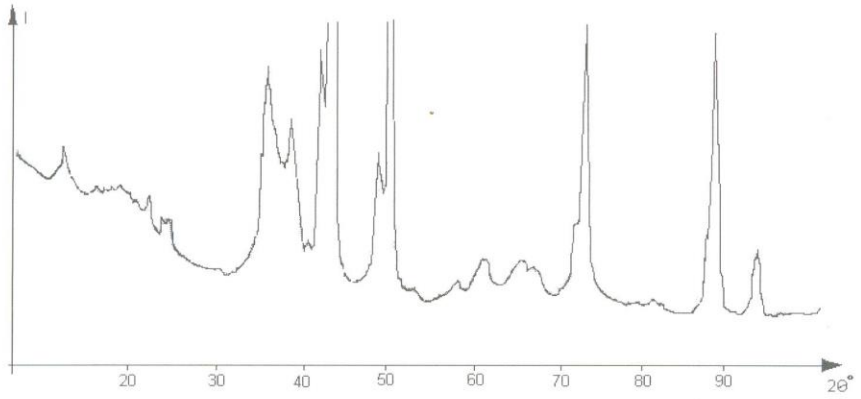

Figure 6 – Diffraction pattern of copper nanopowder irradiated to absorbed doses of 5 MWP

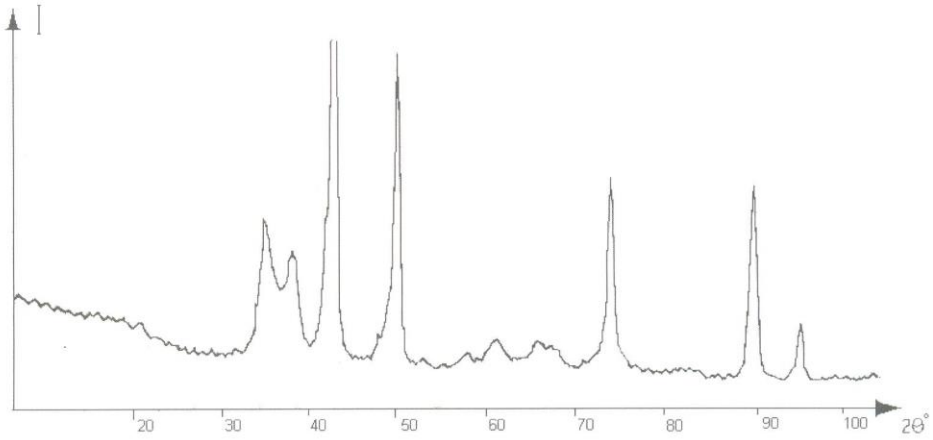

Figure 7 – Diffraction pattern of copper nanopowder irradiated to an absorbed dose of 10 Mrad

Conclusion

It has been established that nano-sizes depend significantly on the electron structure of atoms, and therefore several different structural phases can coexist. The presence of three crystalline phases was detected. A new copper phase with a primitive cubic lattice, not typical of bulk copper crystals, was discovered.

It was found out that at low irradiation doses the ordering processes in the existing crystalline phases dominate, which is caused by the increase in the number of clusters with a stable electron structure of atoms. An increase in the irradiation dose causes, due to the Coulomb explosion [5, 6], splitting of nanoparticles to the magic numbers, as the most stable structures, and agglomeration of nanoparticles.

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