

# Key Engineering Materials

Volume II

Interdisciplinary Concepts and Research

Editors

François Kajzar, PhD

Eli M. Pearce, PhD

Nikolai A. Turovskij, PhD

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Apple Academic Press

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Volume II: Interdisciplinary Concepts and Research



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*Edited by*

**François Kajzar, PhD, Eli M. Pearce, PhD,  
Nikolai A. Turovskij, PhD, and Omari Vasilii Mukbaniani, DSc**

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Apple Academic Press

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TORONTO NEW JERSEY

CRC Press  
Taylor & Francis Group  
6000 Broken Sound Parkway NW, Suite 300  
Boca Raton, FL 33487-2742

Apple Academic Press, Inc  
3333 Mistwell Crescent  
Oakville, ON L6L 0A2  
Canada

© 2014 by Apple Academic Press, Inc.

Exclusive worldwide distribution by CRC Press an imprint of Taylor & Francis Group, an Informa business

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Version Date: 20140124

International Standard Book Number-13: 978-1-4822-2427-6 (eBook - PDF)

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# LIST OF ABBREVIATIONS

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AFM	Atomic force microscopy
ATP	Adenosine triphosphate
BGAF	Benzoguanamine formaldehyde resins
BSA	Bovine serum albumin
CNR	Chlorinated natural rubber
CP	Critical point
DC	Dupli-color
DEX	Dextran
DLS	Dynamic light scattering
DM	Dry matter
DSS	Dextran sulfate sodium
DTGS	Deuterated triglycine sulfate
EDX	Energy-dispersive X-ray
ELPP	Elastomeric polypropylene
EPDM	Ethylene propylene diene monomer
EPR	Ethylene propylene rubber
ESEM	Environment scanning electron microscope
ESR	Electron spin resonance
FG	Fibrinogen
FID	Flame ionization detector
FMR	Ferromagnetic resonance
FPLC	Fast protein liquid chromatography
FTIR	Fourier transform infrared
GAG	Glycosaminoglycan
GC	Gas chromatograph
GFU	Gas fractionation unit
HC	Hydrocarbons
HCO	Hydrocarbon oxidizing
HDPE	High density polyethylene
HPLC	High-performance liquid chromatography
HT	Heterotrophic bacteria
IEF	Iso-electric focusing
IPP	Isotactic polypropylene
IR	Infrared
IR MDCIR	Infrared microscopy of multiply disturbed complete inner reflection
LDPE	Low density polyethylene
MBTS	Dibenzothiazole disulfide
MFI	Melt flow index

MLR	Mass loss rates
MNPs	Magnetic nanoparticles
MNSs	Magnetically targeted nanosystems
MPN	Most probably number
NMR MAS	Nuclear magnetic resonance, magic-angle spinning
OM	Optical microscopy
OSR	Oxidized starch reagent
PE	Polyethylenes
PEG	Poly(ethylene glycol)
PIB	Polyisobutylene
PMPA	Polyelectrolyte-mediated protein adsorption
PMPAS	Polyelectrolyte mediated protein association
PP	Polypropylene
PVC	Polyvinyl chloride
RHR	Rate of heat release
SA	Sodium alginate
SALS	Small angle light scattering
SBR	Styrene-butadiene rubber
SBS	Styrene-butadiene-styrene
SC	Sodium caseinate
SA	sodium alginate
SEM	Scanning electron microscopy
SiH	Silicon hydride
SLS	Static light scattering
SP	Softening point
TEAT	Triethanolaminotitanate
TMTD	Tetramethylthiuram disulfide
TPEs	Thermoplastic elastomers
TPV	Thermoplastic vulcanizates
Trp	Tryptophan
WS	Water steam
XPS	X-Ray photoelectron spectroscopy

# PREFACE

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This book, *Key Engineering Materials: Volume II: Interdisciplinary Concepts and Research*, provides both a rigorous view and a more practical and understandable view of key engineering materials for graduate students and scientists in related fields. This book will satisfy readers with both direct and lateral interests in the discipline.

This volume is structured into different parts devoted to key engineering materials and their applications. Every section of this book has been expanded, where relevant, to take account of significant new discoveries and realizations of the importance of key concepts. Furthermore, emphases are placed on the underlying fundamentals and on acquisition of a broad and comprehensive grasp of the field as a whole.

This book contains innovative chapters on the growth of educational, scientific, and industrial research activities among chemists, biologists, and polymer and chemical engineers and provides a medium for mutual communication between international academia and the industry. This book presents significant research and reviews reporting new methodologies and important applications in the fields of industrial chemistry, industrial polymers, and biotechnology as well as includes the latest coverage of chemical databases and the development of new computational methods and efficient algorithms for chemical software and polymer engineering.

This book's aim is to provide comprehensive coverage on the latest developments of research in the ever-expanding area of polymers and advanced materials and their applications to broad scientific fields spanning physics, chemistry, biology, materials, and so on.

This new book:

- provides physical principles in explaining and rationalizing polymeric phenomena
- features classical topics that are conventionally considered part of chemical technology
- covers the chemical principles from a modern point of view
- analyzes theories to formulate and prove the polymer principles
- presents future outlook on application of bioscience in chemical concepts
- focuses on topics with more advanced methods

— **François Kajzar, PhD, Eli M. Pearce, PhD,  
Nikolai A. Turovskij, PhD, and Omari Vasilii Mukbaniani, DSc**



# CHAPTER 1

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## CASE STUDIES ON KEY ENGINEERING MATERIALS IN NANOSCALE: KEY CONCEPTS AND CRITERIA

A. K. HAGHI and G. E. ZAIKOV

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## 1.1 INTRODUCTION

Technical and technological development demands the creation of new materials, which are stronger, more reliable, and more durable than materials with new properties. Up-to-date projects in creation of new materials go along the way of nanotechnology.

Nanotechnology can be referred to as a qualitatively new round in human progress. This is a wide enough concept, which can concern any area like information technologies, medicine, military equipment, robotics and so on. We narrow the concept of nanotechnology and consider it with the reference to polymeric materials as well as composites on their basis.

The prefix nano- means that in the context of these concepts the technologies based on the materials, elements of constructions and objects are considered, whose sizes make  $10^{-9}$  meters. As fantastically as it may sound but the science reached the nanolevel long ago. Unfortunately, everything connected with such developments and technologies for now is impossible to apply to mass production because of their low productivity and high cost.

That means nanotechnology and nanomaterials are only accessible in research laboratories for now but it is only a matter of time. What sort of benefits and advantages will the manufacturers have after the implementation of nanotechnologies in their manufactures and starting to use nanomaterials? Nanoparticles of any material have absolutely different properties rather than micro- or macroparticles. This results from the fact that alongside with the reduction of particles' sizes of the materials to nanometric sizes, physical properties of a substance change too. For example, the transition of palladium to nanocrystals leads to the increase in its thermal capacity in more than 1.5 times, it causes the increase of solubility of bismuth in copper in 4000 times and the increase of self-diffusion coefficient of copper at a room temperature on 21 orders.

Such changes in properties of substances are explained by the quantitative change of surface and volume atoms' ratio of individual particles that is by the high-surface area. Insertion of such nanoparticles in a polymeric matrix while using the apparently old and known materials gives a chance of receiving the qualitatively and quantitatively new possibilities in their use.

Nanocomposites based on thermoplastic matrix and containing natural, laminated inorganic structures are referred to as laminated nanocomposites. Such materials are produced on the basis of ceramics and polymers however, with the use of natural laminated inorganic structures such as montmorillonite or vermiculite which are present, for example, in clays. A layer of filler  $\sim 1$  nm thick is saturated with monomer solution and later polymerized. The laminated nanocomposites in comparison with initial polymeric matrix possess much smaller permeability for liquids and gases. These properties allow applying them to medical and food processing industry. Such materials can be used in manufacture of pipes and containers for the carbonated beverages.

These composite materials are eco-friendly, absolutely harmless to the person and possess fire-resistant properties. The derived thermoplastic laboratory samples have been tested and really confirmed those statements.

It should be noted that manufacturing technique of thermoplastic materials causes difficulties for today, notably dispersion of silicate nanoparticles in monomer solution. To solve this problem it is necessary to develop the dispersion technique, which could be transferred from laboratory conditions into the industrial ones.

What advantages the manufacturers can have, if they decide to reorganize their manufacture for the use of such materials, can be predicted even today. As these materials possess more mechanical and gas barrier potential in comparison with the initial thermoplastic materials, then their application in manufacture of plastic containers or pipes will lead to raw materials' saving by means of reduction of product thickness.

On the other hand, the improvement of physical and mechanical properties allows applying nanocomposite products under higher pressures and temperatures. For example, the problem of thermal treatment of plastic containers can be solved. Another example of the application of the valuable properties of laminated nanocomposites concerns the motor industry.

As mentioned earlier, another group of materials is metal containing nanocomposites. Thanks to the ability of metal particles to create the ordered structures (clusters), metal containing nanocomposites can possess a complex of valuable properties. The typical sizes of metal clusters from 1 to 10 nm correspond to their huge specific surface area. Such nanocomposites demonstrate the superparamagnetism and catalytic properties; therefore, they can be used while manufacturing semiconductors, catalysts, optical and luminescent devices, and so on.

Such valuable materials can be produced in several ways, for example, by means of chemical or electrochemical reactions of isolation of metal particles from solutions. In this case, the major problem is not so much the problem of metal restoration but the preservation of its particles that is the prevention of agglutination and formation of large metal pieces.

For example under laboratory conditions metal is deposited in such a way on the thin polymeric films capable to catch nano-sized particles. Metal can be evaporated by means of high energy and nano-sized particles can be produced, which then should be preserved. Metal can be evaporated while using explosive energy and high voltage electric discharge or simply high temperatures in special furnaces.

The practical application of metal-containing nanocomposites (not going into details about high technologies) can involve the creation of polymers possessing some valuable properties of metals. For example, the polyethylene plate with the tenth fractions of palladium possesses the catalytically properties similar to the plate made of pure palladium.

An example of applying metallic composite is the production of packing materials containing silver and possessing bactericidal properties. By the way, some countries have already been applying the paints and the polymeric coverings with silver nanoparticles. Owing to their bactericidal properties, they are applied in public facilities (painting of walls, coating of handrails, and so on).

The technology of polymeric nanocomposites manufacture forges ahead, its development is directed to simplification and cheapening the production processes of composite materials with nanoparticles in their structure. However, the nanotechnolo-

gies develop high rates; what seemed impossible yesterday, will be accessible to the introduction on a commercial scale tomorrow.

The prospects in the field of polymeric composite materials upgrading are retained by nanotechnologies. Ever increasing manufacturers' demand for new and superior materials stimulates the scientists to find new ways of solving tasks on the qualitatively new nanolevel.

The desired event of fast implementation of nanomaterials in mass production depends on the efficiency of cooperation between the scientists and the manufacturers in many respects. Today's high technology problems of applied character are successfully solved in close consolidation of scientific and business worlds.

Nanocomposites are polymers containing nanofillers. The microstructure of nanocomposites has inhomogeneities in the scale range of nanometers. Nanocomposite materials cover the range between inorganic glasses and organic polymers. Fillers of polymers have been used for a long time with the goal of enhanced performance of polymers and especially of rubber.

Nanofillers lists increased within years as well as the matrix in which they are used and interactions with traditional fillers. Nowadays, the development of polymer nanocomposites is one of the most active areas of development of nanomaterials. The properties imparted by the nanoparticles are various and focus particularly on strengthening the electrical conduction and barrier properties to temperature, gases, and liquids as well as the possible improvement of fire behavior. As a method which consists of reinforcing polymer chains at the molecular scale in the same way than the fibers at the macroscopic scale, nanocomposites represent the new generation of two-phased materials, associating a basic matrix to nanofillers inserted between polymer chains. Nanofillers can significantly improve or adjust the different properties of the materials into which they are incorporated. The properties of composite materials can be significantly impacted by the mixture ratio between the organic matrix and the nanofillers.

Fillers play important roles in modifying the desirable properties of polymers and reducing the cost of their composites. In conventional polymer composites, many inorganic fillers with dimensions in the micrometer range, for example calcium carbonate, glass beads, and talc have been used extensively to enhance the mechanical properties of polymers. Such properties can indeed be tailored by changing the volume fraction, shape, and size of the filler particles. A further improvement of the mechanical properties can be achieved by using filler materials with a larger aspect ratio such as short glass fibers. It is logical to anticipate that the dispersion of fillers with dimensions in the nanometer level having very large aspect ratio and stiffness in a polymer matrix could lead to even higher mechanical performances. These fillers include layered silicates and carbon nanotubes. Rigid inorganic nanoparticles with a smaller aspect ratio are also promising reinforcing and/or toughening materials for the polymers. The dispersion of nanofillers in the polymers is rather poor due to their incompatibility with polymers and large surface-to-volume ratio. Therefore, organic surfactant and compatibility additions are needed in order to improve the dispersion of these nanofillers in polymeric matrices. For example, layered silicate surfaces are hydrophilic and proper modification of the clay surfaces through the use of organic surfactants is needed. The obtained product is known as 'organoclay'. In this context, organoclays can be readily

delaminated into nanoscale platelets by the polymer molecules, leading to the formation of polymer clay nanocomposites. These nanocomposites belong to an emerging class of organic–inorganic hybrid materials that exhibit improved mechanical properties at very low loading levels compared with conventional microcomposites.

The behavior of polymer–nanofiller composites is directly related to their hierarchical microstructures.

Therefore, the mechanical properties of polymer–nanofiller composites are controlled by several microstructural parameters such as properties of the matrix, properties and distribution of the filler as well as interfacial bonding, and by the synthetic or processing methods. The interfaces may affect the effectiveness of load transfer from the polymer matrix to nanofillers. Thus, surface modification of nanofillers is needed to promote better dispersion of fillers and to enhance the interfacial adhesion between the matrix and fillers. Fabrication of homogeneous polymer nanocomposites and advanced computational techniques remains a major scientific challenge for materials scientists.

## 1.2 CASE STUDY-I

In the present case study, the formation of chemical bond between the atoms of polymer coating components and carbon metal-containing nanostructures with additions of silver or zinc is investigated for improving electrical conduction in coatings.

The analysis has been conducted by the X-ray photoelectron spectroscopy (XPS) method. The XPS allows to investigate an electronic structure, chemical bond, and nearest surrounding of an atom.

The investigation was conducted on a unique automated X-ray electron magnetic spectrometer with double focusing allowing the investigation of samples in both solid and liquid state, which has the following performance specifications: the resolution is  $10^{-4}$  and luminosity is 0.185% [1-10].

The electron magnetic spectrometer has a number of advantages in comparison with electrostatic spectrometers, which are the constancy of luminosity and resolution independent of the electron energy, and high contrast of spectra. The XPS method is a non-destructive method of investigation which is especially important for studying metastable systems.

Two samples of polymer coatings were studied:

- Silver-containing coating modified with carbon metal-containing nanostructures (70% Ag and 1% nanostructures) and
- Zinc-containing coating modified with carbon metal-containing nanostructures (60% Zn, and 1% nanostructures).

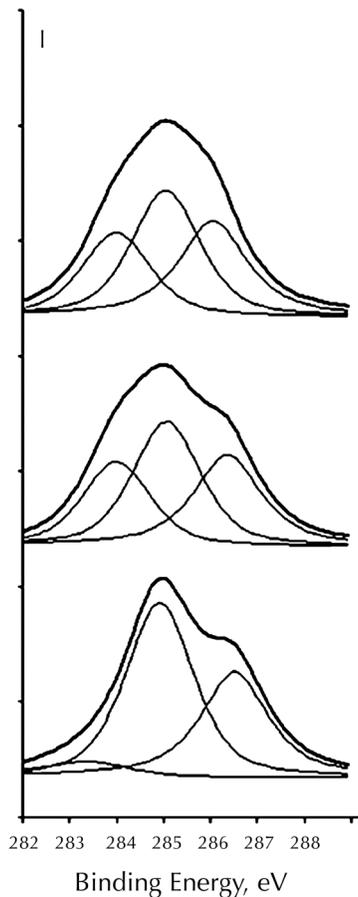
The carbon metal-containing nanostructure samples were prepared by low temperature synthesis. Carbon copper-containing nanostructures were mixed with polyethylene-polyamine  $H_2N[CH_2-CH_2-NH]_mH$ , where  $m = 1-8$ , through mechanic activation.

For improving the interaction of the polymer coating and carbon metal-containing nanostructures, the interaction of nanostructures with d metals, that is Ag and Zn, was used. The spectra of the C1s, Ag3d, Ag3p, and Zn2p core levels and the spectra of valence bands of the composites prepared were studied. The composites were carbon metal-containing nanostructures containing silver, a polymer coating with addition

of carbon copper-containing nanostructures functionalized with silver. The spectra of reference samples, that is Ag, Zn, and carbon copper-containing nanostructures, were studied as well. The cleanness of the sample surface was controlled by the O1s-spectrum. At heating to 300°C, oxygen on the surface is absent.

The decomposition of the spectra into components was performed with the help of a program based on the least squares method. For the spectrum decomposition, energy position, width of spectrum components and components' intensity based on the data obtained from the reference samples' spectra were entered into the program. The accuracy in the determination of the peak positions was 0.1 eV. The error in the determination of the contrast of the electronic spectra was less than 5%.

The C1s-spectrum (Figure 1 (a)) of carbon copper-containing nanostructures consists of three components: C-Cu(283 eV), C-H (285 eV), and C-O (287 eV).

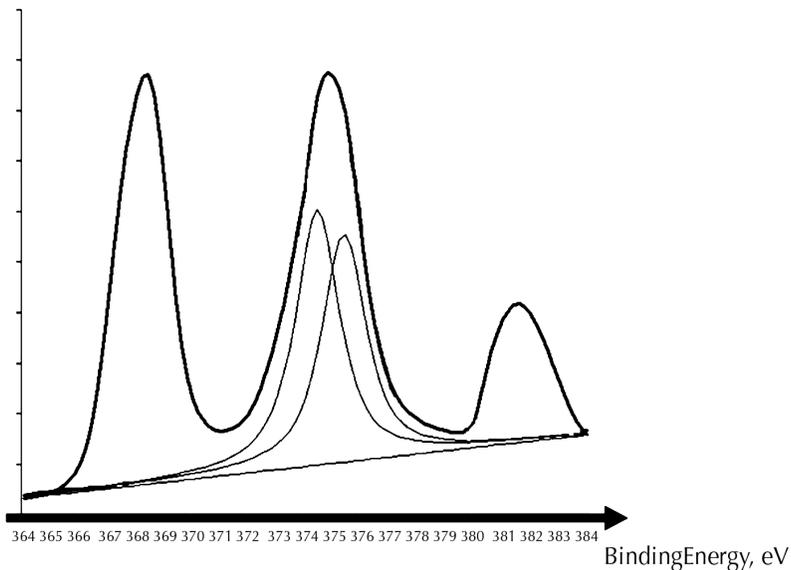


**FIGURE 1** C1s spectrum ((a) C1s spectrum of the copper/carbon nanocomposite, (b) C1s spectrum of the copper/carbon nanocomposite with silver, and (c) C1s spectrum coating) filled by silver and modified by copper/carbon nanocomposite.

In the C1s-spectrum (Figure 1 (b)) of the studied composite consisting of carbon copper-containing nanostructures functionalized with silver, the intensity of the first component C-Me significantly increases and the binding energy changes (283.8 eV), which corresponds to the data from experimental works and is associated with a larger localization of d electrons in silver than that in copper.

There are models, which describes the connection of the parameters of multiplet splitting of the XPS 3s spectra with a spin state, namely, the relative intensity of the maxima of the multiplets in the 3s spectra correlates with the value of the magnetic moment of the atoms in the d-metal systems; the distance between the maxima of the multiplets ( $\Delta$ ) provide the information about the exchange interaction of the 3s–3d shells. The change of their overlapping is associated with changes in the distance between the atoms and average atomic volume. The presence of changes in the shape of the 3s spectra provides the information about the changes in the chemical bond of the atoms in the nearest surrounding in the composite.

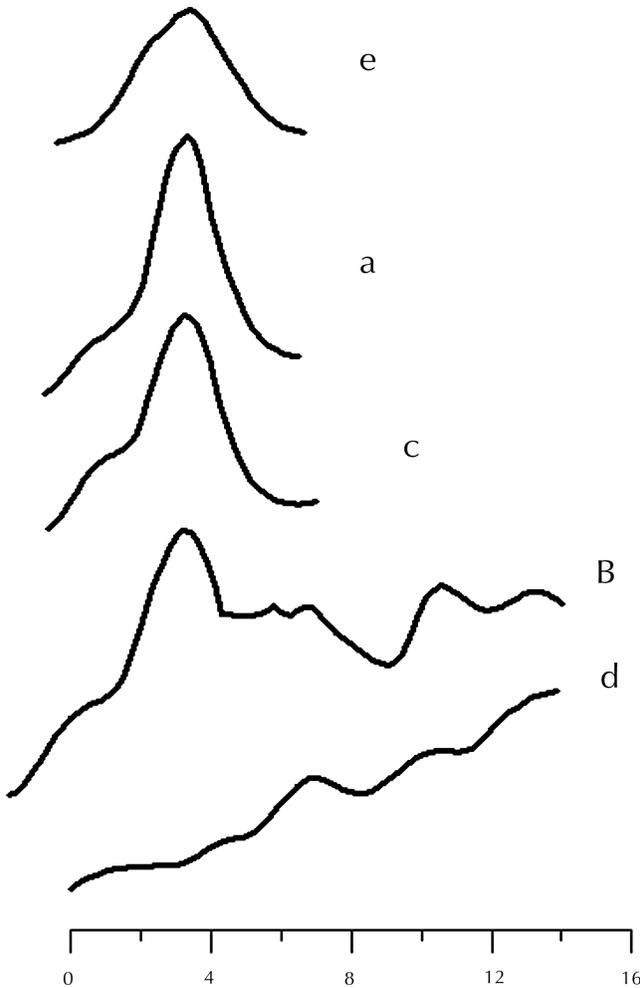
The analysis of the parameters of the multiplet splitting in the Cu3s and Ag4s spectra shows the presence of the atomic magnetic moments on the copper atoms (1.6 mB,  $\Delta = 2.5$  eV) and the argenterum atoms (2.2 mB,  $\Delta = 2.0$  eV). In contrast to carbon copper-containing nanostructures, a decrease in the distance between the multiplets indicates the enhancement of the chemical bond between the copper d electrons and carbon p electrons and the formation of a strong covalent bond. The appearance of the magnetic moment on the silver atoms is associated with the formation of non-compensated d electrons on the silver atoms and the involvement of the d electrons of the silver atoms into the covalent bond with the carbon atoms.



**FIGURE 2** Ag3d spectrum ((a) Ag3d spectrum of the carbon copper-containing nanostructures at interaction with silver and (b) Ag3d spectrum of coating).

The pure silver  $\text{Ag}3d_{5/2,3/2}$  spectra are formed by two components of the spin-orbital splitting (Figure 2 (a)). Similar situation is observed in carbon copper-containing nanostructures functionalized with silver (Figure 2 (b)).

The complex composite  $\text{Ag}3d$  spectrum (Figure 2 (c)) consists of the following maxima: the first—Ag or Ag-C-Cu, and at the distance of 7 eV from it there is a less intensive maximum corresponding to an ionic component of the chemical bond between silver and carbon.



**FIGURE 3** The spectrum of the valence band (a) spectrum of the valence band nanostructures interacted with silver, (b) spectrum of the valence band coating, (c) spectrum of the valence band  $\text{Ag}_2\text{O}$ , (d) spectrum of the valence band C, and (e) spectrum of the valence band pure Ag.

To clarify the nature of the first Ag or Ag-C component, the spectrum of the valence band of the studied composite has been taken (Figure 3). In contrast to pure silver, the growth of an additional maximum at  $E_f$  and a similar maximum in the  $\text{Ag}_2\text{O}$  valence band indicates the hybridization of  $\text{Ag}4d5s$ -electrons with  $2p$  electrons of the second component —carbon. The shape and intensity of the valence band at the distance of 7 eV is associated with the presence of the Ag-C-O component, which is confirmed by the coincidence of them with the maxima in the valence band of pure graphite [4] and the calculations of the oxygen density of states.

The increase of the density of states at  $E_f$  leads to the growth of the electron density of the polymer composite, and, correspondingly, of the electrical conduction in it, similar to that observed for  $\text{Ag}_2\text{O}$  which is used for increasing conduction and is an obligatory element in fabricating conductive glass [15-30].

The data on the measurement of electrical resistance show that when 1% carbon metal-containing nanostructures is added in polymer, the electrical resistance decreases from  $10^{-4}$  down to  $10^{-5}$   $\Omega$  cm.

### 1.2.1 CONCLUSION

It is shown that nanomodification of the argentum-containing polymer coating improves the electrical conduction in it by one order of magnitude.

The analysis of the X-ray photoelectron spectra of the nanomodified composite shows the presence of the covalent bond of the Ag-C-Cu atoms and the growth of the electron density at  $E_f$  due to the hybridization of the  $\text{C}2p$  and  $\text{Ag}4d5sp$  electrons.

## 1.3 CASE STUDY II

The modification of functional groups in the composition of a protein macromolecule is one of the approaches in the development of biotechnology for pharmaceuticals. The virus protection of pharmaceutical preparations of plasma is an acute international task. It is necessary to find albumin modifiers which do not negatively influence human organism.

The main task of the present investigation is the establishment of the regularities of the formation of the energy spectra of electrons and the determination of the chemical bond between the atoms of protein and a modifier by X-ray photoelectron spectroscopy, which allows to define the direction in the investigation of an increase in the protein stability and to choose an optimal modifier for albumin.

The XPS method has been chosen for the above purpose because in contrast to methods using ion and electron beams it is a non-destructive method. The choice of an X-ray electron magnetic spectrometer is conditioned by a number of advantages over electrostatic spectrometers that is constant luminosity and resolution independent of the electron energy and high contrast of spectra. In addition, the constructional separation of the magnetic type energy analyzer from the spectrometer vacuum chamber allows differently effect a sample in vacuum directly during spectra taking [30-37].

The present investigation tasks are as follows:

- The development of the method for the decomposition of X-ray photoelectron spectra into components for finding the spectra parameters indicating the transition of protein atoms into the state of stabilization.
- The development of the method for the determination of the temperature of the protein change and the establishment of a criterion for structural transitions.
- The investigation of the spectra of ordinary and compound amino acids with the purpose of the interpretation of the protein C1s, O1s, and N1s spectra.
- The study of the formation of the chemical bond between the atoms of protein and modifiers, namely, copolymers, super-dispersed particles of d metals and carbon metal-containing nanoforms.
- The study of the influence of the degree of the modification of protein with polymer (vinyl pyrrolidone–acrolein diacetal copolymer) on the protein thermal stability.
- The study of the influence of the protein modification on the protein thermal stability
- The selection of an optimal modifier for protein, which would provide the best protein thermal stability.

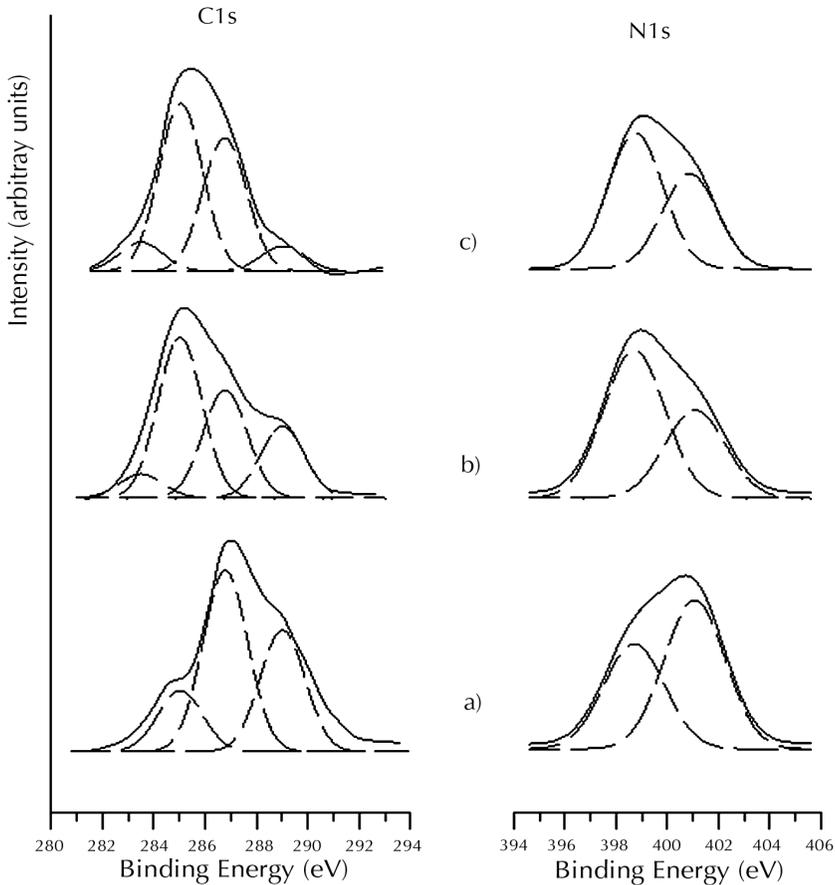
The objects of investigation are the native form of protein and modified protein. Protein was modified with carbon metal-containing nanostructures and additions of functional sp groups for increasing the activity of the interaction of nanostructures with the environment, NiO super-dispersed powder and vinyl pyrrolidone–acrolein diacetal copolymer at the temperature changing from room temperature to 623K.

Carbon metal-containing nanostructures are multilayer nanotubes growing on a metal particle due to the penetration of carbon atoms and carbon adsorption on the particle surface. Samples were prepared by the low energy synthesis method from polymers in the presence of metal systems. 3d metals (Cu and Ni) were used in the form of oxides and super-dispersed particles [12-20]. To increase the activity of the synthesis, the functional sp elements of ammonium polyphosphate were used [13-16].

The investigation of the formation of bionanostructures of a certain form and their properties is based on the concept of studying the interatomic interaction of initial components, the formation of the hybridized chemical bond of d electrons of metal atoms with p electrons of atoms of sp elements.

The C1s, O1s, and N1s spectra of the core levels of the samples of native albumin and modified albumin were studied at the temperatures from room temperature to 573. For investigating the state of atoms of carbon, oxygen, and nitrogen the investigation of reference samples of amino acids (glycine and histidine), copolymer, carbon metal-containing nanostructures, and super-dispersed d metal particles were studied and the data on the electronic structure of graphite and hydrocarbons were used [4].

Figure 4 shows the X-ray photoelectron 1s spectra of carbon and nitrogen taken from glycine and albumin samples at room temperature.



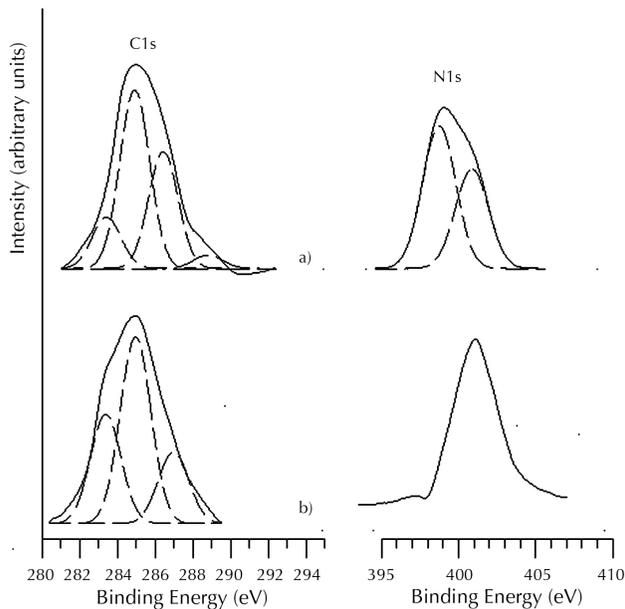
**FIGURE 4** The X-ray photoelectron C1s and N1s spectra of glycine (a), histidine (b), and albumin (c) at 300K.

At room temperature the C1s spectrum of glycine (Figure 4 (a)) consists of three components, bound with different surroundings of carbon atoms, namely, C-H (285 eV), CH-NH (286.5 eV), and COOH (290.1 eV). At room temperature the N1s spectrum of glycine (Figure 4 (b)) consists of two components bound with different surroundings of nitrogen atoms, namely, CH-NH (398.5 eV), and N-O (401 eV).

The histidine C1s spectrum (Figure 4 (b)) consists of four components bound with different surrounding of carbon atoms at room temperature: C-C (283.5 eV), C-H (285 eV), CH-NH (286.5 eV), and COOH (289.1 eV). The histidine N1s spectrum (Figure 4 (b)) consists of two components bound with different surrounding of nitrogen atoms: CH-NH (398.5 eV) and N-O (401 eV). At room temperature, the albumin C1s-spectrum (Figure 4 (c)) also consists of four components bound with different

surrounding of carbon atoms: C-C (283.5 eV), C-H (285 eV), CH-NH (286.5 eV), and COOH (289.1 eV). The presence of the C-C bond is also indicated by a satellite at 306 eV [4]. The albumin N1s spectrum (Figure 3 (a)) consists of two components reflecting the bonds of nitrogen with hydrogen (N-H) and oxygen (N-O). The appearance of oxidized nitrogen can be explained by the oxidation of protein on the sample surface (several tens of Angstroms) or by the formation of the N-O bonds in the protein structure. At temperature growing above 350 K, the spectra shapes of the studied samples change significantly. In the C1s spectrum, the contributions from the components C-C (283.5 eV) and C=O (287.1 eV) appear; and the components CH-NH (286.5 eV) and COOH (290.1 eV) disappear, which indicates the decomposition of the samples at heating, and the spectrum consists of three components C-C, C-H and C=O. In the N1s spectrum the contribution from the CH-NH component disappears at heating, and the spectrum consists of one component reflecting the bond N-O (401 eV).

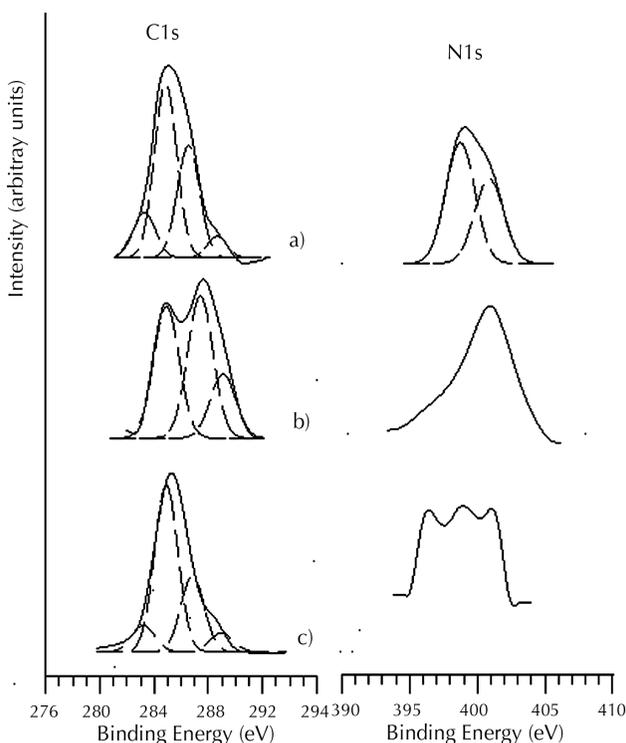
Thus, the oxidation of protein leads to its destruction. The appearance of the carbonyl group C=O indicates the protein destruction (Figure 4 (a), (b), and (c)). The concentration of the carbonyl groups shows the degree of the protein destruction [5]. The growth of the C-C bonds indicates the partial breakage of the C-H bonds. Thus, we have determined the parameters of the X-ray photoelectron spectra characterizing the state of protein. The NH components in the N1s spectrum and COOH in the C1s spectrum indicate the presence of protein. The absence of these components in the N1s and C1s spectra and the growth of N-O and C=O bonds indicate the oxidative destruction of protein. With the change of temperature the amino groups of glycine, histidine, and albumin have similar behavior.



**FIGURE 5** The X-ray photoelectron C1s and N1s spectra of albumin—(a)  $T = 300$  K and (b)  $T = 450$  K.

The samples of vinyl pyrrolidone–acrolein diacetal copolymer have been studied. The copolymer contains 84% of vinyl pyrrolidone and 16 mol% of acrolein diacetal.

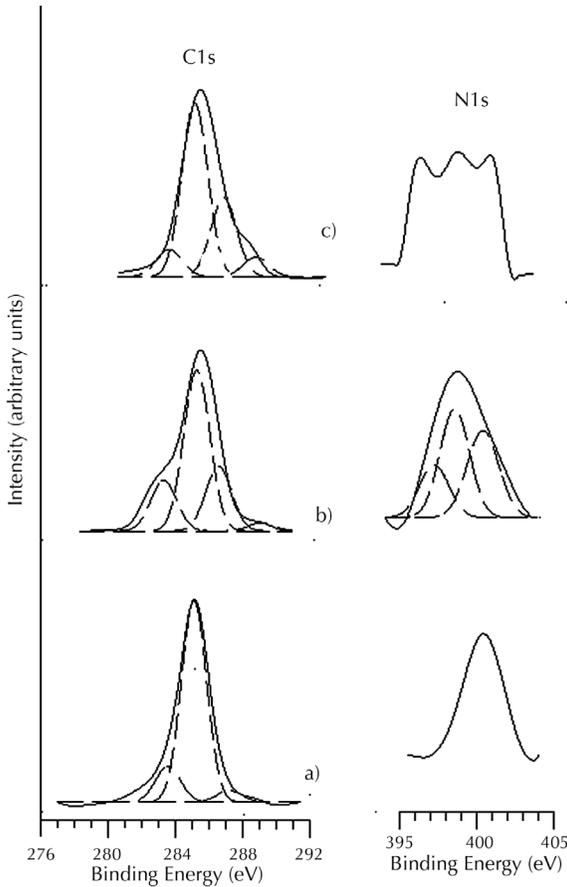
The X-ray photoelectron C1s and N1s spectra of vinyl pyrrolidone–acrolein diacetal copolymer were taken at room temperature and at heating to 473K. At room temperature, the C1s spectrum of vinyl pyrrolidone–acrolein diacetal copolymer consists of three components bound with different surrounding of carbon atoms: C-H (285 eV), N-C (N-CH) (287.3 eV), and COOH (290.1 eV). At the increase of temperature to 373 K, the contribution of the COOH component decreases in the carbon spectra and the components C-H (285 eV) and N-C (N-CH) (287.3 eV) remain. At the temperature above 473, the component C=O (287.1 eV) appears in the C1s spectrum. At room temperature and at the temperatures up to 373K the N1s spectrum consists of two components N-C (397 eV) and N-O (401 eV) and at the temperature above 373K there is one component N-O (401 eV) in the N1s spectrum.



**FIGURE 6** The X-ray photoelectron C1s and N1s spectra of (a) albumin, (b) vinyl pyrrolidone–acrolein diacetal copolymer, and (c) conjugate.

The comparison of the C1s spectra (Figure 6) of albumin, vinyl pyrrolidone–acrolein diacetal copolymer and albumin modified with vinyl pyrrolidone–acrolein diacetal copolymer (conjugate) taken at room temperature shows that in the conjugate prepared from albumin and vinyl pyrrolidone–acrolein diacetal copolymer in the ratio

1:5, there are three components characteristic of albumin, that is C-C (283.5 eV), C-H (285 eV) and COOH (290.1 eV), and the fourth component has the binding energy 286.8 eV characteristic of the CH-NH bond and vinyl pyrrolidone–acrolein diacetal copolymer which has a component with the binding energy 287.3 eV (CH-N). Figure 6 shows the N1s spectra of albumin, vinyl pyrrolidone–acrolein diacetal copolymer and conjugate. In the conjugate N1s spectrum there are components characteristic of vinyl pyrrolidone–acrolein diacetal copolymer and albumin. In contrast to albumin, an increase in the thermal stability of conjugate can be explained by the formation of stronger bonds C-N in it. The dependence of the conjugate thermal stability on the degree of the albumin modification with vinyl pyrrolidone–acrolein diacetal copolymer (1:1, 1:3, and 1:5) has been studied. The samples of albumin modified with vinyl pyrrolidone–acrolein diacetal copolymer in the ratios 1:1, 1:3, and 1:5 were investigated by the XPS method. The C1s and N1s spectra of all the samples (Figure 7) were studied.



**FIGURE 7** The X-ray photoelectron C1s spectra of protein modified with vinyl pyrrolidone–acrolein diacetal copolymer in the ratios—(a) 1:1, (b) 1:3, and (c) 1:5.

In the C1s spectrum (Figure 7 (a)) of the sample with equal content (1:1) of the modifier (vinyl pyrrolidone–acrolein diacetal copolymer) and albumin there are three components C-C, C-H, and C=O. In the N1s spectrum of the sample there is only one component N-O and the contributions from N-H and COOH characteristic of protein are absent at room temperature.

For the sample containing protein and vinyl pyrrolidone–acrolein diacetal copolymer in the ratio 1:3, the C1s spectrum (Figure 7 (b)) shows maxima corresponding to the bonds C-C, C-H, C-NH, and COOH and in the N1s spectrum, maxima characteristic of the C-NH, NH, and N-O bonds are observed. Consequently, there are components N-H and COOH characteristic of protein.

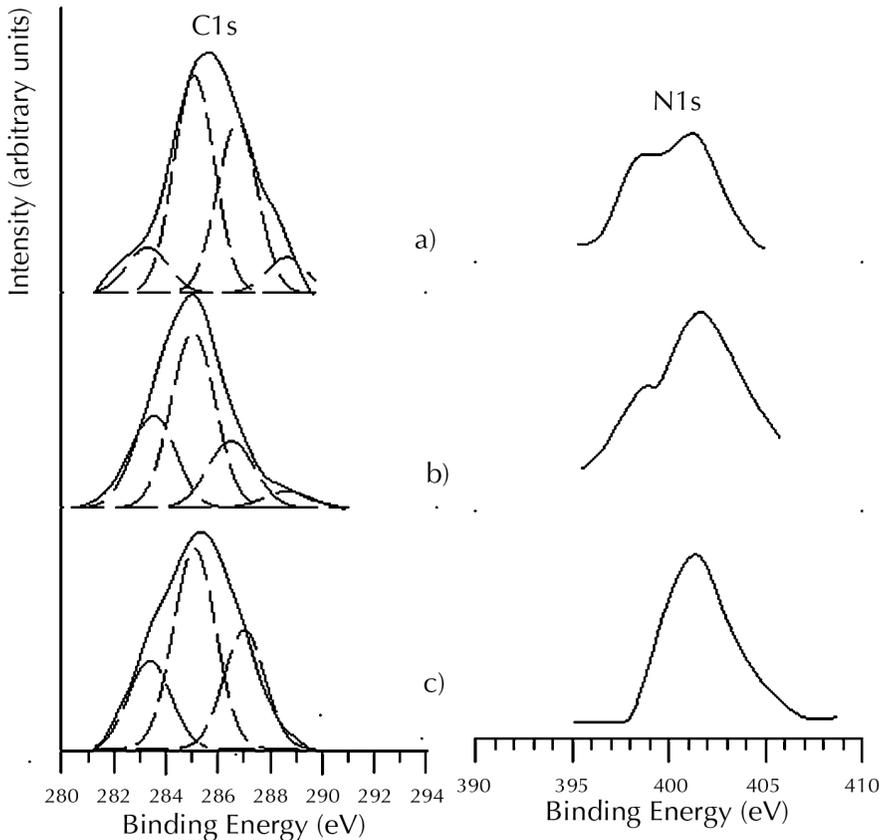
The amino acid group NH is bound with carbon (C-NH) which stabilizes the N-H group and prevents its decomposition. With further growth of the vinyl pyrrolidone–acrolein diacetal copolymer content in protein (5:1), the C-NH, and COOH components' contributions grow relative to that of C-H (Figure 7 (c)). The thermal stability grows with the increase of the relative content of vinyl pyrrolidone–acrolein diacetal copolymer in the conjugate and it reaches 473 K for the 5:1 modification.

For studying the consequences of the interaction of nanobiosystems with artificial nanostructures the modification of protein with nanostructures was conducted. At the protein modification with multilayer carbon copper-containing nanostructures, the position and relative content of the components in the C1s and N1s spectra (Figure 8 (a)) differ from those of the components observed for unmodified protein. For modified protein, in the C1s and N1s spectra, in addition to C-C, CH, and COOH, the C-N(H<sub>2</sub>) components are observed. Heating up to 523K changes insignificantly the shape of spectra (Figure 8 (a) and (b)). Apparently, the bond between protein atoms (N-H) and carbon atoms becomes stronger due to the formation of double or triple bond of C with NH<sub>2</sub> or, which is more likely, the formation of the hybridized sp<sup>3</sup> bond on the C-N(H<sub>2</sub>) atoms. In contrast to the weak bond of the NH<sub>2</sub> groups, the presence of the strong covalent bond C-N(H<sub>2</sub>) leads to an increase in the thermal stability of the protein modified with carbon copper-containing nanostructures to 523 K. With the temperature increase above 523 K, the intensity of the C-N(H<sub>2</sub>) and COOH components decreases in the C1s spectrum and at T = 623 K these components completely disappear. In the C1s spectrum the components similar to destructed albumin that is C-C, C-H, and C=O, remain and in the N1s spectrum the component N-O remains which is characteristic of destructed protein. Sharp worsening of vacuum and the appearance of the Au4f spectrum from the substrate indicate the protein coagulation. Similar to the case of albumin, the growth of C-C bonds is observed.

Nanoparticles can influence protein molecules by penetrating into cells and often destructing them [6-18]. There is a minimal radius of a nanoparticle at which it can be captured inside the cell. Consequently, the biocompatibility of protein and nanoparticles depends on the nanoparticle size that is the surface area can be used as a measure of oxidation (toxicity).

Then, the protein modified by multilayer carbon nickel-containing nanotubes prepared by low temperature synthesis of polymers and nickel oxides was investigated. The multilayer carbon nickel-containing nanotubes have external dimensions much smaller (20–40 nm) than those of the above multilayer copper-containing nanotubes

(from 50 nm and larger). The protein modified by multilayer carbon nickel-containing nanotubes destruction is observed at room temperature. In the C1s spectrum, the COOH carboxyl group is absent, and the C=O carbonyl group and C-C and C-H appear. In the N1s spectrum the N-H group disappears and the component N-O grows.



**FIGURE 8** The X-ray photoelectron C1s and N1s spectra of albumin with multilayer carbon copper-containing nanotubes—(a)  $T = 373\text{K}$ , (b)  $T = 523\text{K}$ , and (c)  $T = 623\text{K}$ .

The same result is observed when protein is modified with NiO nanoparticles which are oxidation catalysts. The destruction of albumin modified with multi-layer carbon nickel-containing nanotubes is observed at room. The decomposition of the spectra into the components shows that in the C1s and N1s spectra the components COOH and N-H are absent and the components C-C, C-H, C=O, and N-O are present similar to the case of the modification with carbon nickel-containing nanostructures, that is the protein destruction takes place at room temperature. Thus, the growth of carbonyl groups, the breakage of the N-H bond and the formation of the N-O bond

occur at an elevated temperature or in the presence of the interaction with a metal catalyst.

### 1.3.1 CONCLUSION

Based on the conducted fundamental investigations, the regularities are obtained, which can be used for the choice of the direction in the purposeful increase of protein stability. The investigations of the protein modification show that:

- Low thermal stability of protein (albumin) is due to the weak bond of the  $\text{NH}_3(\text{NH}_2)$  group and the decrease of the content of  $\text{NH}$  ( $\text{NH}_3$  and  $\text{NH}_2$ ) groups in the protein composition and nitrogen oxidation at heating.
- One of the consequences of the formation of the strong covalent bond between the atoms of the  $\text{NH}_2$  amino group and the carbon atoms (C-NH) at the protein modification is an increase in the thermal stability of the modified protein. The destruction of carboxyl groups (COOH) and the formation of the carbonyl groups (C=O) as it follows from the change of the C1s spectrum at heating indicate the destruction of protein. At the protein destruction, the bond between hydrogen and nitrogen is broken, and nitrogen forms the bond with oxygen.
- The presence of metal catalysts (Ni, NiO) in protein leads to the oxidation and destruction of protein due to the formation of carbonyl groups and the destruction of the N-H groups.

Also:

1. A method for the determination of the temperature of the protein destruction has been developed and the criteria of the protein destruction have been established.
2. At the modification of protein with carbon copper-containing nanotubes a strong covalent bond (C-NH) of the atoms of the N-H amino group with the carbon atoms is formed, which results in the increase of the modified protein thermal stability up to 523–573 K.
3. The compatibility of bio and nanostructures depends on the size of the nanostructures, which can serve as a measure of oxidation.
4. In addition to the influence of the temperature on the oxidative destruction of protein, the presence of metal catalysts (Ni and NiO) in protein leads to the oxidation and destruction of protein due to the formation of carbonyl groups and the decomposition of the N-H groups at room temperature.
5. In contrast to the modification of protein with carbon copper-containing nanotubes, the modification of protein with carbon nickel-containing nanotubes leads to the protein destruction at room temperature due to the presence of Ni atoms.
6. One of the consequences of the formation of the covalent bond C-N(-H) between nitrogen atoms and carbon atoms is an improvement in the thermal stability of the modified protein.
7. The dependence of the thermal stability of protein modified with vinyl pyrrolidone–acrolein diacetal copolymer on its content in the mixture is found. The

growth of the temperature of stabilization with the increasing content of vinyl pyrrolidone–acrolein diacetal copolymer is shown.

8. At the vinyl pyrrolidone–acrolein diacetal copolymer concentration three times smaller than that of protein, the protein destruction is observed at room temperature. With the threefold and more increase of the vinyl pyrrolidone–acrolein diacetal copolymer concentration, the temperature of the protein stability grows and is maximal at the ratio 1:5.

Based on the results obtained some recommendations on the modification of protein for increasing its stability are given, which can be used in pharmaceutical biotechnology.

A model for the protein stabilization is offered on the basis of the formation of the strong hybridized chemical bond of the atoms of protein and a modifier.

The results of the work on choosing an optimal modifier for protein for medicobiological and pharmaceutical technologies show that the highest thermal stability of protein (523–573 K) is achieved at the modification of protein with carbon copper-containing nanotubes having functional groups of sp elements in the ratio 1:0.01, which is more rational in comparison with the protein modification with vinyl pyrrolidone–acrolein diacetal copolymer because in this case the required amount of the modifier is significantly larger (in 3–5 times) than the amount of protein.

#### 1.4 CASE STUDY III

For many years, the improvement of the mechanical properties of structural materials was mainly performed by the development of new alloys with new chemical and phase compositions. Lately, new ways have appeared for improving properties of structural materials, namely by the well-directed formation of micro- and nanocrystalline structure.

The set of the experimental methods that are used for studying the chemical structure of carbon cluster nanostructures is limited. Therefore, one of the main tasks is the development of diagnostic methods, which will allow controlling intermediate and final results in the creation of new materials.

At present, the analysis of numeral works shows that classical methods for determining shapes, sizes, and compositions of carbon nanostructures are transmission electron microscopy, methods based on electron diffraction and Raman spectroscopy. However, more and more publications appear referring to the investigation of nanostructures with the use of the XPS method. Further development of the XPS method and related methods for the surface (from 1 to 10 nm) investigation will lead to an increase in the number of methods for studying compositions, electronic properties, and structures of nanostructures.

The XPS has been used for the determination of the type of carbon structures. The XPS method allows investigating the electron structure, chemical bond, and nearest environment of atoms. One of the important specific features of the method is its non-destructive character of action since the X-ray radiation used for photoelectron excitation does not practically cause any damages in most materials. This cannot be said about the surface analysis methods that involve ion or electron bombardment of a surface. In most cases, a sample can further be used for some other investigations after it has been studied by the XPS method.

In addition, the method provides the possibility to analyze thin layers and films, which are very important for the case of the formation of fullerenes, nanotubes and nanoparticles, and to obtain the information on the sample chemical composition based on spectra, which provides the control over chemical purity of materials.

The XPS method allows investigating electron structure, chemical bond, and the nearest environment of atoms with the use of an X-ray photoelectron magnetic spectrometer. The X-ray photoelectron magnetic spectrometers with automated control system [1] are not inferior to the best foreign spectrometers in their main parameters. The preference is given to the X-ray electron magnetic spectrometer because of a number of advantages compared with electrostatic spectrometers [2], which are the high spectrum contrast, the permanency of optical efficiency and resolution capacity that are not influenced by electron energy. Moreover, the XPS method is a non-destructive investigation method.

In this work, the samples prepared from iron powder modified with fullerenes or graphite was studied with the use of the XPS method. The samples were prepared in two ways—fusion or pressing. The modification was carried out for obtaining nano-carbon structures in metal matrices in order to improve strength properties of a material. The samples were verified with the use of X-ray diffraction, which showed that the sample structures were mainly fcc iron. The description of the samples studied is given in Table 1.

**TABLE 1** The investigated samples

Sample No	Sample composition	Sample form
1	Fe + 0.5% C <sub>60/70</sub>	Ingot (T = 1410°C)
2	Fe + 0.5% graphite	Ingot (T = 1410°C)
3	Fe + 2% C <sub>60/70</sub>	Powder
4	Fe + 2% graphite	Powder
5	Fe + 2% C <sub>60/70</sub>	Pellet (P = 800 MPa)
6	Fe + 2% graphite	Pellet (P = 800 MPa)

The X-ray photoelectron investigations were carried out for studying the changes in the nearest environment of the carbon atoms in the samples prepared in different ways.

The investigations were carried out using the X-ray photoelectron magnetic spectrometer with double focusing and instrumental resolution of 0.1 eV at the excitation of AlK $\alpha$ -lines (1486.6 eV).

For the XPS investigations of carbon-metal cluster nanomaterials, the method of the C1s spectra identification by the satellite structure was employed. To do this, reference samples were studied, the carbon components of which could give the C1s spectrum—C-H—hydrocarbons [1-25], C-C (sp<sup>2</sup>)—graphite [4], and C-C (sp<sup>3</sup>)—dia-

mond [25-37]. The spectra parameters are presented in Table 2, where  $E_b$  is binding energy,  $E_{sat}$  is the energy characterizing the satellite position,  $I_{sat}$  is the satellite intensity, and  $I_0$  is the intensity of the main maximum.

**TABLE 2** The C1s spectra parameters for reference samples

	$E_b, \text{eV}$	$E_{sat}, \text{eV}$	$\Delta E = E_{sat} - E_b, \text{eV}$	FWHM, eV	$I_{sat}/I_0, \Delta = 10\%$
C-H [3] hydrocarbons	$285.0 \pm 0.1$	$292.0 \pm 1.0$	$\sim 6-7$	$2.0 \pm 0.1$	0.10
C-C ( $sp^2$ ) [4] graphite	$284.3 \pm 0.1$	$306.0 \pm 1.0$	$\sim 22$	$1.8 \pm 0.1$	0.10
C-C ( $sp^3$ ) [5] diamond	$286.1 \pm 0.1$	$313.0 \pm 1.0$	$\sim 27$	$1.8 \pm 0.1$	0.15

To identify the structures studied in [6], the C1s spectra of carbon nanostructures were studied. The nanostructures were obtained in the electric arc during graphite electrode sputtering. The carbon nanostructures obtained were fullerenes  $C_{60}$ , single-walled and multi-walled carbon nanotubes and amorphous carbon.

It is shown that in all the C1s spectra there is a satellite structure related to different effects (a shake-up process and characteristic losses—plasmons [17-24]), which allows to create a calibration technique and to determine not only the energy position of the components but their intensities as well. In the C1s spectrum of fullerenes  $C_{60}$ , there is a satellite with binding energy of 313 eV [8-14] and the relative intensity of 15% from the main peak. This satellite is characteristic of the  $sp^2$  hybridization of the valence electrons of the carbon atoms.

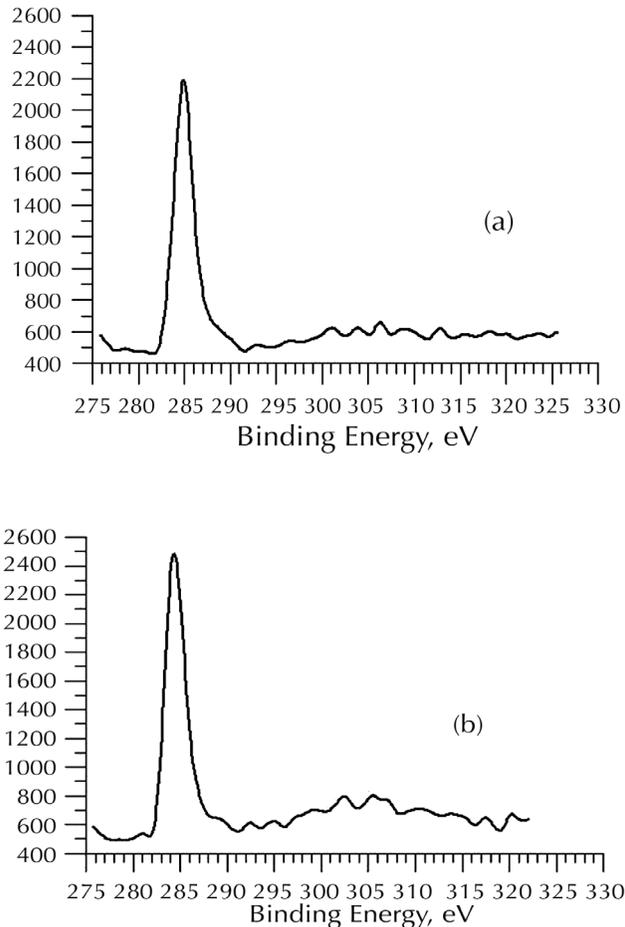
In the C1s spectrum of single-walled carbon nanotubes, in addition to a gradually rising spectrum in the high energy region, two satellites are observed characteristic of the C-C bonds with the  $sp^2$  and  $sp^3$  hybridization of the valence electrons of the carbon atoms. Consequently, in the C1s spectrum of the one-layer nanotubes, there are these two components with the binding energies of 284.3 and 286.1 eV and the intensities of 1:0.1 and 1:0.15 relative to their satellites and the width of 1.8 eV. The ratio between the C-C bonds with the  $sp^2$  and those with  $sp^3$  hybridization of valence electrons is 2. The similar situation is observed for the C1s spectrum of multi-walled carbon nanotubes.

In the region of 313 eV of the amorphous carbon spectrum, there is a satellite characteristic of  $sp^3$  hybridization of the valence electrons with the relative intensity of 15%. Consequently, in the C1s spectrum there is a component characteristic of C-C bond with  $sp^3$  hybridization of the valence electrons at the distance of 27 eV from the satellite. Thus, the amorphous carbon presents carbon inclusions that are like a globe-shaped form of graphite. The development of a calibration method for spectra in the X-ray photoelectron investigations of reference samples allows realizing the decom-

position of the C1s spectrum to the components that determine the chemical bond, the hybridization type of s-p valence electrons of the carbon atoms and the nearest environment of the carbon atoms. Studying the nanoparticles with a known structure gives the possibility of the identification of studied carbon structures by examining the C1s spectra shapes.

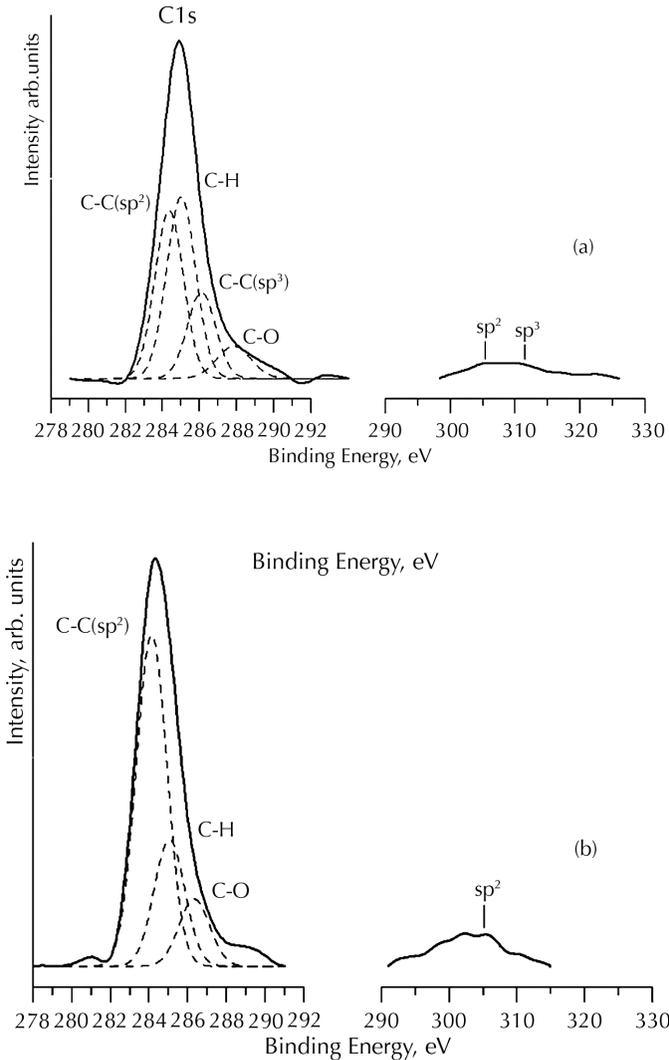
The C1s spectra identification method developed by us was successfully used for the investigation of nanostructures in the iron matrix.

The XPS method was used to obtain the C1s, O1s, and Fe2p spectra. The O1s spectra show that large amounts of adsorbed oxygen and iron oxides are present on the sample surfaces. The Fe2p spectra are also indicative of the presence of the oxidized iron layer on the surfaces of the samples. During the experiment, the shift of the spectra was not observed. The experimental C1s line spectra for samples №1 and №2 are shown in Figure 9 (a) and (b).



**FIGURE 9** The experimental C1s spectra of samples №1 (a) and №2 (b).

The mathematical treatment of the C1s spectra was performed that is the background subtraction and the procedure of the spectra smoothing and decomposition. The results are given in Figure 10.



**FIGURE 10** The X-ray photoelectron C1s spectra obtained from samples №1 (a) and №2 (b) after the spectra were decomposed into their components.

In Figure 10 (a), the X-ray photoelectron spectrum of the C1s line is displayed, which was obtained from sample №1 without heating in the spectrometer chamber. In the high energy region, two satellites are observed, which are characteristic of  $sp^2$  and