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National Centre for Information and Documentation

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NATIONAL SCIENTIFIC PROGRAMMES WITH EUROPEAN DIMENSIONS

MODERN APPROACHES FOR DEVELOPMENT OF CLINICAL INFORMATION SYSTEM (CIS) FOR PEDIATRIC SURGICAL DISEASES MONITORING (PedSurgCIS)

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Abstract

In modern concepts for development of e-health one of the main directions in research is the employment of Internet technologies, Web technologies and Web services. This tendency is enhanced in the last ten years and it is emphasized in Lisbon' strategy i2010 and EC initiatives for development of e-health systems. Following this process, in 2006 Bulgaria accepts the strategy for development and introduction of e-health systems and national strategy for improvements in healthcare delivery 2008-2013.

Clinical Information Systems (CIS), as an essential part of Hospital Information Systems (HIS), are one of the main directions in concepts for development of e-health. They are separate information systems in clinics and hospital departments performing specific functions concerning collection of patients' status and treatment data, research, management, planning and synchronizing data exchange with the central information system of Ministry of Health (MH) or National Health Insurance Fund (NHIF). Except specific functions concerning the operation of the clinic, a CIS performs traditional tasks associated with the electronic patient records (EPRs), storage and image processing, monitoring, preparation of reports, training and decision-making.

The main goal of the research project is analysis, design and implementation of a service-oriented architecture (SOA)-based clinical information system (CIS) for pediatric surgery diseases monitoring (PedSurgCIS). The development of methods and software tools based on web services and Internet applications for building distributed CIS and related EPRs, clinical archives, algorithms and modules for analysis of treatment-diagnosis data are envisaged. For implementation of SOA-based clinical information system for pediatric surgical diseases monitoring an experimental distributed computer network is designed and developed. The expected applied result will assist successful integration of health care providers to e-health systems applying European standards in this field.

INTRODUCTION

In 2006 Bulgaria accepts the strategy for development and introduction of e-health systems [1] and national strategy for improvements in healthcare delivery 2008-2013 [2]. These strategies are based on the EC initiatives [3] for development of e-health systems and the Lisbon's strategy i2010, which envisage development of integrated centralized electronic health portals in all EC member countries, creation of personal

patient electronic health records (PEHR), centralization and consolidation of information resources and their integration in hospital information systems (HIS).

In 2007 EC published a new strategy [4] to accelerate the increase of electronic healthcare services' market share in Europe. In the strategy, that market share is divided into four areas: clinical information systems; telemedicine and home care; integrated regional and national networks for exchange of health information in the form of distributed electronic patient records; reuse of non-clinical systems. Of those four areas, a particular focus is put on development of clinical information systems (CIS) as an essential part of HIS [4].

However, till the present moment in Bulgaria unified standards for the transition from paper-based health records toward electronic patient records (EPR) and their integration with hospital information systems are not introduced. The majority of the existing information systems in the healthcare domain is serving the needs of National health insurance fund (NHIF) and reports the activities of general practitioners, specialists in medical diagnostic centers, and clinical paths in hospitals. In general, these systems do not provide information which is clinically relevant and useful in the process of diagnosis, management or treatment of a patient.

All these objectives has motivated the initiation of research efforts in the development of clinical information systems in different areas of Bulgarian health care that will be an integral part of e-health, supplementing and extending it in the direction toward integrated system for information sharing among medical staff, educational, scientific, financial and administrative units.

CIS constitute separate information systems in clinics and hospital departments with the following functions [5]:

- to perform specific functions concerning collection of patients' status and treatment data, research, management, planning, and synchronizing data exchange with the central information system of Ministry of Health or NHIF;
- to perform specific functions concerning

the operation of the clinic or appropriate hospital department – cardiology, internal medicine, pediatric surgery, etc.

- to perform traditional tasks associated with the EPR, storage and image processing, monitoring, preparation of reports and epicrises, training and decision-making.

Some of the common problems in implementing such systems in Bulgaria are:

- Lack of XML-based standards for medical documentation;
- Lack of standards for formal representation of diagnosis - treatment relationship;
- Lack of standards for base nomenclatures (for example types of anesthesia);
- Lack of standards for identification codes of laboratory tests;
- Lack of standards for identification codes of drugs;
- Lack of standards for formal representation of medicine – diagnosis relationship;
- Increasing amounts of data related to diagnostic and treatment events and the need for analysis, evaluation and storage.

Modern concepts in the development of e-health, CIS and personalized healthcare systems dictate the use of Internet and web technologies, web-based services, and Service-oriented architectures (SOA) for realization of clinical information systems [6, 7, 8].

PROJECT OBJECTIVES

The goal of the research project is analysis, design and implementation of SOA-based clinical information system for pediatric surgery diseases monitoring (PedSurgCIS). The development of methods and software tools based on web services and Internet applications for building distributed CIS and related EPRs, clinical archives, algorithms and modules for analysis of treatment-diagnosis data are envisaged for implementation. Hence, the following phases are necessary to be realized:

- System analysis of treatment-diagnosis events and design of XML-based electronic medical records for pediatric surgery department;
- Development of methods and libraries for analysis and processing of treatment-diagnosis data;

- Design and implementation of web-based experimental CIS for analysis of models for integration with other e-health systems (HIS, National e-Health Portal) and the flow of information between their components and building blocks;
- Development of methods and libraries for integration of web applications and services in CIS for pediatric surgical diseases monitoring;
- Development of methods, web-applications and services for integration of CIS with hospital information systems, national integration system of information exchange between employees in healthcare, and national e-health portal;
- Development of methods and software tools for information security, authentication and authorization.

RESEARCH TASKS

Implementation of the project goal involves the following tasks:

Task 1. Preliminary surveys

The objective of this task is to draw the boundaries of the area that the project will be based on and to provide relevant technologies, including:

- Investigation of medical records and documents and their flow in the process of diagnosis and treatment in the departments for pediatric surgery;
- Classification of the data from the records of the treated children according to the organ system involved, nosological units, symptoms or set of symptoms (syndrome);
- Systematization of the laboratory, instrumental and imaging diagnostic information of the treated children;
- Analysis of the paper-based patient records' structure in the departments for pediatric surgery. Systematization of the data from medical records of the treated children from surgery departments for transfer to the EPRs;
- Analysis of technological standards and solutions for data representation of EPRs and medical documents in an open platform independent format;
- Analysis of technological standards and so-

lutions for integration of Web applications in CIS (models, specifications, standards and data formats);

- Investigation of possibilities of different communication media and protocols (wired and wireless) to be used in pediatric surgery department.

Task 2. Theoretical analysis

- Analysis of the data and information flows in the process of diagnosis and treatment in the children's surgery departments using centralized or decentralized architecture of the CIS;
- Analysis of the interaction of the protocols on the application and transport layer of the TCP suite and the data access protocols in the integration of Web application in CIS;
- Comparing analysis of the measurement methods for the parameters of the SOA-based CIS.

Task 3. Investigation and development of the information flow and interaction

The objective of this task is design and development of functional architecture of SOA-based CIS for pediatric surgical diseases monitoring:

- Design of the information flow and interaction in the adaptation of Web applications in CIS;
- Investigation of the techniques for synthesis, monitoring and evaluation of HTTP traffic in CIS;
- Analysis of models for distributed storage of EPRs on different layers of the model;
- Design of information services for remote access to third party systems for e-Health;
- Investigation of the data flow between the nodes in network of the HIS;
- Analysis of attacks and methods for Web services protection in CIS.

Task 4. Design and development of an experimental system

The objective of the task is development of an experimental distributed clinical information system together with all concerned EPRs, clinical archive and tools for analysis and processing of information for diagnosis and treatment, based on Web service and application integration:

- Design of multi-layer CIS for department of pediatric surgery with integrated Web servic-

es;

- Design and development of a computer network in the department that will be used for realization of CIS, Web applications and distributed data storage of diagnostic information and patient records;
- Software implementation of libraries for Web applications and services for visualization, archiving and processing of diagnostic and treatment information;
- Installation and configuration of network gateways for integration of CIS and HIS and third party services for e-Health;
- Software implementation of methods for Web service and application protection in CIS.

Task 5. Experimental analysis

- Performing test-bed experiments in different configurations of the system and various parameters of the communication media;
- Working with real data from pediatric surgery departments, presentation and visualization of patients' medical parameters;
- Estimation of the system's dynamic, operation and its potential for integration with third party systems for e-Health.

METHODS AND RESEARCH TECHNIQUES EMPLOYED

Methods

- Structural modeling of information flows in distributed CIS – data format, data flow, transfer protocols;
- Simulation study of the data traffic in dis-

tributed CIS based on Web applications;

- Data validation and verification of the information flows in CIS.

Research techniques

- Test-bed experiments for investigation of the specifics of wireless data transfer and its influence on integration of Web applications in CIS;
- Test-bed experiments for evaluation of application protocols and their optimal integration in Web application for CIS;
- Test-bed experiments for investigation of the factors that influence the complex effectiveness of the CIS with integrated Web applications and services.

DISTRIBUTED EXPERIMENTAL COMPUTER NETWORK FOR PedSurgCIS

In most of the current research projects and scientific papers a general structure of a SOA-based CIS [6] is proposed regardless of the target clinic or hospital department. An example architecture of a SOA-based CIS is presented on Figure 1.

The CIS architecture is based on the four layers model, where:

- The first layer is called data layer and consists of all data storage and database management systems (DBMS) that include electronic patient records (EPRs) and other clinical and diagnostic information;
- The second layer consists of application servers that implement the functions for data and information processing and medical anal-

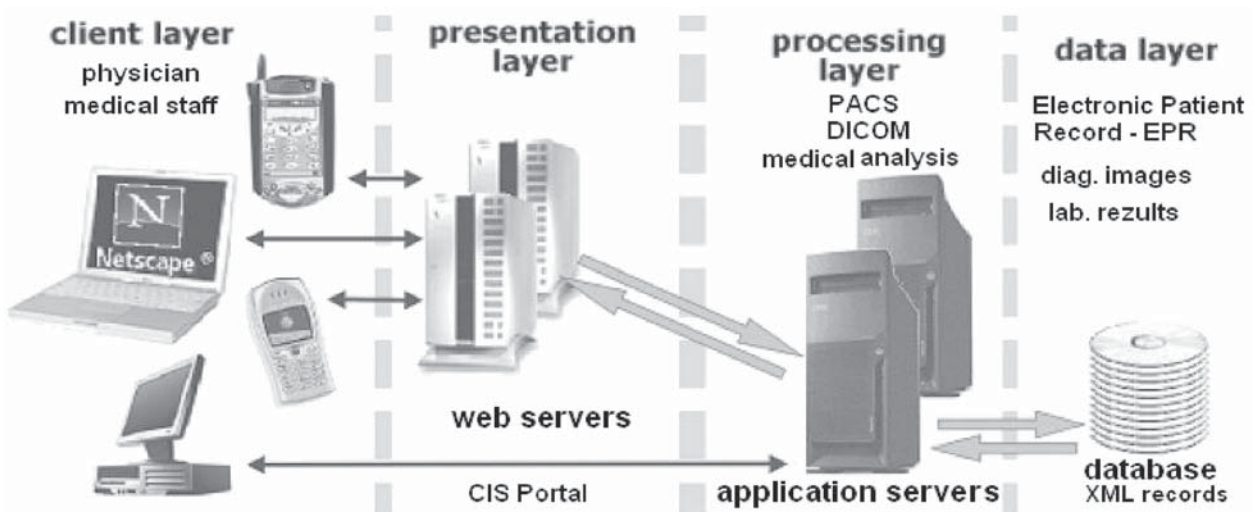


Fig. 1. Four layers model of a CIS

ysis for the purposes of diagnosis and treatment;

- The third layer is responsible for presentation of information and usually is realized as Web portal that provides a single point of entry to all services for diagnosis and treatment in corresponding department or clinic;
- The forth layer is the client layer that is commonly presented by Web browsers. Medical staff and physicians can access the services and data through desktop, laptop computers or mobile phones.

For implementation of SOA-based clinical information system for pediatric surgical diseases monitoring an experimental distributed computer network is designed and developed. It is based on the results of the performed system analysis and its structure is shown on Figure 2.

The distributed computer network is built of two parts connected via Internet. The main part (kernel) is situated in the Pediatric surgery clinic in "Saint George" Hospital, Medical University of

Plovdiv. The development part of the network is situated in Laboratory on "Distributed systems and networking" (DSNET V-Lab) at Faculty of Electronics and Automation, TU-Sofia, Plovdiv branch.

The main part (the kernel) of the distributed computer network comprises the following sub-systems:

- Data security system, based on SmoothWall UTM-100, with Firewall and system for intrusion detection and protection (IPS).
- Layer 3 switch, based on HP 5120-24g EI, for development of virtual local networks for different types of users of PedSurgCIS and providing IP routing in the network.
- Servers situated in DMZ zones, comprising: Database server for electronic patient records in Pediatric surgery clinic (PedSurg EPR) and application server (AppServer).
- Layer 2 switches based on HP 2620-24 for development of virtual local networks with user workstations.
- Workstations for PedSurgCIS users, involving

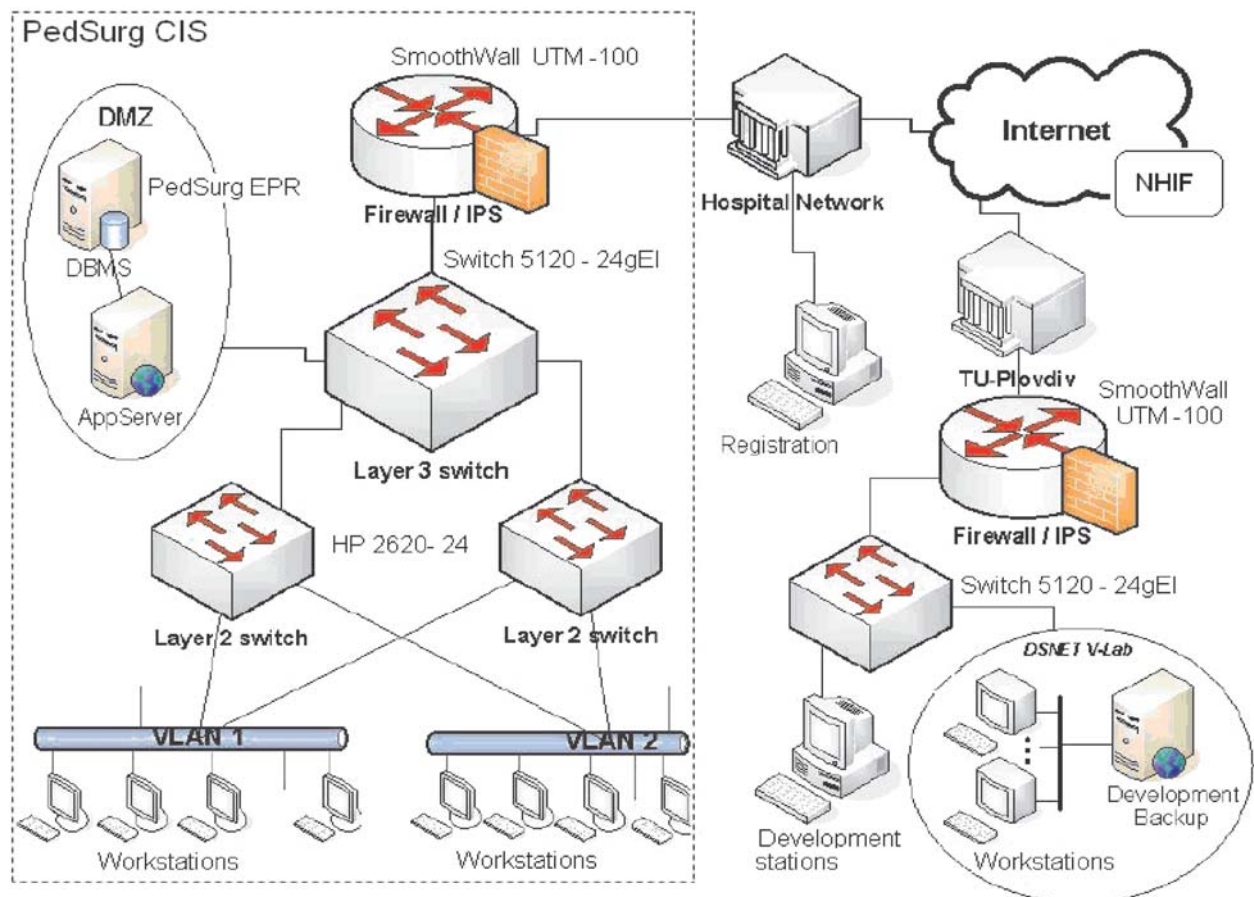


Fig. 2. Distributed computer network for PedSurgCIS

medical and administrative staff.

The development part of the distributed computer network comprises the mirror image of the first two sub-systems from the main part (SmoothWall UTM-100 and HP 5120-24g EI), the Development Backup server and the Workstations.

EXPECTED EFFECTS AND RESULTS

The results from the current project could be drawn in general conclusions into the following aspects:

Theoretical and applied results

- Transfer of developed technologies for integration of Web applications in the area of e-health and CIS;
- Development of simulation models for investigation of integrated Web applications in CIS;
- Development of Database with EPRs containing information with many specific features: heterogeneous, voluminous, low level of formalization, noise-prone, free-text data entered by clinicians about the condition of a patient during all stages of his treatment;
- Development of methods and libraries for integration of Web applications in CIS;
- Development of methods and tools for complex estimation of effectiveness of the integrated Web applications in CIS.

Strategic benefits of the project

- The development of a unified Electronic Patient Record gives opportunities for standardization of methods for extraction of medical data according to the type of activities;
- The development of CIS will allow each treated child to have precise medical record containing full information about surgical reason (congenital or acquired), issue of disease, monitoring during longer period of time, etc. The analysis of treated children in horizontal and vertical aspects will create a basis for future research and statistical processing of different nosological units. The developed CIS will allow archiving of all diagnostic and treatment activities, thus keeping this information for future education needs anytime and anywhere.
- The proposed CIS will introduce into prac-

tice long time monitoring, distant consultations and expertise from European and world-wide pediatric surgeons and will trace opportunities for introduction of telemedicine in pediatric surgery in the near future.

- The developed database will facilitate qualification and continuous education of medical doctors – surgeons, pediatricians, neonatologists, residents, etc.
- The created EPRs will facilitate development and implementation of the complex Hospital Information Systems (HIS) integrated with additional external applications.
- The introduction of CIS in medical practice is a complex interaction of advances in information and communication technologies with human factor. This interaction leads to important social changes, the success and benefits of which are dependant on the multidisciplinary approach to the subject of medical doctors, engineers and users.

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СЪВРЕМЕННИ ПОДХОДИ ЗА ИЗГРАЖДАНЕ НА КЛИНИЧНА ИНФОРМАЦИОННА СИСТЕМА (КИС) ЗА ПРОСЛЕДЯВАНЕ НА ДЕЦА С ХИРУРГИЧНИ ЗАБОЛЯВАНИЯ (PedSurgCIS)

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Резюме

В съвременните концепции за развитие на електронното здравеопазване, клиничните информационни системи и системите за персонализирано здравеопазване една от основните насоки за провеждане на научни изследвания е използването на Internet, уеб технологиите, уеб услугите и базираната на тях Service-Oriented-Architecture (SOA). Целта на текущия проект е изследване, проектиране и реализиране на SOA базирана клинична информационна система (КИС) за проследяване на деца с хирургични заболявания. Предвижда се създаването на методи и програмни средства, базирани на уеб услуги и интернет приложения, за изграждане на разпределена КИС и свързаните с нея електронни записи за пациенти (EPRs), клиничен архив, средства за анализ и обработка на лечебно-диагностична информация. Данните, които се поддържат от КИС за всеки пациент, определят структурата на електронни записи за пациента. Характерна специфика за EPR в хирургично отделение е, че в основната си част

информацията е предимно описателна, представена в свободен текст и не подлежи на формализация и стандартизация. Друг съществен проблем е, че информацията постъпва от различни източници, с различна вероятност за допускане на грешки. Това поставя сериозни предизвикателства и редица проблеми за решаване свързани с избора на архитектура на системата, базата данни и системата за управление на базата данни при проектирането и реализацията на КИС за проследяване на деца с хирургични заболявания.

Основните етапи и дейности в процеса на изследване, проектиране и реализация на информационната система включват:

- Системен анализ на лечебно-диагностичните мероприятия и проектиране на XML базирани електронни медицински досиета за детски хирургични отделения.

- Разработване на методи и библиотеки за анализ и обработка на лечебно-диагностична информация.

- Проектиране и реализиране на уеб базирана експериментална КИС за изследване на модели на интегриране с други системи от електронното здравеопазване (болнични информационни системи, национален електронен здравен портал) и информационното взаимодействие между отделни техни елементи и структури.

- Разработване на методи и библиотеки за интегриране на уеб приложения и услуги в КИС за проследяване на деца с хирургични заболявания.

- Разработване на методи, уеб приложения и услуги за интегриране на КИС към болнична информационна система, национална интегрирана система за обмен на информация между заетите в сферата на здравеопазването и към национален електронен здравен портал.

- Разработване на методи за защита на информацията и оторизиране на достъпа в КИС.

За целите на провежданото изследване и реализация на SOA базирана КИС за проследяване на деца с хирургични заболявания е проектирана и изградена разпределена експериментална компютърна мрежа, разположена на територията на Клиниката по Детска хирургия в УМБАЛ „Свети Георги“ на МУ - Пловдив и Лабораторията по Компютърни мрежи и разпределени системи в ТУ - София, филиал Пловдив.

FERROFLUID HYPERTHERMIA FOR BREAST CANCER THERAPY

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Abstract

Electromagnetic field distribution in biological structures is a challenging multidisciplinary problem that may offer many new opportunities for precise medical diagnosis and therapy due to modern scientific approaches. Investigation of electromagnetic fields, processes and phenomena is significantly improved by new highly precise computational models and field reconstruction strategies. In this work, method of magnetic fluid hyperthermia for breast cancer therapy is modeled and investigated. Coupled field modeling of ferrofluid transport and heating in tumor tissue is presented. A 3D electromagnetic – thermal - fluid dynamic finite element method model is developed. The model uses anatomically precise multilevel geometrical model of human with real cancer sample acquired by surgical procedure. Thermal field results are verified by infrared thermograph imaging.

INTRODUCTION

Investigation of processes and phenomena during electromagnetic medical diagnosis and therapy is significantly improved by new highly precise computational models and field reconstruction strategies. Magnetic fluid hyperthermia is one of promising recently developed methods for cancer therapy. In this method magnetic field selectively heats up tissues by inducing alternating current to targeted magnetic fluid [1-4]. Magnetic fluid distribution determines thermal field inside tissues under therapy process. Inversely the magnetic fluid transport and distribution rearranges the electromagnetic field that dramatically changes the thermal field in that sensitive live tissue domain. Anatomy objects under investigation are particularly complex structures, which exhibit considerable variability from person to person. Electromagnetic and thermal tissue properties are anisotropic, frequency and

time varying and in general are not clearly determined for all tissues. All of these, as well as absence of explicit shape models that capture anatomy specifics, makes modeling task challenging. The infrared thermography is a reliable and perspective contactless technique and recently has been significantly developed [5, 6]. It offers the possibility of fast imaging and appears as a powerful quantitative tool to obtain the mapping of temperature and to investigate the heat exchange between objects under considerations. Modern thermo-vision cameras are used for a noninvasive and effective method for early breast cancer screening. In that case the metabolic heat generation differences between normal and cancer tumor tissues are used for diagnosis recognition and can be applied for magnetic hyperthermia effects measurements. However, this method has a poor sensitivity to deeper or smaller tumors. Also, the thermal property parameters were generally specified for population averages, which might substantially depend from individual values. This leads to a major barrier to accurate estimation of the tumor-induced thermal contrast on the breast surface, because of the uncertainty of corresponding non-tumor thermal background, which needs to be removed from the thermograph image [2-5]. Because of that developing of a precise model for magnetic hyperthermia processes, fields and phenomena investigation is of paramount importance.

In this work, coupled field modeling of ferrofluid transport and heating process in tumor tissue is presented. A forward 3D electromagnetic - fluid dynamics – thermal finite element method (FEM) model is developed. Results obtained from modeling are verified experimentally by a sensitive infrared thermograph camera. Experiments are carried out by the real cancer

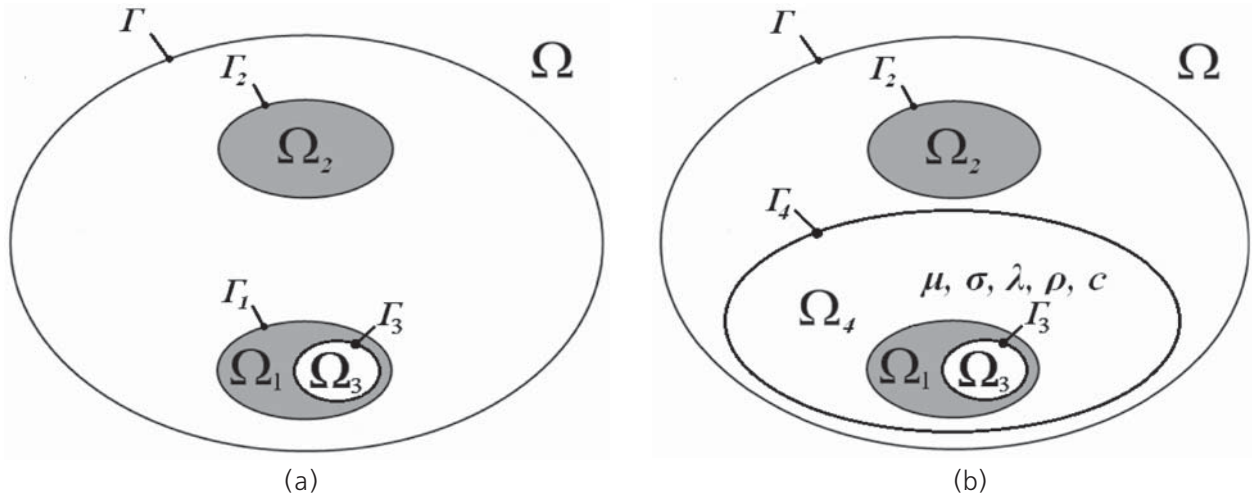


Fig. 1. Schematic diagram of domains used in problem formulation, simplified model (a), full coupled field model (b)

and normal tissue samples, which 3D models are used in numerical coupled field calculations.

PROBLEM FORMULATION

Ferrofluid particles being subjected to a magnetic AC field show remarkable heating effects related to losses during the magnetization process and Joule heating of the particles. The temperature enhancement which occurs in a magnetic ferrofluid system under the influence of an external high frequency magnetic field has found applications in tumor hyperthermia treatment therapy. The main objectives are the uniformity of the temperature distribution and the target value of temperature to be up to 42°C in the controlled region for magnetic hyperthermia treatment.

For determination of the thermal field distribution in magnetic hyperthermia therapy, a coupled electromagnetic – thermal - fluid dynamic field model is established. The electromagnetic field distribution inside the conductive tissue region depends on the time varying magnetic flux density. The heat sources are defined by the electric losses in tissue, acquired by the solution of the electromagnetic field problem. The analysis was carried out on a three-dimensional transient electromagnetic problem according FEM formulation.

The FEM model uses anatomically precise multilevel geometrical model of human breast with known electrical tissue properties, blood and liquor flow speeds in its vessels. The model contains information about real cancer structure

sample acquired by surgical procedure. Cancer and normal electrical tissue properties are directly measured for this sample by precise measurement system [5].

The Scheme of the domains used for the FEM model formulation is shown in Fig. 1. Because of the complexity of the process two schemes are used for the analysis. On Fig. 1(a) a simplified model is shown, where Ω is the whole domain, Ω_1 is the treated tissue domain, Ω_2 is the magnetic field source domain and Ω_3 is the ferrofluid domain. For precise modeling a full scheme is applied, it consists of all mentioned domains and a new one is included – Ω_4 . It represents the body domain, containing the treated tumor tissue domain Ω_1 . For all live tissue domains (Ω_1 , Ω_3 and Ω_4) electromagnetic and thermal properties are defined and in Ω_4 ferrofluid properties are used. Boundaries Γ_1 , Γ_2 , Γ_3 and Γ_4 correspond to the domains Ω_1 , Ω_2 , Ω_3 and Ω_4 , respectively.

Electromagnetic FEM Formulation

The electromagnetic field distribution inside the conductive tissue region depends on the time varying magnetic flux density. The magnetic vector potential \mathbf{A} and electric scalar potential V_e formulation is used for electromagnetic modeling. Equation (1) is the governing equation for the (A-V, A) formulation.

$$\nabla \times \frac{1}{\mu} \nabla \times \mathbf{A} + \sigma \left(\frac{\partial \mathbf{A}}{\partial t} + \nabla V_e \right) + \nabla \times \mathbf{M} = \mathbf{J}, \quad (1)$$

where μ , σ , \mathbf{J} and \mathbf{M} are the magnetic per-

meability, the specific electric conductivity of the tissue, the source current density and ferrofluid magnetization vector, respectively.

$$\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M}) \quad (2)$$

where \mathbf{B} , μ_0 , \mathbf{H} are the magnetic flux density, the magnetic permeability of vacuum and the magnetic field intensity, respectively.

A three-dimensional transient electromagnetic problem according FEM formulation was solved for the analysis.

The Scheme of the domains used for the electromagnetic FEM model is shown in Fig.1. In Ω_1 and Ω_3 domains the \mathbf{A} and V_ϵ exist. The domain Ω is the surrounding free space with only magnetic vector potential distribution. Electromagnetic field source domain Ω_2 is represented with its current density. Zero value Dirichlet boundary condition for the free space boundary Γ is applied.

The induced current density in tissue is expressed by $\sigma(\partial\mathbf{A}/\partial t + \nabla V_\epsilon)$. Heating effect on the tissues and ferrofluid particles is calculated as Joule heating Q by (3) in Ω_1 and Ω_3 .

$$Q = J^2 / \sigma. \quad (3)$$

Magnetic force \mathbf{F}_M acting on ferrofluid particle volumes in domain Ω_3 is

$$\mathbf{F}_M = M\nabla\mathbf{H}. \quad (4)$$

Fluid dynamics

The effect of magnetic field on the magnetic nanoparticles volume concentration is governed by Navier–Stokes equation for the fluid velocities \mathbf{v}

$$\rho\left(\frac{\partial\mathbf{v}}{\partial t} + \mathbf{v}\nabla\mathbf{v}\right) = \nabla p + \eta\nabla^2\mathbf{v} + \mathbf{F}_M, \quad (5)$$

where ρ and η are the density and viscosity of ferrofluid, respectively.

Equation (5) is solved with suitable boundary conditions specifying the contact between the fluid and the domain walls, $\mathbf{v} = 0$ on Γ_3 , and zero traction force at the outflow, $(\rho_n - \mathbf{v}_n) = 0$ on Γ_3 cross-section.

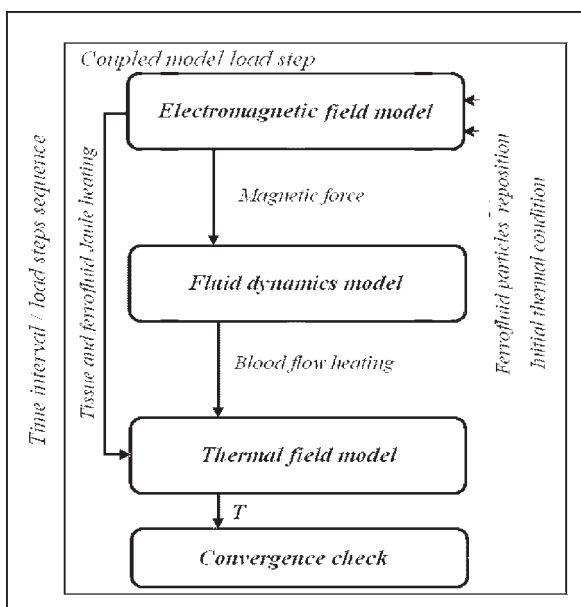
Thermal Field Modeling

The physical process is governed by the bio-heat transfer equation (6), which is a heat conduction equation with specific terms for the generation of heat due to Joule losses Q , blood perfusion Q_p and for metabolic heat Q_m . The equation for a homogeneous isotropic medium is

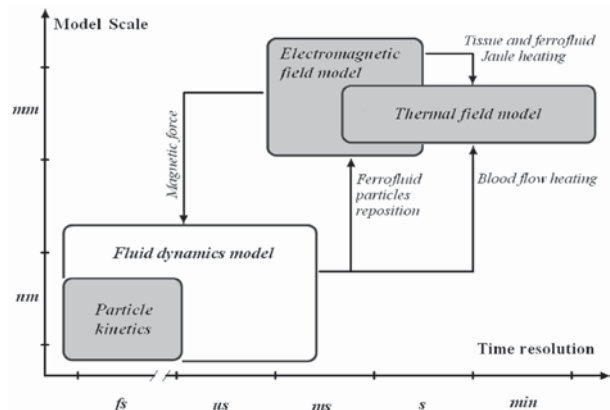
$$\rho c \frac{\partial T}{\partial t} = \lambda \nabla^2 T + Q + Q_p + Q_m, \quad (6)$$

where λ , ρ , c , T are the thermal conductivity, density, specific heat and local temperature of the tissues, respectively. The heat source Q_p due to blood perfusion is given

$$\text{by } Q_p = \omega \rho c_b (T_b - T), \quad (7)$$



(a)



(b)

Fig. 2. Flowchart of the coupled field model (a) and model scale and connectivity diagram (b)

where ω is the blood perfusion rate, expressed by blood flow speed \mathbf{v} in milliliters per second per volume of tissue, c_b is the specific heat of blood and T_b is the temperature of the arterial blood circulating in tissue [8].

The boundary conditions used to solve (6) are heat transfer by convection between the surface of the breast and the external environment Γ_1 or Γ_4 . FEM is used for the thermal field analysis.

Initial temperature of the breast surface is equal to 37°C. The heat transfer coefficient expresses the convection and radiation and it is equal to 10.5 W/m² °C. The metabolic heat Q_m is 7.2 kW/m³. The thermophysical properties were considered in each region of the breast.

Coupled Field Problem

For determination of the thermal field distribution a coupled electromagnetic-fluid dynamic-thermal field problem is built. The heat sources are defined by the electric losses in tissue, acquired by the solution of the electromagnetic field problem. Weak sequential coupling [6] is used where the coupling sequence is shown in the most general form in flowchart in Fig. 2. The coupling of the three fields is in both directions. The heat source is dependent on the results of the electromagnetic and fluid dynamics field analysis. Convergence of the coupled field problem is followed by the temperature of the model for each time step of the modeling process.

TISSUE PROPERTIES

Electromagnetic properties of tissues were obtained by direct measurements on surgically extracted human tissue samples. Investigated probe of breast tumor with surrounding tissue types is presented in Fig. 3. Electric properties of each tissue type are measured with bio-impedance measurement system. Impedance amplitude and angle are stored and visualized for

broad frequency range from 100Hz to 10MHz. Using these data the electromagnetic properties of samples are acquired [5]. The cancer sample consists of tumor and normal tissues. These tissues are histologically recognized and mapped for tumor volume, Fig. 3.

Thermal properties for all tissue types included in the model are defined and presented in Table 1.

The properties of the used water-based magnetic fluid at 40°C are: density $\rho = 1190$ kg/m³, viscosity is $\eta = 4.75$ kg/s•m, initial relative magnetic permeability $\mu_r = 1.214$, magnetization $M = 107$ kA/m, mean particle size 10 - 12 nm, electric conductivity $\sigma = 1.27$ S/m.

Table 1. Model Thermal Properties

Tissue	Density ρ (kg/m ³)	Thermal conductivity λ (W/m°C)	Heat capacity c (J/kg°C)
Tumor	1060	0.6	3200
Skin	1016	0.5	3500
Fat	970	0.45	2110
Lobules	1060	1.25	3000
Blood	1125	1.45	3594
Ferrofluid	1190	0.67	4100

TUMOR MODEL BUILDING

According to the developed coupled field problem formulation, the two models of magnetic hyperthermia are applied. The realistic tumor model, shown in Fig. 3, and 3D breast model, shown in Fig. 4 with tumor are built. The models contain information about real tumor structure sample acquired by surgical procedure. It is a breast cancer tumor sample in medical stage T2N2M1 with maximal size of 25 mm. Sample volume is 317 mm³.

Tumor geometry model and whole breast

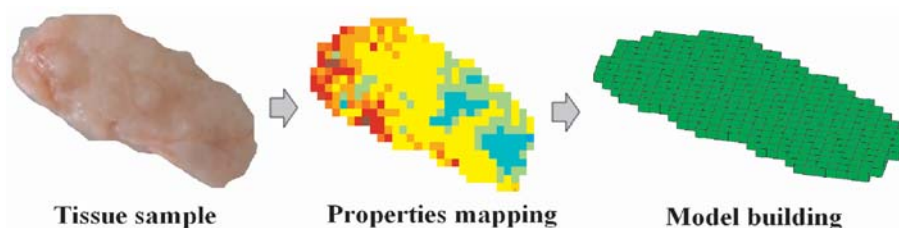


Fig. 3. Tumor model building process

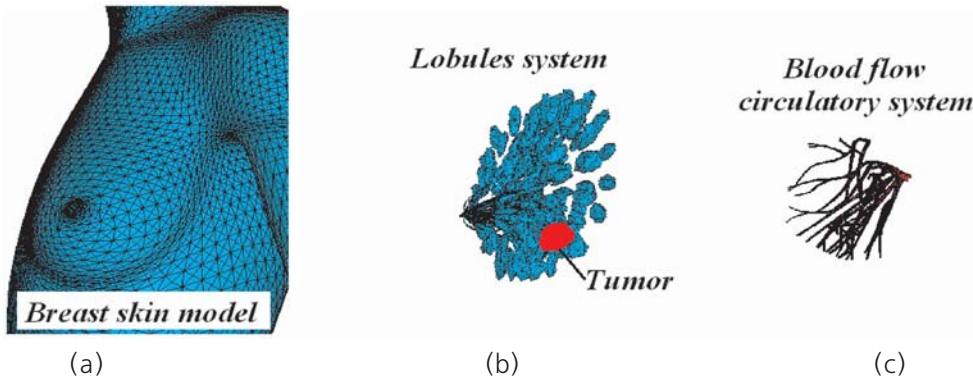


Fig. 4. 3D breast model, surface skin mesh (a), lobules and tumor (b) and blood flow circulatory system

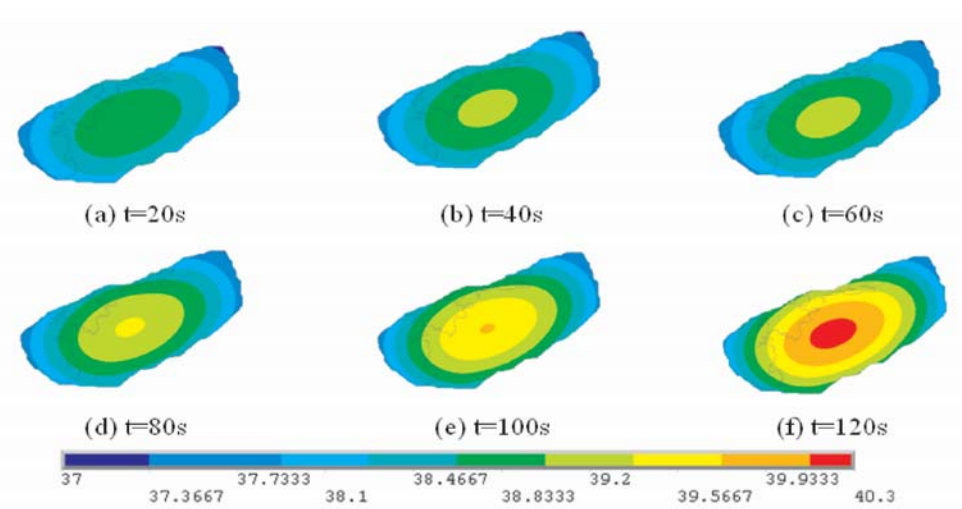


Fig. 5. Thermal field distribution in tumor model for time period of 120s. Images represent the thermal field distribution time sequence of tumor inner layer without ferrofluid used in it.

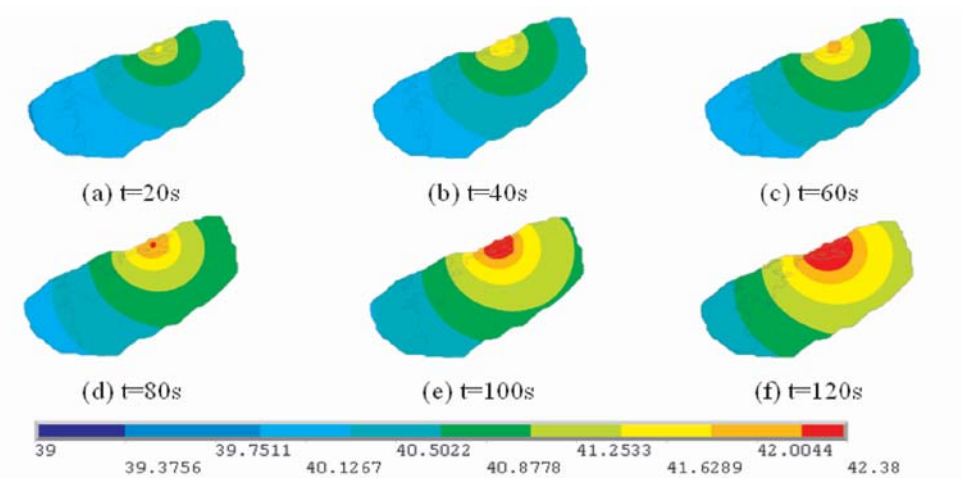


Fig. 6. Thermal field distribution in tumor model for time period of 120s. Images represent the thermal field distribution time sequence of tumor inner layer with presence of ferrofluid in the upper side of the object.

model are built by 3D CT image stack, using sophisticated algorithm for image segmentation and volume model building [9, 10].

Breast model contains the main tissue types as skin, sub-skin fat, lobules tissue, tumor and blood vessels. These tissues form the main inves-

tigated systems in the breast as lobules system, tumor system and blood flow circulatory system.

Fig. 3 shows the structure of real cancer sample acquired by surgical procedure. The 3D geometry model of the same cancer structure reconstructed for the model is implemented in anatomically precise breast model.

Electromagnetic field source is a circular coil with inner diameter $D_1=84\text{mm}$, outer diameter $D_2 = 126\text{mm}$ and thickness $h = 15\text{mm}$. Total number of the coil turns is $w = 20$, wire diameter is 1mm . The coil impedance at frequency of 500kHz and temperature of 25°C is with resistance $R=2.8\text{Ohm}$ and inductance $L=114\mu\text{H}$.

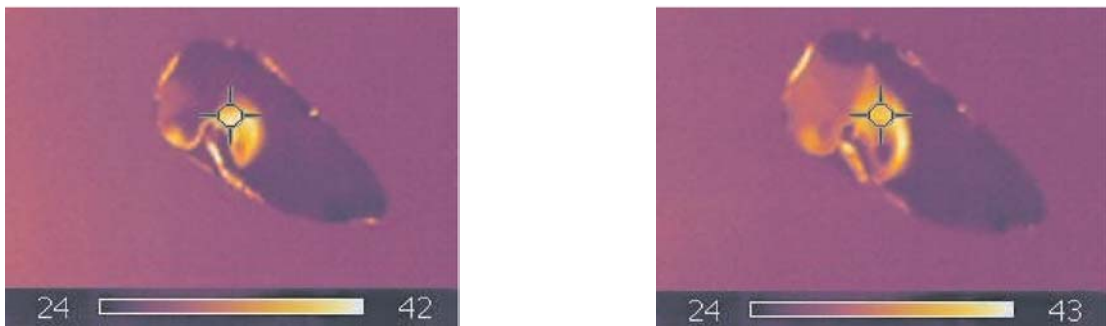
Ferrofluid solution is injected at cancer sample. Ferrofluid filled volume in sample is 24mm^3 .

Thermal field distributions in cancer model for time period of 120s are presented in Fig. 5.

Images (a) to (f) represent the thermal field distribution of tumor inner layer without ferrofluid solution. Maximal temperature acquired is 40.3°C . Fig. 6 represents the calculated thermal field distribution of tumor inner layer with presence of ferrofluid in upper side of the object. Ferrofluid volume concentrates the thermal field maximum and it is the main thermal field source in the sample. Maximal temperature acquired is 42.4°C .

Calculated surface thermal field distribution in breast model is shown in Fig. 8. Temperature maximum represents the position of tumor tissue volume. On Fig. 9 is shown maximal temperature in cancer sample for frequencies from 400kHz to 500kHz , for time period of 120s .

Validation of thermal distribution for breast model is difficult to perform. This leads to a



(a) Tumor tissue sample at $t = 60\text{s}$

(b) Tumor tissue sample at $t = 120\text{s}$

Fig. 7. Infrared thermography of breast cancer sample.

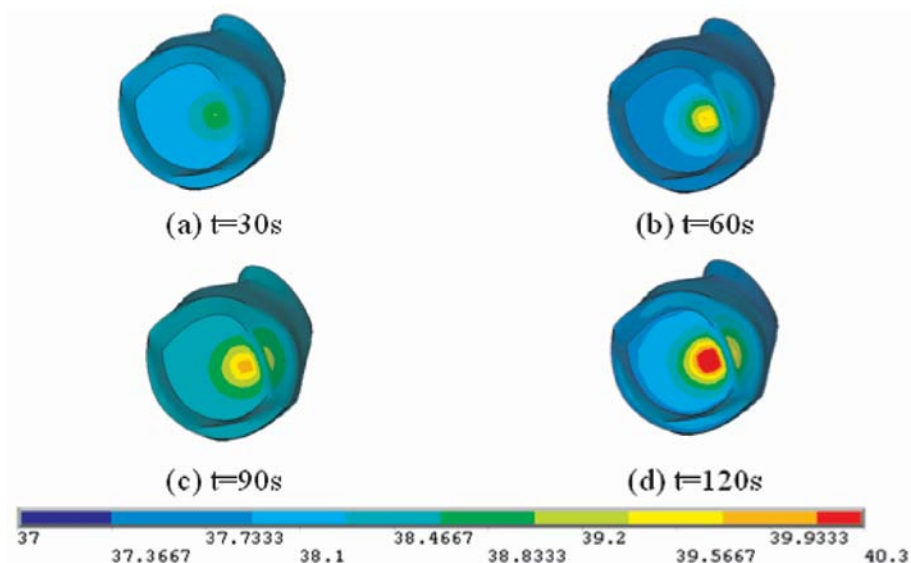


Fig. 8. Thermal field distribution in breast model for time period of 120s

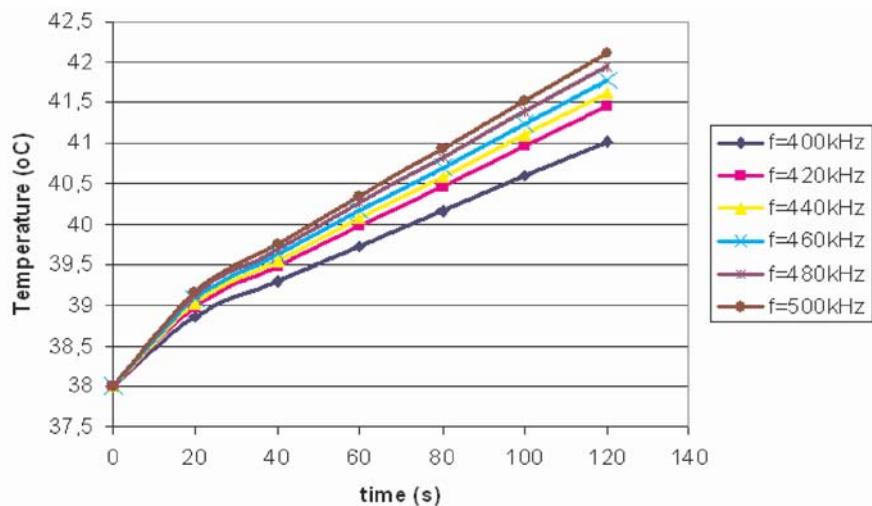


Fig. 9. Temperature in cancer sample for frequencies from 400kHz to 500kHz, for time period of 120s

major barrier to accurate estimation of the tumor thermal contrast on the breast surface, because of the uncertainty of corresponding non-tumor thermal background, which needs to be subtracted from the thermograph.

Results from this model are validated by infrared thermography measurements of the sample. Infrared thermography of breast cancer sample at $t = 60s$ and $t = 120s$ are shown in Fig. 7. Maximal temperature acquired is $43^{\circ}C$. Temperature maximum represents the position of ferrofluid volume. Field values and distributions correspond well to these shown on Fig. 6.

CONCLUSION

A coupled electromagnetic-fluid dynamics-thermal field FEM modeling is developed to determine temperature distribution in breast tumor and to investigate the phenomena during magnetic ferrofluid hyperthermia.

The FEM model uses anatomically a precise multilevel geometrical model of real tumor structure sample acquired by surgical procedure. Electric properties are directly measured for the same sample. Infrared thermal imaging is used for model validation. The results obtained from modeling coincide well with measurements by infrared thermography.

The coupled electromagnetic-fluid dynamics-thermal field FEM modeling is capable to investigate the magnetic ferrofluid hyperthermia processes and phenomena. The developed model can be used for design and optimization of elec-

tromagnetic interaction between electromagnetic devices and biological structures.

Acknowledgment

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ФЕРОФЛУИДНА ХИПЕРТЕРМИЯ ПРИ ТЕРАПИЯ НА РАК НА ГЪРДАТА

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Резюме

Определянето на електромагнитното поле в биологичните обекти е важна интердисциплинарна задача, решаването на която може да предложи много нови възможности за медицинска диагностика и терапия, благодарение на разработените нови методи и средства. Изграждането на нови изчислителни модели и подходи дават възможност за прецизно изследване на ефектите от електромагнитните полета и процеси. В статията е изследвано приложението на магнитна хипертермия при терапия на рак на гърдата. Разработен е 3D смесен модел, обединяващ електромагнитно, топлинно поле и флуидна динамика, за изследване на загряването на туморно образуване. Моделът използва прецизен многосвързан, геометричен модел на реално туморно образуване. Получените резултати за топлинното поле са сравнени с измерени с инфрачервена термографска камера.

INTEGRATED STUDY ON INDOOR ENVIRONMENT IMPACT ON HUMAN PERFORMANCE, COMFORT AND HEALTH, AND EFFECTIVE ENERGY UTILIZATION

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Abstract

The present project deals with an **integrated study on indoor environment impact on human performance, comfort and health, and effective energy utilization**. The study focuses on up-to-date scientific problem with multiple socio-economic effects. It is innovative and the first one for Bulgaria.

The research tasks defined are:

- Design of a specialized laboratory with controlled indoor environment by means of CFD simulation of the room air flow based on a correct mathematical model – the

Reynolds averaged Navier-Stokes equation closed with an adequate turbulence mode;

- Establishing of a specialized laboratory with controlled indoor environment for the purpose of the planned study under the project with groups of subjects (pupils, students, engineers and office workers) performing intensive mental work;
- Development of both a methodology and a procedure for both objective and subjective evaluation of the quality of the indoor environment;
- Development of both a methodology and a

procedure for evaluation of the performance of the subjects taking part in the study – pupils, students, engineers and office workers.

Main results achieved during the first stage of the project (January 2011 to June 2012) can be summarized as follows:

- *Specialized laboratory for controlled indoor environment parameters was designed and equipped using CFD based simulations;*
- *Procedures for performance assessment of occupants with intensive mental work (students, pupils in schools, office workers) were developed;*
- *Preliminary studies using the developed procedures were performed.*

INTRODUCTION

The project faces three important priority areas – human health, environment and energy efficient buildings.

Generally speaking, the environment strongly concerns the world as it evidently affects all aspects of the life on the planet through the global warming, several local sources of pollution, etc. Therefore problems related with the outdoor environment are visible and look very familiar for all of us. However, people are very much directly affected by the indoor environment in their everyday life. Indoor environment directly influences their comfort of life, health, performance and productivity at the end, no matter what they do.

In 1983 World Health Organization (WHO) published a report [14], where the term “Sick Building Syndrome” (SBS) was defined. There is no doubt that the Indoor Environment Quality (IEQ) affects human health, human well-being, employee performance and productivity at work, but still it is not known enough about how different factors of IEQ influence this effect.

At the same time the society spends a lot of money to maintain the indoor environment in acceptable conditions as more than 40% of the energy used in EU belong to the building sector. Therefore several measures were taken in the last decades for energy saving in buildings. These measures directly affect the indoor environment, since they introduce changes in ventilation

and air-conditioning in order to save energy. Usually the result is reduction of air supply rate and reduction of infiltration caused by the new air-tight windows and doors. As a result the quality of the indoor air significantly decreases thus affecting the people’s life, including remarkable increase of health problems (allergies and asthma), and discomfort, as well as decrease of performance and productivity. The respective socio-economic effect is measured by the lower quality of life, lower performance, illness, sick leave, increasing number of people dissatisfied, etc. Hence, the importance of indoor environment quality affects not only the individuals but the society and economy as well, having its strong negative socio-economic impact.

In scientific literature evidences are provided, which show that the indoor environment affects the occupants’ comfort and performance in the short term but in the long term impaired performance and comfort dissatisfaction leads to potential acute health problems. Moreover, usually the occupants cannot feel and assess without bias how the poor indoor environment affects them due to the ability of humans to adapt. Once the occupant can feel discomfort indoors he can change his behavior in terms of changing some of the indoor environment parameters, but if the occupant is already adapted to the environment he is no more able to control his physiological and psychological needs (which predetermine human’s behavior).

Over the last decade huge number of people in Bulgaria replaced their old wood framed doors and windows with new air-tight PVC or aluminum or wood framed glazing units. This is done on the public buildings too. The result of such replacement is visualized on Figure 1 by the CO₂ volume fraction time variation in a classroom of the private primary school St. Kliment Ohridski in Sofia. It is obvious that during almost the whole day students are exposed to levels of CO₂ above the worst level prescribed by БДC EN 15251:2007 standard. This makes the problem with the poor microclimate extremely actual for Bulgaria, especially in schools, universities and offices, where a large number of people is concentrated. That is why in the present study exactly the occupants of these buildings are an object of in-

terest and investigation.

The importance of the indoor environment related with the energy saving problems reflects in an intensive research in the field. There are great number of studies and papers in the literature related with this topic. In a critical review Mendel [9] reports that there exists evidence that indoor environmental quality (IEQ) has direct association to the performance or attendance. Mendel and Heath [10] show also that poor IEQ in schools is common and adversely influences the performance and attendance of students, primarily through health effects from indoor pollutants, which justifies (i) immediate actions to assess and improve IEQ in schools and (ii) focused research to guide IEQ improvements in schools. This conclusion is also supported by the work of Berner et al. [4], Braganza et al. [5], Bakó-Biro et al. [2].

There are several studies where the effect of different indoor environment parameters influences the performance of workers (mainly of office work), such SBS: Mendell [9]; Seppanen [11], Warkocki [14], effect of noise: Weinstein [15, 16], ventilation rate: Seppanen et al. [11, 12], Bako-Biro [1, 2, 3], temperature: Seppanen [13]. All these studies and others have established evident dependence of people's performance and productivity on the indoor environment quality.

The referred papers together with several others, clarify the present status of the studies in the field which can be summarized as follows:

- There is still no clear understanding about the physiological mechanisms behind the effects of the indoor environment on the performance.
- The relation between the adaptation to thermal environment and its impact on the performance is still not clarified.
- There is still no clear understanding about the combined effects of the indoor environment factors on the performance.
- It is still not clear how to measure performance under the real conditions as well as whether it is possible to estimate the self-reported performance and how.
- There is clear evidence that further studies are needed to understand better the effect of IEQ on human wellbeing.

OBJECTIVES

The main objective of the project is to give significant input into the knowledge in the field on the basis of an integrated study on the indoor environment impact on human performance, comfort and health and effective energy utilization.

In order to achieve this, there were defined the following tasks:

- Field studies on the influence of the indoor environment on the occupants' performance, comfort and health in real conditions;
- Field studies on the influence of the indoor environment on the occupants' performance, comfort and health in controlled laboratory conditions.

These two studies will be carried out for three groups of subjects:

- Pupils in a school (in a Private Primary School "St. Kliment Ohridski") in the real classroom conditions (the conditions in the chosen school are very appropriate in terms of both standards applied and requirements of the study);
- Students from Technical University of Sofia under the real classroom conditions; both Bulgarian and foreign students who study engineering subject in English are involved in the study.

RESULTS ACHIEVED AT THAT STAGE

1. Design and establishing of a specialized laboratory with controlled indoor environment by means of CFD simulation.

The research is based on numerical modelling of different working regimes of the ventilation and acclimatization system in laboratory room 2225, situated in Technical University – Sofia. The simulation research is based on Computational Fluid Mechanics (CFD). The indoor quality analysis takes into account the airflow parameters as well as the comfort and basic micro climate parameters. Important aspect of the research is the Drought Rate (DR), the Predicted Mean Vote (PMV) and the Predicted Percentage Dissatisfied (PPD). The goal of the simulation research is to identify suitable positions for the ventilation and acclimatization system as well as to evaluate the performance of different work-

ing regimes. This will guarantee the efficiency and will ensure the controlled conditions in the environment.

Figure 2 shows the geometrical layout, the developed computational grid and the contours of all objects in the investigated room. The total number of computational cells is 187446. The structured computational grid reduces the simulation error and speeds up the convergence of the solution, which is required in such long term numerical studies.

Several conditions with respect to air terminal devices type, size and location as well as modes of operation were simulated in order to achieve the required parameters of the indoor environment such as homogeneous velocity and temperature field and based on this general thermal comfort indexes PMV and PPD and local thermal discomfort parameter DR were evaluated.

Figure 3 to figure 7 show the visualized numerical results for the above parameters. As it can be seen, the achieved distribution of these parameters and indexes satisfy the standards.

Figure 8 and figure 9 show views of the established laboratory with the installed equipment.

2. Procedures for objective assessment and subjective evaluation of indoor environment quality

Indoor environment is a complex integrity of various interrelated elements, which must be combined to ensure human comfort and satisfaction with the environment. Over the years it became clear that indoor environment with good quality could be designed only by teams which think the indoor environment in its complexity. The relationship between indoor environment components and human performance is schematically presented on Figure 10. It is obvious that the impact of the indoor environment parameters on human has physiological and psychological concern and they both can be assessed using different approaches.

Both the objective and subjective assessment of the indoor environment elements are addressed in the blue boxes of Figure 10.

Objective assessment of thermal environment

will be done following the ISO 7730 standard procedure with measuring instruments which cover the requirements of ISO 7726 standard. More details can be found in the standards referred to, as well as in Markov [6]. Subjective assessment of both general thermal comfort and local thermal discomfort will be done by questionnaires Markov [6].

Objective assessment of indoor air quality will be done based on continuous measurements of CO₂ concentration and relative humidity of indoor air. The methodology for assessment of indoor air quality follows the requirement of CEN CR1752 document. Subjective evaluation of indoor air quality will be performed by questionnaires. All details are presented in Markov [7, 8].

Visual and acoustic environment will be assessed by measurement of the illuminance at each work place and the sound power level in a single point. Subjective evaluation of these elements of the indoor environment will be done by a questionnaire designed to collect subject's perception of the general comfort in the room.

3. Procedures for subject's performance evaluation

It is obvious that the impact of the indoor environment parameters on human has physiological and psychological concern and they both can be assessed using different approaches. The main concern of this paper is the *psychological effects* caused by the indoor environment factors, namely the five symptoms relevant to performance: arousal, logical thinking, short term memory, alertness of mind and effort.

For pupils there are two differences: instead of short term memory is tested concentration and fatigue, and the efforts self-assessment tests are omitted. The Tsai-Partington test is used for examination of arousal level. Logical thinking tests comprise "Figural reasoning" and "Exclude the unnecessary word". Concentration and fatigue are examined by two tests: "Find the hidden word" and "Find the proper combination of the given letters/ symbols", and three mental performance tasks are selected – addition, subtraction, number comparison. All those tests and procedures are presented in Simova et al. [2012b].

4. Improvement of the indoor air quality in Private primary school "St. Kliment Ohridski", Sofia

An immediate result from the work under the project is the adequate reaction of the school authorities with respect to indoor air quality at the school. Based on the results of the measurements performed in the school the teaching staff was trained how to maintain the indoor air quality by regular aeration of the classrooms during the breaks. Students are also much more concerned about the quality of the indoor air even at home. This way positive effect was multiplied in the families of the students as well.

RESEARCH TASKS STILL TO BE DONE

1. Development of a methodology for implementation of the laboratory study on the performance of various groups of subjects (pupils, students, engineers and office workers) under controlled indoor environment conditions.

2. Development of a methodology for implementation of the field study on human subjects' performance at their workplace under non-controlled indoor environment conditions.

Investigation on the impact of the indoor environment quality on the performance of human subjects involved in intensive mental work.

3. Development of a database of the study with data obtained under both the laboratory and field studies on the performance of the various groups of subjects – pupils, students, engineers and office workers. This database will be established in a format allowing exchange of the data with specialized European and worldwide organizations and research centers such as ISIAQ (International Society of Indoor Air Quality and Climate), ICIEE (International Center for Indoor Environment and Energy), etc.

4. Analysis of the data obtained on the impact of the indoor environment on the performance and comfort of the investigated groups of subjects at the specific character of their activities.

5. Development of a model for evaluation of the potential human subject performance at the design stage of the indoor environment through mathematical modeling and computer simulation

of the room air movement in ventilated and air-conditioned spaces.

6. Development of practical recommendations for designing of the indoor environment, which are focused on achieving the maximum possible performance of the occupants and effective utilization of the energy.

DISSEMINATION OF THE RESULTS

In terms of dissemination of the results, the team has performed the following activities:

- Development and support of project website: <http://www.perfecten.tu-sofia.bg>.
- Organization of a scientific seminar for the partners as well as for wide audience.
- Regular work meetings and round table discussions with the team members and the partners.
- Development of a brochure in English and Bulgarian languages, with the most important outcomes from the different parts of the project.
- Project presentations have been performed in Denmark, Germany, Bulgaria.
- The following papers concerning the project were published or submitted and accepted for publishing:
 - Pichurov G., P. Stankov. "Computation of the ventilation efficiency based on computer simulation of the flow", "Energetica" Journal, 3' 2012, pp. 35-40, 2012;
 - Mijorski S., D. Markov, G. Pichurov, P. Stankov. CFD based design of ventilated space, Central European Journal of Engineering, submitted for publishing;
 - Markov D. CFD based design of a ventilated and air-conditioned space, Proceedings of Eighth International Course for Young Researchers "Computational Engineering", ISSN 1314-0779, Pamporovo, Bulgaria, pp. 83-94, 2012;
 - Simova I., D. Markov, P. Stankov. "Battery for assessment of the indoor environment impact on the performance of students, teachers and office workers", Proceedings of XVII Scientific Conference with International Participation EMΦ 2012, pp. 64-72, 2012;
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CONCLUSIONS

The literature survey as well as the preliminary measurements performed within the present project clearly illustrate that the indoor environment quality strongly affects the occupants' health, quality of life and productivity.

The study planned for the second stage of the project will go more deeply into the problem as the newly established laboratory with controlled indoor environment parameters allows systematic investigation to be performed.

Acknowledgment

This study is financially supported by Bulgarian Science Fund with the Ministry of Education Youth and Science under the ДДВУ-02-8/17.12.2010 grant.

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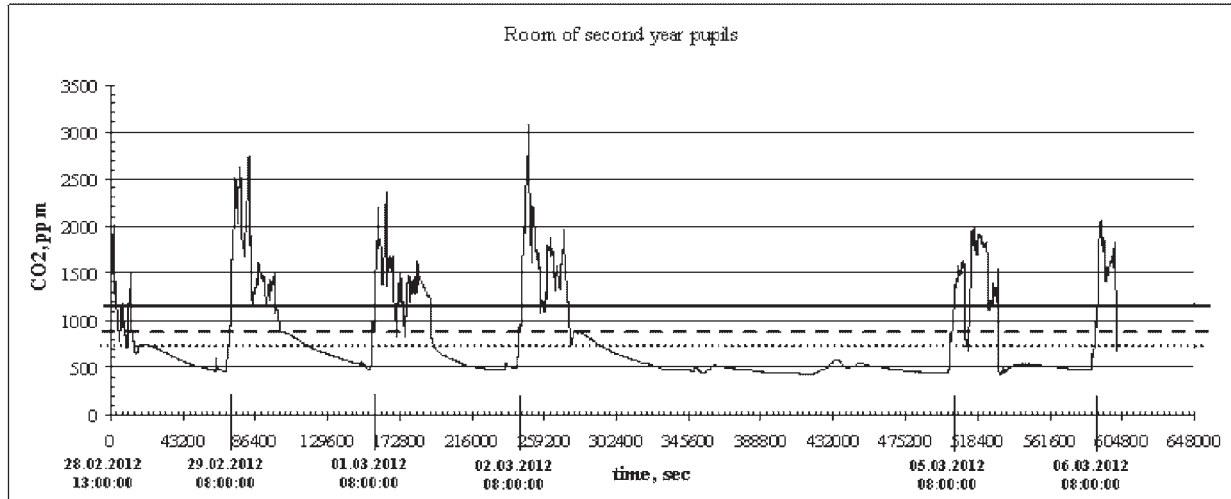
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Outdoor CO₂ concentration: 400 ppm
 Category I: 350 + 400 = 750 ppm
 Category II: 500 + 400 = 900 ppm
 Category III: 800 + 400 = 1200 ppm

Fig. 1. CO₂ volume fraction time variation in a classroom of the private primary school “St. Kliment Ohridski” in Sofia

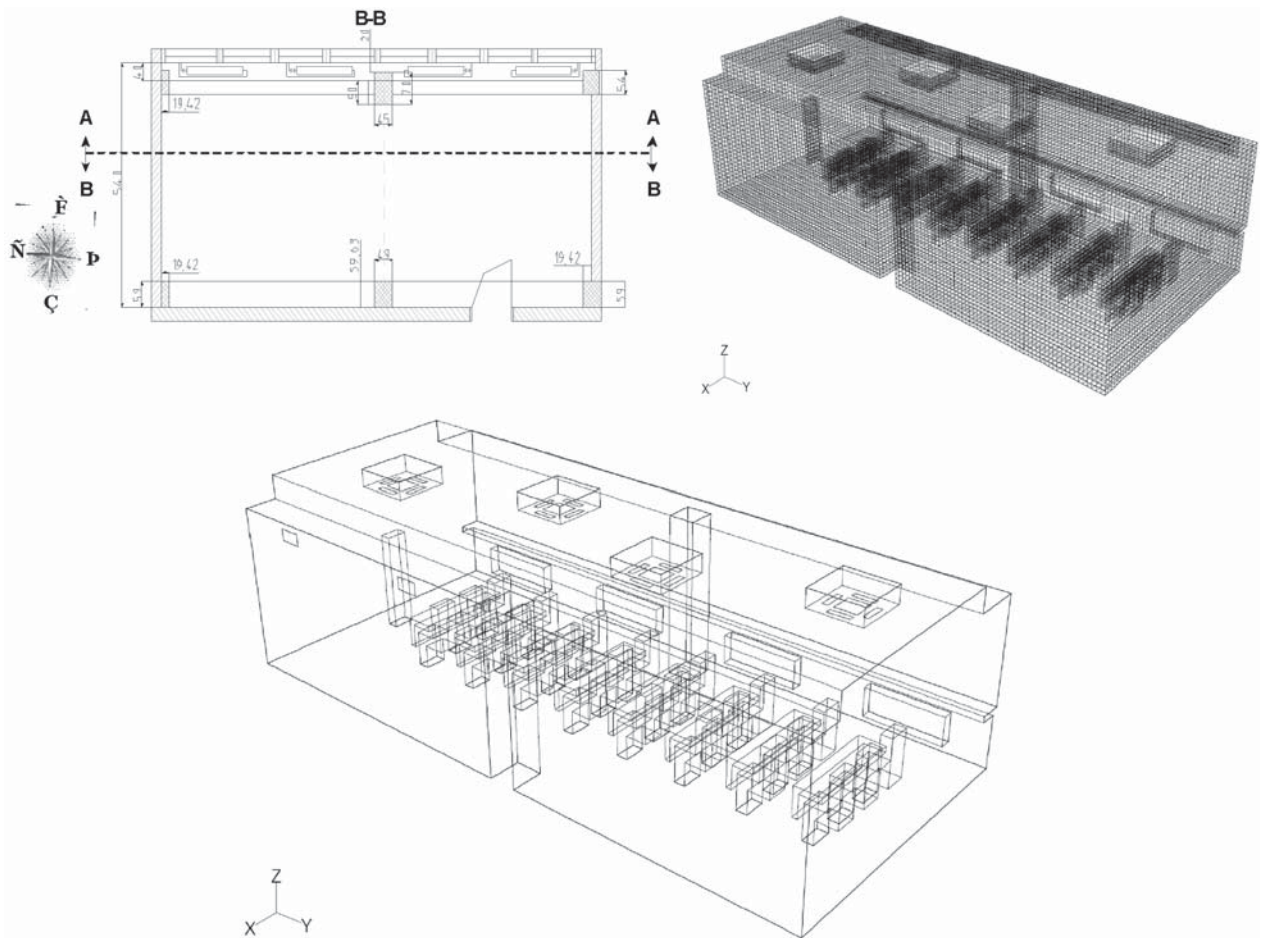


Fig. 2. Geometry, computational grid and contours of the objects in the investigated room

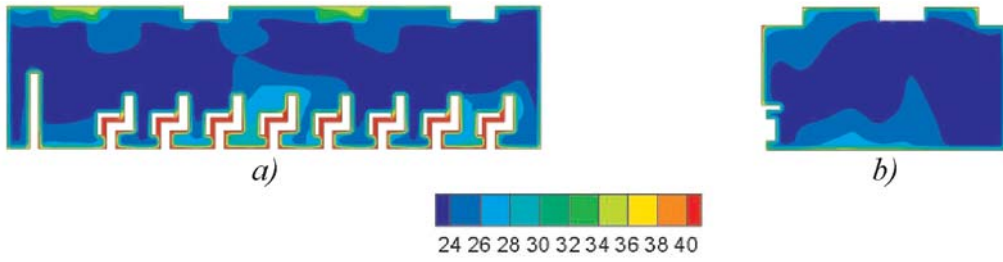


Fig. 3. Temperature field – a) X=2.6; b) Y=1.5

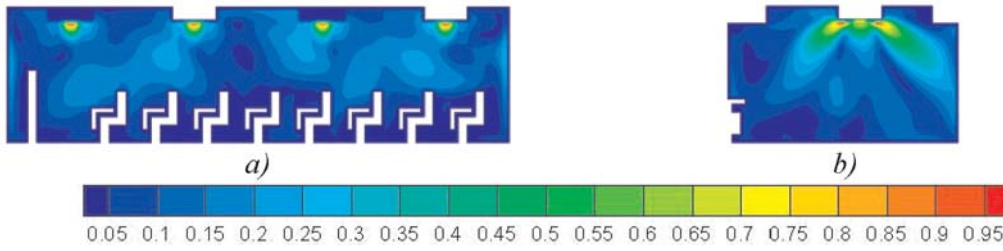


Fig. 4. Velocity field – a) X=2.6; b) Y=1.5

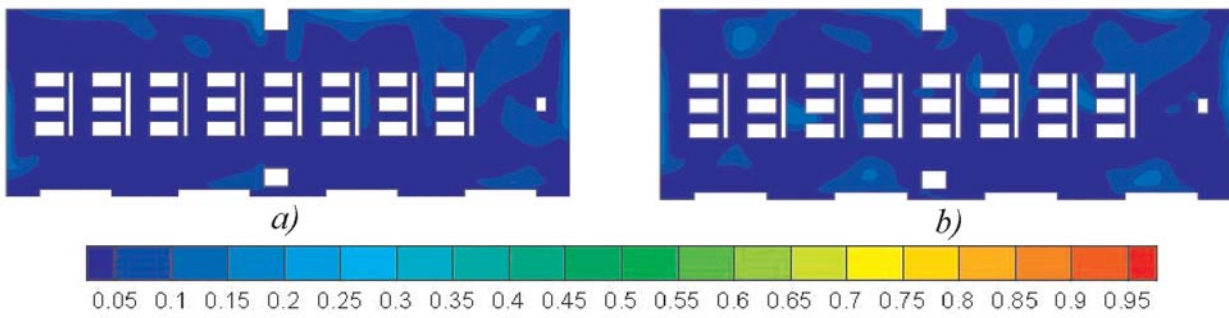


Fig. 5. DR, Z=0.6, 80cm – a) 25°; b) 30°

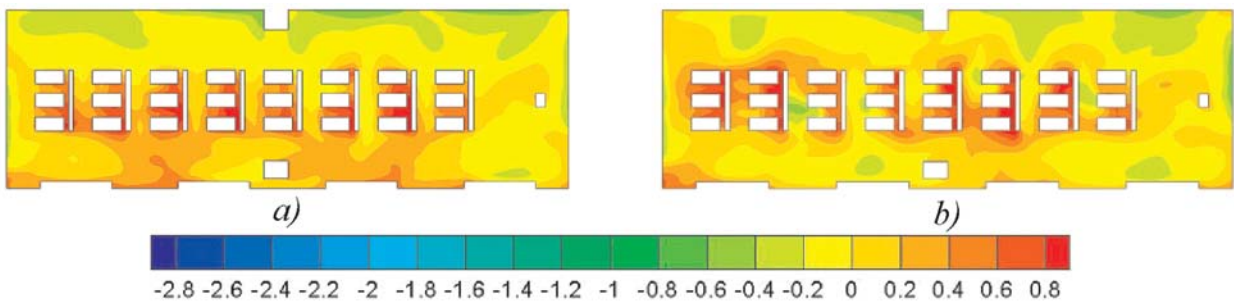


Fig. 6. PMV, Z=0.6, 80cm – a) 25°; b) 30°

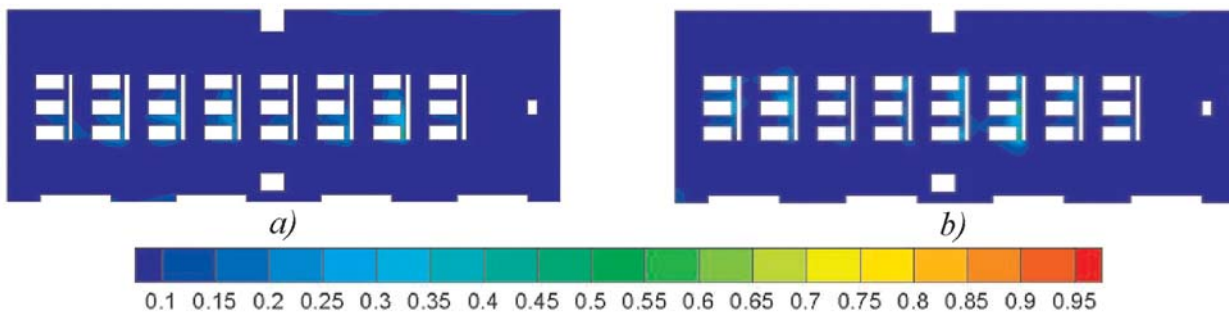


Fig. 7. PPD, Z=0.6, 80cm – a) 25°; b) 30°



Fig. 8. Left side view of the established laboratory with the installed equipment



Fig. 9. Right side view of the established laboratory with the installed equipment

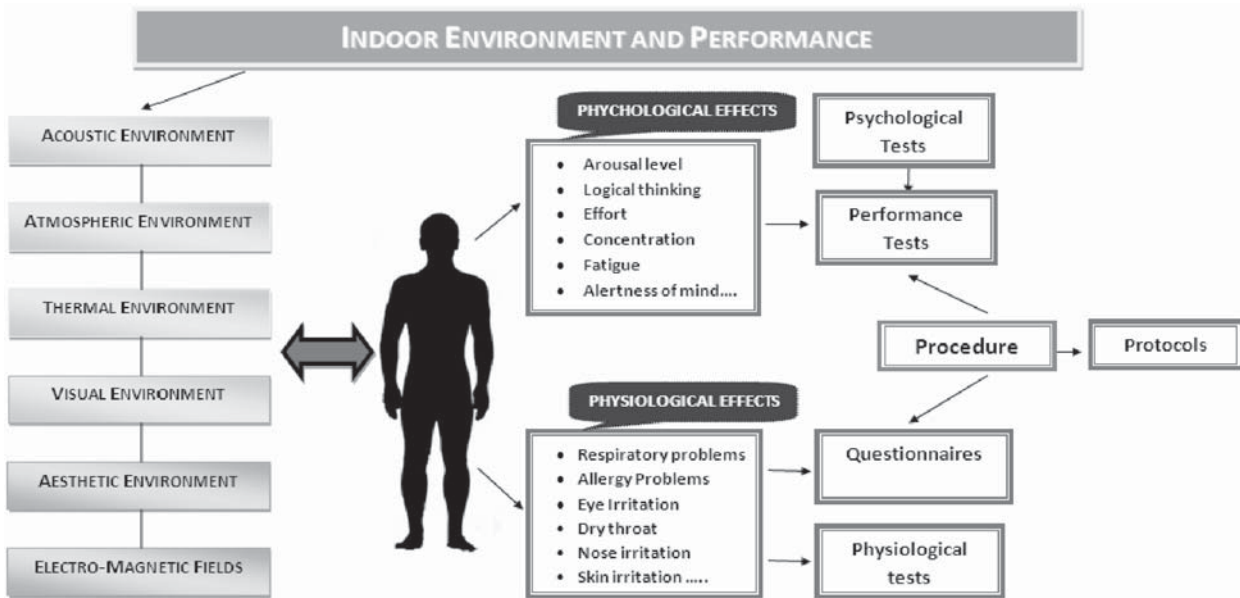


Fig. 10. Relationship between indoor environment components and human performance

КОМПЛЕКСНО ИЗСЛЕДВАНЕ НА ВЛИЯНИЕТО НА ВЪТРЕШНАТА СРЕДА (МИКРОКЛИМАТ) ВЪРХУ РАБОТОСПОСОБНОСТТА, КОМФОРТА И ЗДРАВЕТО НА ХОРАТА И ЕФЕКТИВНО ИЗПОЛЗВАНЕ НА ЕНЕРГИЯТА

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Резюме

Настоящият проект е свързан с комплексно изследване на влиянието на вътрешната среда (микроклимат) върху работоспособността, комфорта и здравето на хората и ефективно използване на енергията. Изследването е иновативно и първо по рода си за България.

Поставените цели на изследването са:

- Проектиране на специализирана лаборатория с контролирана вътрешна среда с помощта на симулация на въздушните течения в стаята, основано на коректен математически модел – осреднените по Рейнолдс уравнения на Навие – Стокс и оценка на топлинния комфорт на обектите на

изследването чрез термо - физиологичен модел.

- Създаване на специализирана лаборатория с контролирана вътрешна среда за целите на планираното по проекта изследване с групи от обекти (ученици, студенти, инженери и офис работници) извършващи интензивна умствена дейност.
- Разработване на методология и процедура за обективно и субективно оценяване на качеството на вътрешната среда.
- Разработване на методология и процедура за оценяване на производителността на обектите, които участват в изследването – ученици, студенти, инженери и офис работници.

Основните резултати, които са постигнати по време на първия етап от изследването (януари 2011 – юни 2012), могат да бъдат обобщени както следва:

- Проектирана е и е изградена специализирана лаборатория за контролиране на параметрите на вътрешната среда с помощта на симулация на течението.
- Разработена е процедура за оценка на производителността на обитателите, извършващи активна умствена дейност (студенти, ученици и офис работници).
- Извършени са редица предварителни експериментални изследвания с разработените процедури.

EXPERIMENTAL RESEARCH OF WIND TURBINE GENERATOR POWER CONTROL IN A HYBRID LABORATORY TEST BENCH

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Abstract

The paper describes the developed power control system for wind turbine generator based on a hybrid laboratory test bench. The structure and hardware configuration of the control system is represented. The mathematical model which describes the drive train and experimental determination of the model parameters are considered. Some experimental results in accordance with the maximal power extraction and power reference tracking control strategies are shown. A PC based HMI system for processes control and visualization is developed.

INTRODUCTION

The priority development of renewable energy sources (RES) determines the actuality of the task of modeling and analyzing their work in electric power system (EPS). The stochastic nature of wind speed determines relevant change in the magnitude of produced power to the EPS. At the same time power consumption of EPS has a stochastic nature. Thus, in the EPS there are already two random processes with a variable power. Random variation of the power output of wind power plants (WPP) makes difficult to forecast and to keep the balance between power production and load, and therefore the forecasting and control processes of the normal operation of EPS. This imposes the increase of spinning reserves and complicates control systems for the EPS normal operation. Wind plants must be treated as an integral part of the electric system [1]. Wind energy utilization in some countries comprises wind turbines integration in the frequency-power control system, which is a significant step to wind turbine participation in the operation control of the EPS [3]. *Therefore the WPP operation may include the wind turbine power control in order to extract maximum energy from the wind (if there is a permission for*

such mode of operation by the system controller) as well as the operation on a partial power output (as a part of the available power of the wind) determined from the steady-state "frequency-power" characteristic [7].

The wind turbine power change with respect to EPS frequency deviation is determined from the steady-state "frequency-power" characteristic. It establishes the frequency upper and lower limits in which the wind turbine remains connected to the grid, as well as the power output change (as a part of the available power) depending on the current wind speed versus frequency between the upper and lower limits. The linearized model of the wind generator may be considered as a time-variant system whose parameters depend on the wind velocity. Mathematical description of such systems is convenient to be done in the state space by using the so-called linear parametrically varying transformations (LPV). In this way control of a nonlinear time-variant system may be realized by using time-invariant controllers designed by linear control theory application. The controller design can be accomplished by implementation of the optimal filtering theory (Kalman and Wiener filters). The usage of such a procedure in practice is made difficult by the fact that wind velocity can't be measured accurately and that several generator parameters depend on its aerodynamics and may be determined only approximately. For this reason it is necessary to use design methods for robust controllers that take into account the uncertainties in generator parameters as well as the presence of unstructured uncertainty in its description. Here one may apply methods based on the H_∞ - norm of the closed-loop system in which the gain-scheduled controller is determined by optimization procedure using the so-called linear matrix inequalities (LMI). A powerful method for controller design in the

presence of parametric uncertainty is the μ -synthesis which may be applied to the design of gain scheduled controllers [4]. There is no information about practical implementation of this method to the design of wind generators, the possible cause being the high order of the controllers obtained by the μ -synthesis. With improvement of the hardware used in the implementation of modern digital controllers one may expect that higher order controllers will be used which will help to achieve better performance in the control of wind generators. In this research work a hybrid laboratory test bench is described, which offers convenient tools for modelling, design and implementation of advanced control algorithms for RES operation in power system.

SYSTEM CONFIGURATION DESCRIPTION

The modeling system [8] components are shown in Fig. 1. It comprises the following subsystems:

- Mechanical subsystem: asynchronous motor (ASM) connected with encoder, flywheel and synchronous motor (SM);

- Power components: *Sensor module* that provides the connection with the *Control Unit*; *Single Motor Modules* and *Active Line Module*;
- Control subsystem: Programmable Logical Controller (PLC) and *Touch Panel*;
- Computer system with installed Step 7 – PLC program environment, WinCC Flexible – *Touch Panel* and SCADA system program environment, Matlab/Simulink – program environment for system components modeling – wind and aero dynamical system models, as well as the models of the electric power system (EPS) components.
- Communication networks – Ethernet, Profibus, Drive-Clq.

The ASM is intended for modeling of some wind turbine components. It ensures torque and rotational speed corresponding to the wind parameters. The synchronous motor combined with electronic power converters provides electrical power to the grid. The flywheel is a model of inertia of all rotating elements – turbine, shaft, multiplicator, etc.

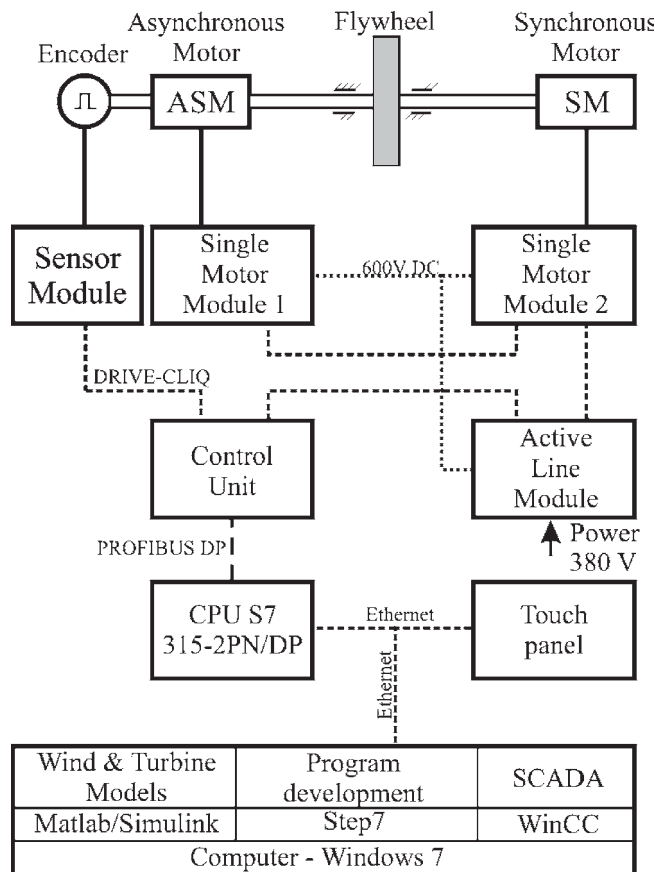


Fig. 1. Modeling system components

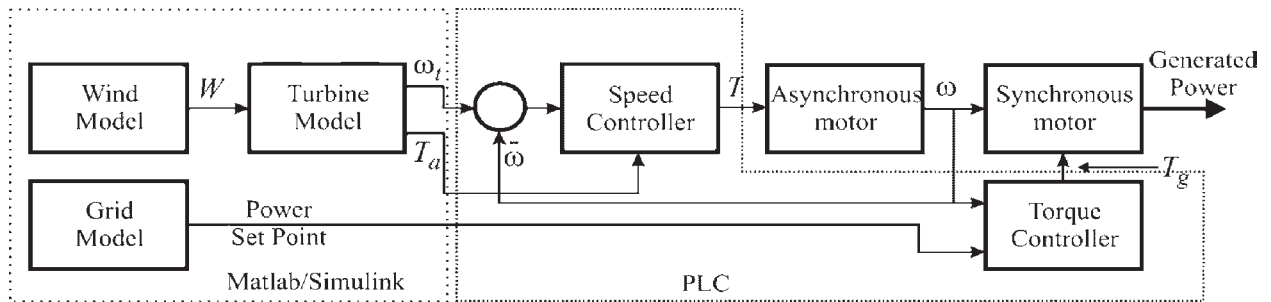


Fig. 2. Block diagram of the wind generator modeling and control system

WIND GENERATOR MODELING

The block diagram of the wind turbine modeling and control system is shown in Fig. 2.

The control system block diagram is shown in Fig. 3, and the test bench system – in Fig. 4. The models of the wind and wind turbine dy-

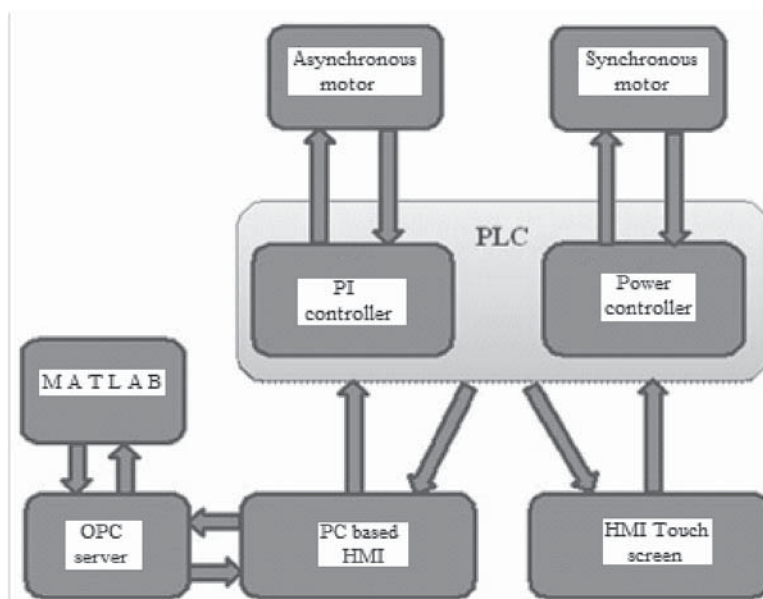


Fig. 3. Control system block diagram

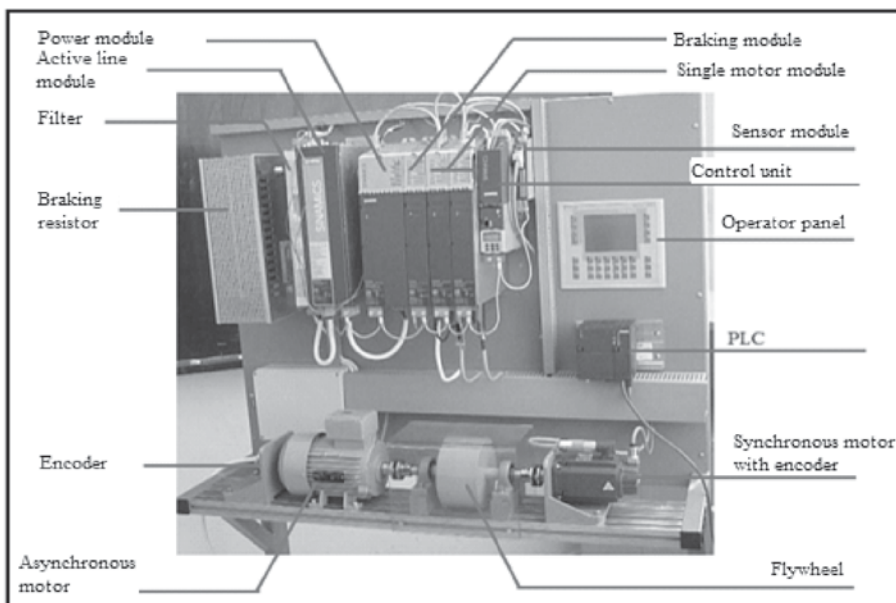


Fig. 4. Laboratory test bench

namics are realized in the Matlab/Simulink software environment. They are designed as a real time model with a sample time 10 s. The outputs of the turbine model are the maximum aerodynamical torque T_a and the turbine rotational speed ω . The asynchronous motor (ASM) and its control system provide a physical model of the wind turbine rotational speed ω under torque limitation by T_a . The electric power system model is also realized in the Matlab/Simulink software package. In accordance with the accepted wind generator control strategy (maximum power extracted from the wind or partial power control mode) the power reference is formed. This power is transformed by the synchronous motor, operating as a generator into electrical torque T_g . The aero dynamical torque created by the turbine depends on the wind speed square value as well as on the torque coefficient as follows [2, 5, 6, 9]:

$$T_a = 0.5\pi\rho R^3 v^2 C_T(v, \beta, \omega), \quad (1)$$

where

ρ is the air mass density, [kg/m^3];

R - rotor radius, [m];

v - wind speed;

$C_T(v, \beta, \omega)$ - aero dynamical system torque coefficient that depends on a wind speed value, blade pitch angle and rotational speed.

By analogy to (1) an expression may be written for the turbine power:

$$P_w = 0.5\pi\rho R^2 v^3 C_p(v, \beta, \omega), \quad (2)$$

where the relation between the aero dynamical torque coefficient and the power coefficient is

$$C_T(\lambda, \beta) = \frac{C_p(\lambda, \beta)}{\lambda}, \quad (3)$$

where the tip-speed ratio λ may be determined from the expression:

$$\lambda = \frac{\omega R}{v}. \quad (4)$$

The nonlinear relationship $C_p(\lambda, \beta)$ is usually approximated by the expression:

$$C_p(\lambda, \beta) = c_1 \left(c_2 \frac{1}{\lambda} - c_3 \beta - c_4 \beta^x - c_5 \right) e^{-c_6 \frac{1}{\lambda}} \quad (5)$$

where

$$\frac{1}{\Lambda} = \frac{1}{\lambda + 0.08\beta} - \frac{0.035}{1 + \beta^3}. \quad (6)$$

According to [6] the coefficients c_i are proposed as equal to $c_1=0.5$; $c_2=116$; $c_3=0.4$; $c_4=0$, $c_5=5$, $c_6=21$.

Taking into account (1) and (3), the aerodynamical torque is represented finally in the following form:

$$T_a(v, \omega, \beta) = \frac{0.5\pi\rho R^3 v^2 C_p(\lambda, \beta)}{\lambda} \quad (7)$$

It can be seen that aerodynamical torque is represented by nonlinear relationship of wind speed value v , turbine rotational speed ω , and blades pitch angle β . The expression (7) can be linearized in terms of small perturbations from the operating point (O.P.) $x_0 = (\omega_0, v_0, \beta_0)$. The representation of (7) in Taylor series about the operating point is:

$$\Delta T_a = \theta \Delta v + \gamma \Delta \omega + \delta \Delta \beta, \quad (8)$$

where the coefficients are

$$\theta = C_0 \left[\frac{2v_0 C_p(\lambda_0, \beta_0)}{\lambda_0} + \frac{v_0^2}{\lambda_0} \frac{\partial C_p}{\partial \lambda} \frac{\partial \lambda}{\partial v} \Big|_{OP} - \frac{v_0^2 C_p(\lambda_0, \beta_0)}{\lambda_0^2} \frac{\partial \lambda}{\partial v} \Big|_{OP} \right],$$

$$\gamma = \frac{C_0 R v_0}{\lambda_0^2} \left(\lambda_0 \frac{\partial C_p}{\partial \lambda} \Big|_{OP} - C_p(\lambda_0, \beta_0) \right),$$

$$\delta = C_0 \frac{v_0^2}{\lambda_0} \frac{\partial C_p}{\partial \beta} \Big|_{OP},$$

$$C_0 = 0.5\pi\rho R^3, \quad \lambda_0 = \frac{\omega_0 R}{v_0}$$

The one-mass drive train model is described by the equation

$$T_a - T_g = J_r \frac{d\omega}{dt} + B_r \omega, \quad (9)$$

where

T_a is the wind wheel torque, [N.m];

T_g - generator torque, [N.m];

ω - turbine rotational speed, [rad/s];

B_r - damping coefficient in the mechanical subsystem [N.m.s];

J_r - turbine inertia, [$kg \cdot m^2$].

In accordance with the aero dynamical torque linearization around the operating point represented by Eq. (8), the following linearized form of Eq. (9) holds

$$\theta \Delta v + \gamma \Delta \omega + \delta \Delta \beta - \Delta T_g = J_r \frac{d\Delta \omega}{dt} + B_r \Delta \omega. \quad (10)$$

The physical model of wind turbine generator system represented by one-mass model is studied

$$J_r \frac{d\omega}{dt} + B_r \omega = T_a - T_g, \quad (11)$$

where T_a is the motor torque, and T_g - resistance torque of the SM. The transfer function with respect to the motor torque is

$$W(s) = \frac{\omega(s)}{T_a(s)} = \frac{k}{Ts + 1}, \quad (12)$$

where $k = \frac{1}{B_r}$, $T = \frac{J_r}{B_r}$.

The mathematical model parameters are obtained by experiments under variable torque magnitude applied as a step input 0.25Nm, 0.5Nm, 0.75Nm, 1.0Nm, 1.25Nm и 1.5Nm. The experimental results are shown in Fig. 5. In order to ensure safety experiments, the motor velocity is restricted to 1500 rpm that is less than the admissible angular velocity in the system. The parameters k and T are obtained by identification procedure applied to the experimental data.

For example, model parameters are

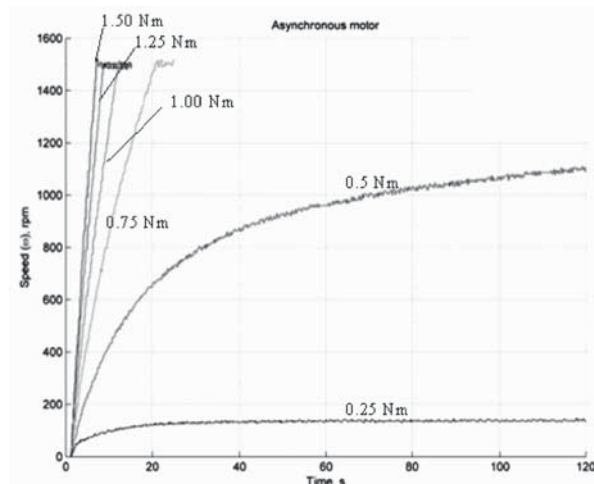


Fig. 5. Motor velocity under variable torque

$k=4897.9$, $T=20.45$ s if the torque reference is 1.25 Nm. In Fig. 6 a comparison of the motor velocity obtained from the laboratory test bench and the identification procedure under torque reference signal of 0.75 Nm is shown. Similar experiments have been carried out under variable torque reference magnitude. They confirm the identification model accuracy. Significant deviations between experimental data and identification model exist in the cases of small torque values when the aero dynamical torque is comparable to the friction losses when in fact the wind turbine generator system doesn't oper-

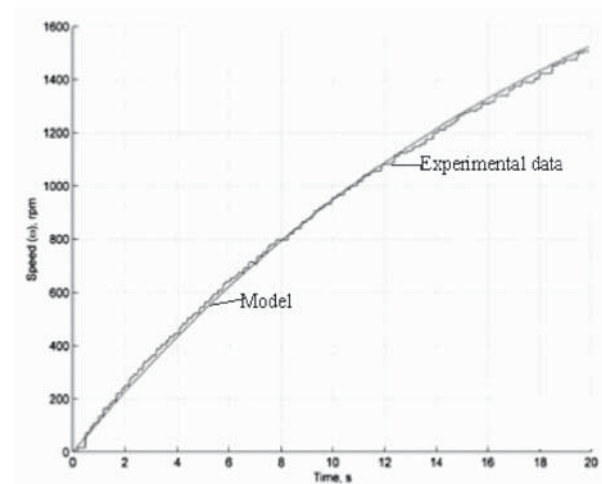


Fig. 6. Motor velocity results comparison (laboratory test bench and identification model) under torque reference of 0.75Nm

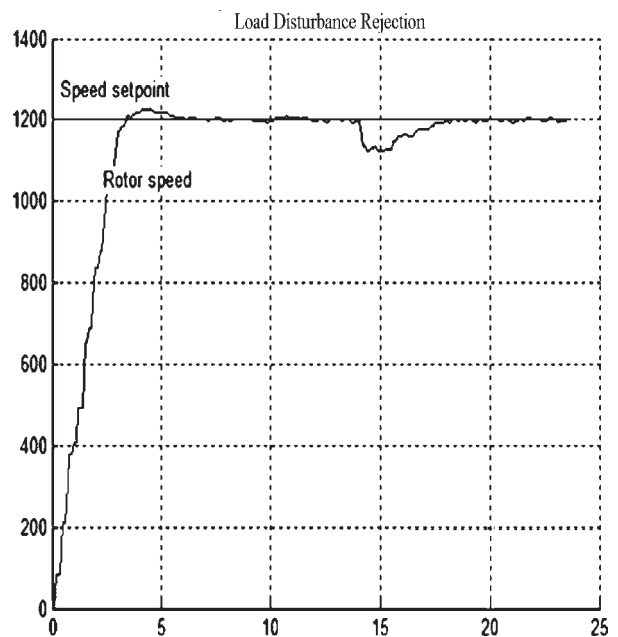


Fig. 7. Experimental results by load disturbance rejection

ate.

The speed control loop is accomplished by PI controller (see Fig. 2) which has an additional input, providing the torque maximal value to the system and which is intended to saturate the controller output. In Fig. 7 the speed control and disturbance rejection experiments obtained by laboratory test bench is shown.

WIND TURBINE GENERATOR POWER CONTROL

The range of the wind turbine generator power depends on its mode of operation. The relationship between the generated power and the wind turbine aero dynamical torque is

$$P = T_g \omega. \tag{13}$$

In the ideal case the maximum power will be generated at maximum rotational speed and maximum load applied to the generator. In real situations the friction losses should be taken into account. For their determination several experiments are carried out. They use different rotational speed values - [500, 750, 1000, 1250, 1500] rpm and control signal limitation up to 1.5Nm. The generator torque is formed as a ramp function in range of 0÷1.3Nm. In Fig. 8 the experimentally obtained losses in the motor-generator system are shown.

PROCESS VIZUALIZATION TOOLS

The system control is implemented by the operator panels of SCADA system, developed in the WinCC Flexible Software environment of Siemens [10]. For easier data transfer between MATLAB/Simulink the OPC server of WinCC Flexible is utilized. In Fig. 9 some of the operator panels are shown.

PC based HMI system ensures system remote control and processes real time visualization. It provides the input information of the control loops – speed reference of the asynchronous motor and the power reference of the synchronous motor. The controller parameters, the sample time and the control signal limit may be adjusted from the control panel of SCADA system. Another function of the HMI system is the real time visualization of the technological process parameters– the control signal value, the PID controller components values, and the generat-

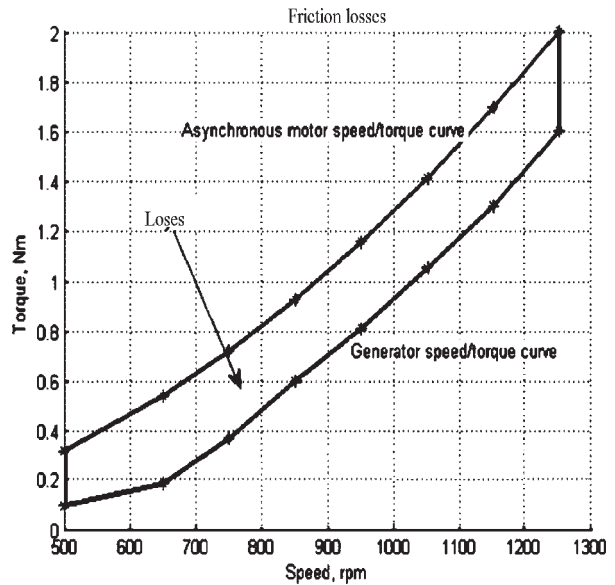


Fig. 8. Friction losses in the motor-generator system

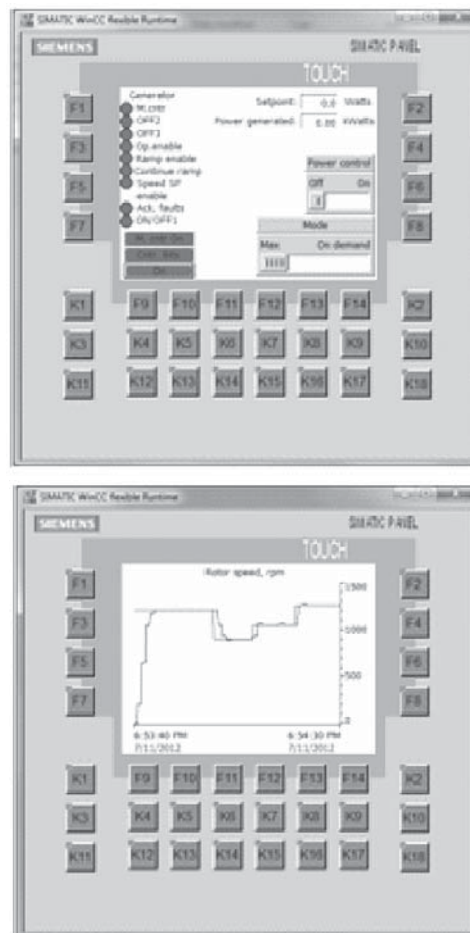


Fig. 9. Panels for control and visualization of power value, as well as visualization of the rotational speed and the power as a function of time. An important function of the HMI system is the control of power supply and invertors of a

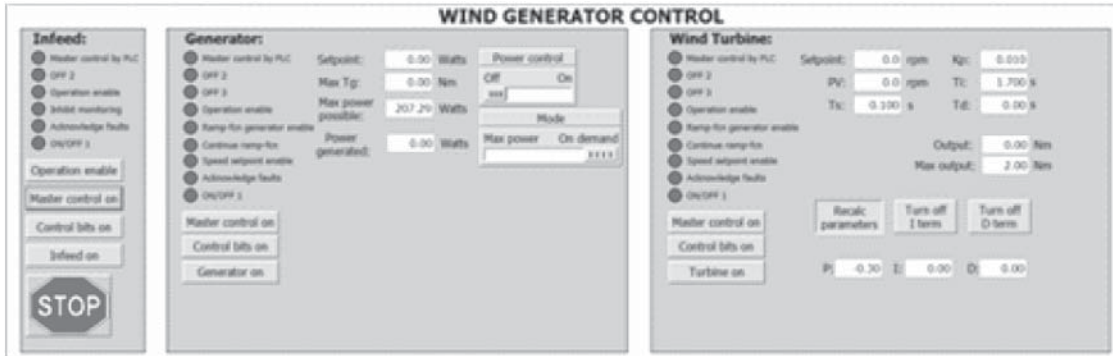


Fig. 10. Control panel of SCADA system

servo system. The SCADA system control panel for the wind generator speed and power control is shown in Fig. 10.

The OPC server utilization enables application of different program languages for graphical interfaces implementation between the system and operators. The part of the system model that emulates the wind dynamics and the wind turbine model utilizes the OPC server for the parameters transfer to the system. This system part model calculates in a real time the wind speed and the aero dynamical torque. Based on this function the ASM speed reference can be determined. Another option is a power reference determination, if a *Power control mode* is selected. In this mode of operation the power produced from the wind depends on the power demand, unlike the aim of the *Maximum power*

extraction strategy is to generate the maximum available power from the wind. The developed software application comprises functions for data and signals recording (rotational speed, generated power, PI control signal, etc.), as well as real time visualization of some processes (wind speed, aero dynamical torque, generated power, load torque). User interface is implemented in the graphical user environment of Matlab "Guide". In Fig. 11 the operator panel window is shown. It is designed for the purpose of processes control and visualization of the wind turbine generator operation.

EXPERIMENTAL RESULTS

The goal of the experiments is to investigate two different control strategies:

- Maximum power extraction strategy;
- Power generation in accordance with the

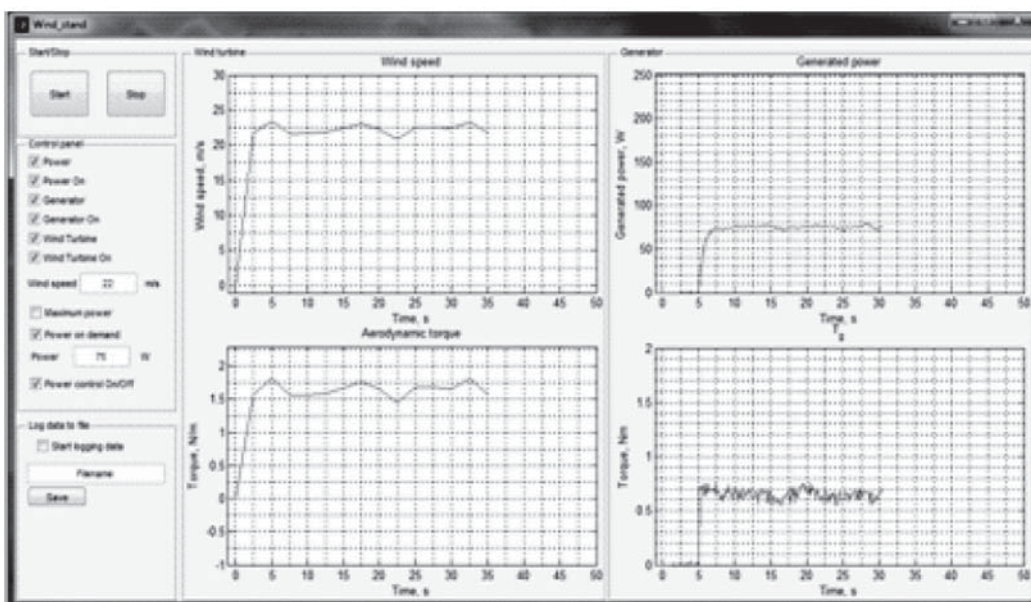


Fig. 11. Graphical user interface in MATLAB

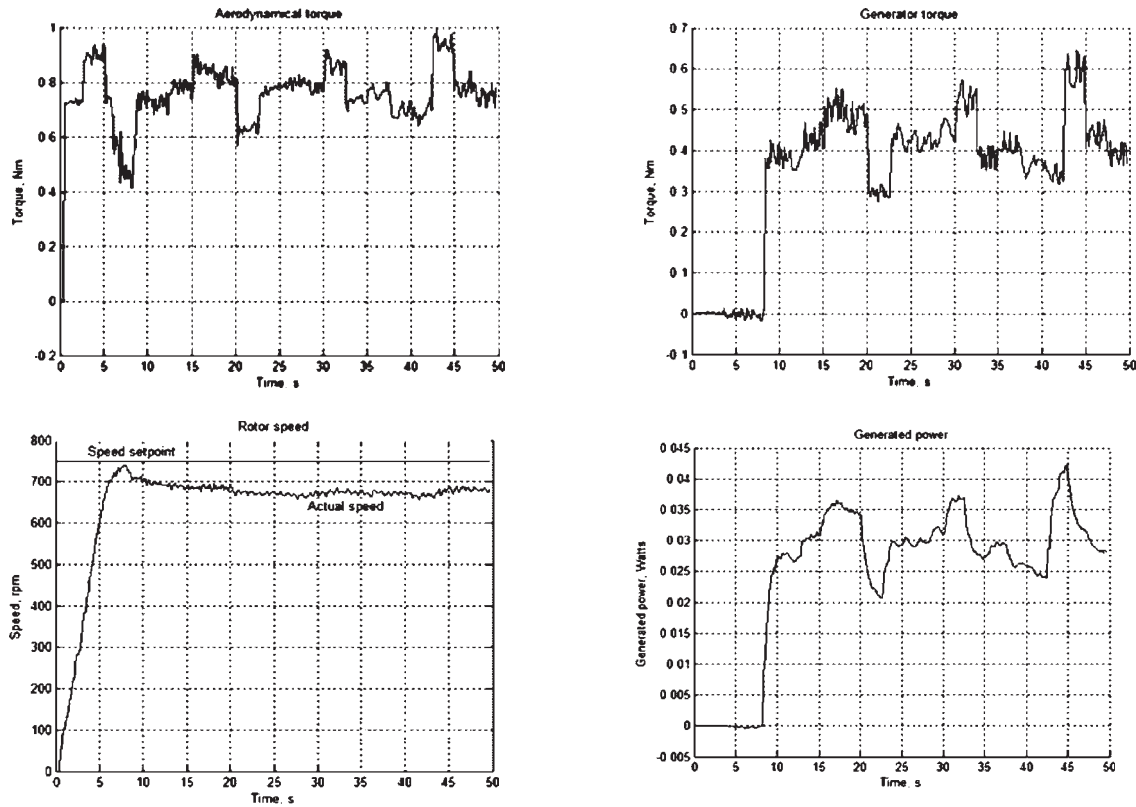


Fig. 12. Experimental results by wind speed of 15 m/s

power reference tracking.

In Fig. 12 experimental results under these control strategies and rotational speed of 750 rpm, (corresponding to the wind speed of 15 m/s) are shown.

CONCLUSION

Accomplishment of the main part of the hybrid laboratory test bench for renewable energy sources modeling and control is presented in this paper. Experiments under different wind turbine generator system control strategies are shown. They comprise maximal power extraction strategy under variable wind speed (Fig. 12) and power reference tracking strategy. The developed PC based HMI system ensures remote control and visualization of the technological processes. Future investigations are related to implementation of the optimal filtering theory (Kalman and Wiener filters) to the WTG speed and power control and development of powerful algorithms for controller design in the presence of parametric uncertainty.

Acknowledgement

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ЕКСПЕРИМЕНТАЛНИ ИЗСЛЕДВАНИЯ НА ПРОЦЕСИТЕ НА РЕГУЛИРАНЕ НА МОЩНОСТТА НА ВЕТРОГЕНЕРАТОР В ХИБРИДНА ЛАБОРАТОРНА СРЕДА

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Резюме

В статията се разглежда разработената система за управление на мощността на ветрогенератор, реализирана в хибридна лабораторна среда. Представена е структурата и хардуерната конфигурация на системата за управление. Разгледан е математическият модел на турбината и експерименталното определяне на параметрите му. Показани са резултати от експерименти при управление по критерии извличане на максимална мощност от вятъра и задание по мощност. Разработена е РС базирана HMI система за визуализация и управление на процесите.

SYNTHESIS AND PHYSICO-CHEMICAL STUDY OF POROUS NANOCOMPOSITES BASED ON CARBON FOAM AND Cu/Cu-Sn NANOPARTICLES FOR LI-ION BATTERY ELECTRODE MATERIALS

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Abstract

In this work results obtained in the first stage of the Project DDVU 02/10 "Porous nanocomposite electrodes for new generation electrochemical power sources based on carbon foam and metallic nanoparticles" supported by the Fund "Scientific investigations" of the Ministry of Education, Youth and Science – Bulgaria have been presented.

Metallic (Cu, Sn) and intermetallic (Cu-Sn) nanoparticles have been synthesized through a chemical reduction in water solution of chloride salts ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ or their mixture) with NaBH_4 at room temperature and atmospheric pressure. A template synthesis of Cu and Cu-Sn nanoparticles using a carbon foam (C-foam) as a support has been also carried out. For the first time in this work, Cu and Cu-Sn nanoparticles have been synthesized directly in the C-foam pores through the borohydride reduction. Porous nanocomposites based on the C-foam and the synthesized in its pores Cu/Cu-Sn nanoparticles have been obtained. In the second stage of the Project they will be tested as elec-

trodes in electrochemical power sources.

The Cu nanoparticles have been synthesized in the C-foam pores using $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solutions with a concentration in the interval of 0.2 to 2.0M, while the Cu-Sn nanoparticles - from a mixture of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ solutions with the same concentration at a different mass ratio of Cu:Sn (Cu:Sn=40:60, 50:50 and 60:40).

The morphology, structure and phase composition of the synthesized nanoparticles have been studied by electron microscopy (TEM/SEM), including surface electron diffraction (SAED) and X-ray electron diffraction (XRD) analysis. The SEM/TEM images have shown the existence of crystalline nanoparticles regular and irregular by shape. Cu_6Sn_7 , Cu_3Sn , $\text{Cu}_{10}\text{Sn}_3$ Cu, and Sn phases have been established.

INTRODUCTION

The nanoparticles with a slight dispersion (monodisperse nanoparticles) exhibit unique conductive, magnetic, optical, and mechanical properties. The particles in size of 1 to 100 nm are characterized by properties greatly different

from those of the bulk materials with the same chemical composition. One of the techniques used to synthesize monodisperse nanoparticles is the so-called in the nanotechnology "down-up" technique by chemical or electrochemical methods alternative to the mechanical "up-down" grinding and alloying by ball-milling technique. An appropriate method for obtaining nanoparticles is a template synthesis using porous supports through a chemical reduction of the suitable metallic ion with NaBH_4 in the support pores formed between the support structure grains. Porous ceramic materials like SiO_2 and molecular sieves of type MCM-41 (SiMCM, AlMCM) are used as a template.

In our opinion carbon foam (C-foam) characterized by a porous structure is of interest as a support for a template synthesis. This is due to its unique properties such as low material cost and light weight, high electrical conductivity, low thermal conductivity, low thermal expansion coefficient, high mechanical strength [1-4]. Among the applications, battery and fuel cell electrodes have been of significant interest to a research. The C-foam could be a light weight support for electrodes, because it combines a good electrochemical behavior, good electrical conductivity, corrosion stability, environmental friendly and low cost.

As compared to graphite electrodes the C-foam porous materials offer great benefits for battery and fuel cell applications due to their electrical conductivity, smaller cell size and better component connectivity. Among the various metallic nanoparticles, Cu, Sn and Cu-Sn nanoparticles have attracted considerable attention because they are important metallic materials in modern technologies. Significant interest has been focused on these nanoparticles due to their unusual optical, catalytic, mechanical and electrical properties. At present porous composite materials based on C-foam and intermetallic (Cu-Sn) nanoparticles are perspective electrode materials (for anodes) in new generation of energy storage systems. Nanoparticles are characterized by a high developed specific surface area (SSA) and surface active properties. High SSA determines their application as active components in the electrode materials. Metallic nano-

particles synthesized through a borohydride reduction contain bonded hydrogen, which is a pre-condition for good electrochemical characteristics.

Recently, there has been interest in the use of composite materials consisting of an active metal (metal that alloys with Li, i.e. Sn) dispersed within an inactive matrix (i.e. Cu) as replacement anodes for graphite in Li-ion batteries [5, 6]. Dispersing the alloy within a matrix reduces mechanical stresses associated with Li insertion/removal during charging/discharging and improves the cycle life compared to the alloy alone. One approach to improve the cycle life of active/inactive composites is to reduce their particle size. For example, in the Cu-Sn system ($\text{Li}_{4.4}\text{Sn}$ alloy surrounded by a Cu matrix) a significant improvement in cycle life is exhibited as the particle size is reduced.

The unique C-foam properties and its porous structure have generated our idea to use C-foam as a support for a direct template synthesis of Cu and Cu-Sn nanoparticles in its pores through a borohydride reduction to prepare porous composite materials with C-foam matrix and Cu/Cu-Sn nanoparticles appropriate for application as electrodes in electrochemical power sources. The porous nanocomposite materials combining the unique properties of the C-foam as an inert matrix and those of the intermetallic nanoparticles are characterized by a lower specific capacity compared with those of the graphite and other carbon materials, which are nowadays used for electrode materials in Li-ion batteries [7-18].

The main purpose of this work is to realize a synthesis of Cu, Sn and Cu-Sn nanoparticles through a borohydride reduction with NaBH_4 in water solutions of chloride salts ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ or their mixture) at room temperature and atmospheric pressure. *The second aim* is to carry out a template synthesis of Cu and Cu-Sn nanoparticles using C-foam as a support through the borohydride reduction in the C-foam pores, as well as to prepare porous nanocomposite materials with a C-foam matrix and active components such as Cu-Sn nanoparticles. *Thirdly*, to modify the commercial C-foam to be used as a support applying a treatment with different

impregnating solutions to create in the foam pores nucleolus centers and suitable conditions for nanoparticle synthesis. *The fourth goal* is to investigate the morphology, structure and phase composition of the synthesized in the C-foam pores nanoparticles by electron microscopy (SEM/TEM), surface electron diffraction (SAED) and X-ray diffraction (XRD), as well as to determine the specific surface area by BET and the porous characteristics such as volume and pore radius, respectively porosity and relative density. It is expected thus obtained porous C-foam/Cu (Cu-Sn) nanoparticles composites to be appropriate materials for application as electrodes in the new generation electrochemical power sources.

EXPERIMENTAL SET-UP

1. Synthesis of Cu, Sn and Cu-Sn nanoparticles through a borohydride reduction

Cu, Sn and Cu-Sn nanoparticles have been synthesized through a borohydride reduction in water solutions of copper and tin chloride salts with NaBH_4 . The synthesis has been carried out in a reactor ensuring consecutive introduction of the initial solutions of the salts and reducing agent applying continuous mechanical stirring by a magnetic stirrer during the synthesis. Solutions of 0.2M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 0.2M $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and 0,17M NaBH_4 have been used for the synthesis of Cu and Sn nanoparticles. NaOH has been added to NaBH_4 solution to prevent its decomposition. To synthesize Cu-Sn nanoparticles the copper and tin solutions have been mixed at mass ratios of Cu:Sn=60:40 and 50:50. The reducing solution has been added to the mixture applying continuous mechanical mixing. The mixing time was two minutes. The obtained fine particles were filtrated and washed with distilled water and ethyl alcohol and dried in vacuum at 80 °C for 24 hours.

2. Template synthesis of Cu and Cu-Sn nanoparticles in the pores of C-foam used as a support

For the first time in our work a template synthesis of Cu and Cu-Sn nanoparticles directly in the pores of a modified commercial C-foam used as a support is executed from $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and respectively, a mixture of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ at a mass ratio of Cu:Sn=40:60, 50:50 and 60:40. The template synthesis has

been carried out in the same reactor at same conditions ensuring a regime of a consecutive introduction of the both modified support (impregnated C-foam with a corresponding reaction solution) and the reducing solution (NaBH_4).

In the case of Cu nanoparticles the C-foam has been preliminarily wetted with the copper salt solution (0.2M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) and then introduced into the reducing solution (0.2M NaBH_4).

Cu-Sn nanoparticles have been synthesized also in the C-foam pores through a reduction with 4.4M NaBH_4 in 14M NaOH using a mixture of both $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ solutions with three different concentrations (2.0M, 1.5M and 1.0M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) at mass ratio Cu:Sn= 40:60, and Cu-Sn nanoparticles have been also synthesized in the C-foam pores with 0.2M NaBH_4 using a mixture of 0.2M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.2M $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ at mass ratios Cu: Sn=50:50 and 60:40.

3. Modifying a commercial C-foam

The support used for the template synthesis is a commercial C-foam, which has been previously modified through impregnation with different solutions to create nucleus centers and appropriate conditions for nanoparticle deposition. The C-foam modification has been carried out through reaction solutions of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with a different concentration (0.2M - 2.0M), as well as using a mixture of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ with the same concentration at mass ratio Cu:Sn=40:60. The solutions with lower concentrations have been obtained through a diluting of the 2M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 2M $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ solutions.

4. Investigation techniques used

The synthesized porous nanocomposite materials based on modified commercial C-foam as a matrix and Cu and Cu-Sn nanoparticles as components were investigated by electron microscopy (SEM/TEM) including a specific surface area diffraction (SAED) and also by XRD analysis.

The morphology of the samples was examined by JEOL JSM 5300 (Japan) SEM microscope at accelerating voltage of 20 kV. The TEM images of the structure of the commercial C-foam and Cu/Cu-Sn nanoparticles synthesized in the C-foam pores was obtained on a JEOL2100 (Japan) transmission electron microscope with an accel-

erating voltage of 200 kV. X-ray diffraction patterns of carbon foam and the synthesized Cu/Cu-Sn nanoparticles using the impregnated commercial C-foam as a support were collected within the 2θ range from 10° to 95° with a constant step 0.03° and counting time 1 s/step on Philips PW 1050 diffractometer using $\text{CuK}\alpha$ radiation.

The specific surface (SSA) was determined by the so-called Kliachko-Gurvich express method (BET method) using a silicon manometer. Both the pore volume and the bulk density of the samples were determined by Hg porometry using Micrometric Auto-Pore 9200 appliance. The measurement was carried out in the pressure interval of $5 \cdot 10^{-3}$ to $2 \cdot 10^2$ MPa, which corresponds to a pore radius from $3,60 \cdot 10^{-3}$ to $1,35 \cdot 10^2$ μm . Before the measurement the samples were dried at 110°C for 48 hours.

RESULTS AND DISCUSSION

1. Results from the SEM investigation of the Cu, Sn and Cu-Sn nanoparticles synthesized through a borohydride reduction

SEM images of Cu nanoparticles at different magnification are shown in Fig. 1. Tetrahedral by shape nanoparticles are observed. Figure 2 shows SEM images of Sn nanoparticles at different magnification. Nanoparticles irregular by shape, which display a tendency to aggregate, can be seen. SEM images of Cu-Sn nanoparticles at

mass ratio Cu: Sn=60:40 at different magnification are given in Fig. 3, while in Fig. 4 SEM images of Cu-Sn nanoparticles obtained at mass ratio Cu: Sn = 50:50 at different magnification are shown.

On the SEM images of the Cu-Sn nanoparticles regardless of the mass ratio Cu: Sn (60:40, 50:50) regular (tetrahedral) and irregular by shape nanoparticles are observed. It is observed that the particles display a tendency to aggregate because of the high surface activity as a result of the existence of unsaturated bonds on their surface, which is typical for the nanostate.

2. Results from the SEM investigation of the Cu and Cu-Sn nanoparticles synthesized by a template technique in the C-foam pores used as a support

SEM images of Cu nanoparticles obtained from 0.2 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solution by a template technique in the C-foam pores used as a support are shown in Fig. 5, while in Figs. 6, 7 and 8 SEM images of Cu-Sn nanoparticles prepared by the same technique from a mixture of solutions with concentrations 2M, 1.5M and 1.0M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, respectively 2M, 1.5M and 1.0M $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ at mass ratio Cu:Sn =40:60 are presented. The SEM images show that regardless of the concentration of the initial copper and tin solutions at mass ratio Cu:Sn = 40:60, Cu and Cu-Sn nano-

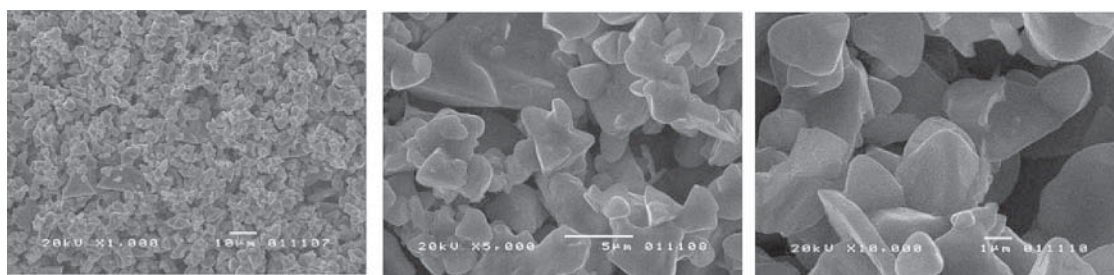


Fig. 1. SEM images of Cu nanoparticles at different magnifications

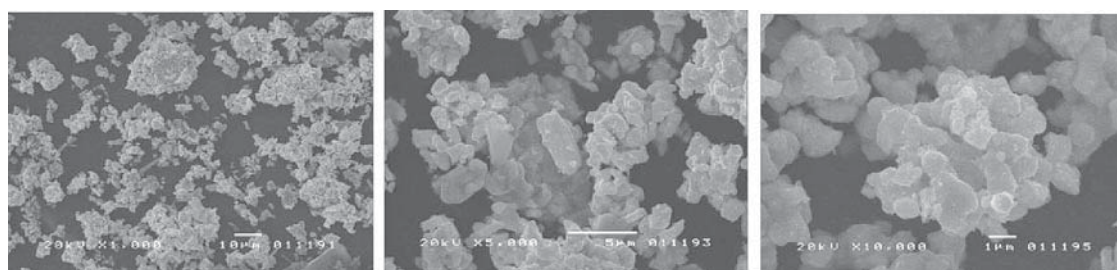


Fig. 2. SEM images of Sn nanoparticles at different magnifications

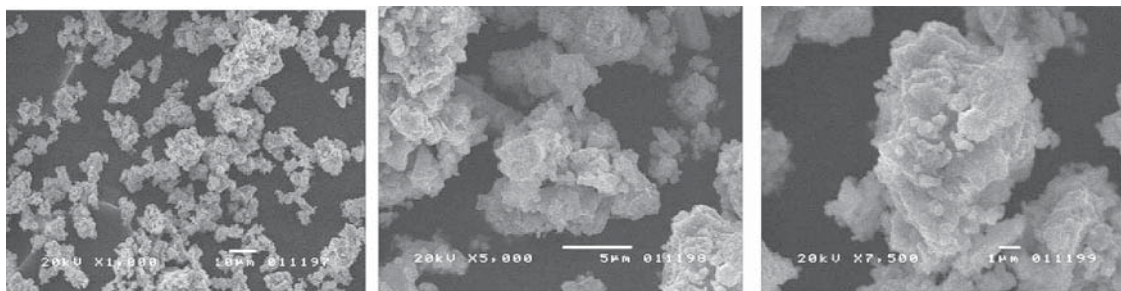


Fig. 3. SEM images of Cu-Sn nanoparticles obtained at a mass ratio Cu:Sn=60:40 at different magnifications

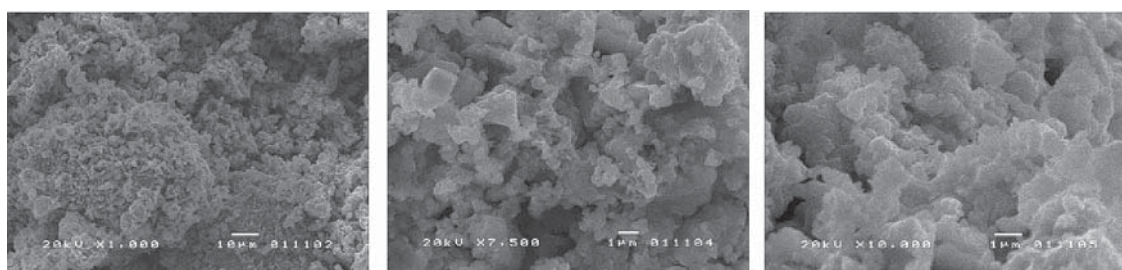


Fig. 4. SEM images of Cu-Sn nanoparticles synthesized at a mass ratio Cu: Sn=50:50 at different magnifications

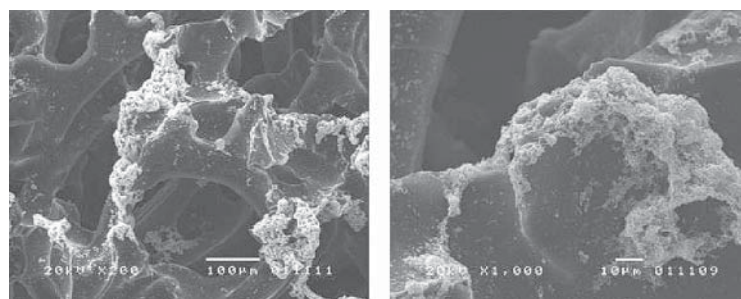


Fig. 5. SEM images of Cu nanoparticles obtained from 0.2M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ using C-foam: a-x 200, b-x 1 000

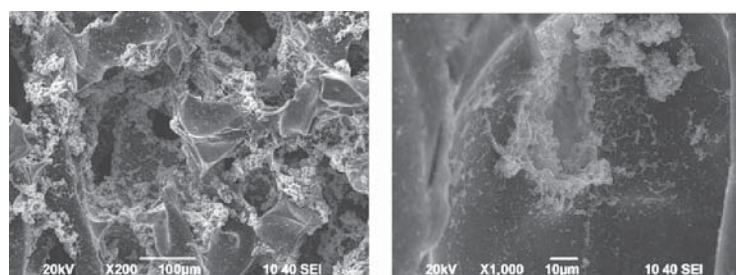


Fig. 6. SEM images of Cu-Sn nanoparticles obtained from 2M chloride solution (Cu: Sn=40:60) using C-foam: a-x 200, b-x 1000

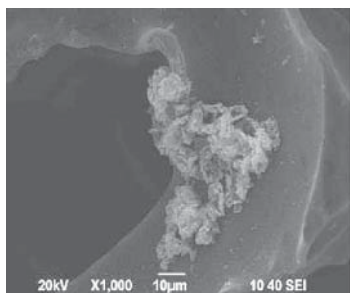


Fig. 7. SEM image of Cu-Sn nanoparticles obtained from 1.5M chloride solutions (Cu: Sn=40:60)

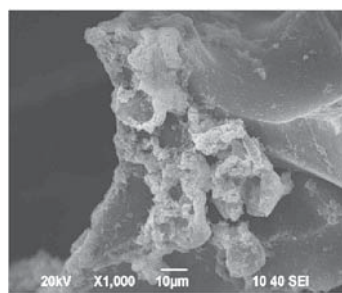


Fig. 8. SEM image of Cu-Sn nanoparticles obtained from 1M chloride solutions (Cu: Sn=40:60)

particles were obtained not only inside the pores formed between the carbon grains, but also on the grain surface. It can be seen that the nanoparticles are closely packaged and aggregated.

3. Results from the SEM analysis of the C-foam

3.1. SEM results for the commercial C-foam

The SEM images of the commercial C-foam are shown in Fig. 9, while Figure 10 presents TEM micrographs of the same C-foam. It can be seen that C-foam is characterized by interconnected micropores formed between the carbon grains. It is observed on the carbon surface the

existence of open pores, uniformly distributed. The pores are irregular by shape and unsteadily arranged inside the foam. The open pores allow the C-foam modification through impregnation with different solutions to be an appropriate place for the Cu and Cu-Sn nanoparticles synthesis. The wetting procedure of the C-foam is of significant importance for the nanoparticle nucleus formation.

3.2. SEM results for the modified commercial C-foam

Figure 11 presents SEM images of a modified commercial C-foam impregnated with 0.2M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solution. The modified C-foam has been put in the reducing solution to realize a

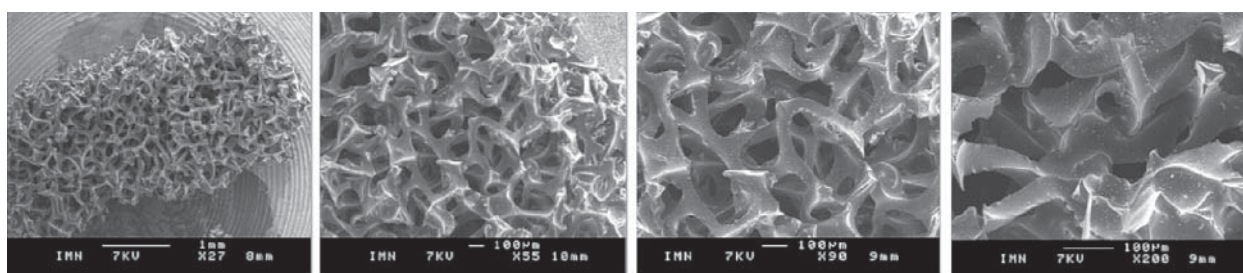


Fig. 9. SEM images of a commercial C-foam: a - x 27; b - x 55; c - x 90, d - x 200

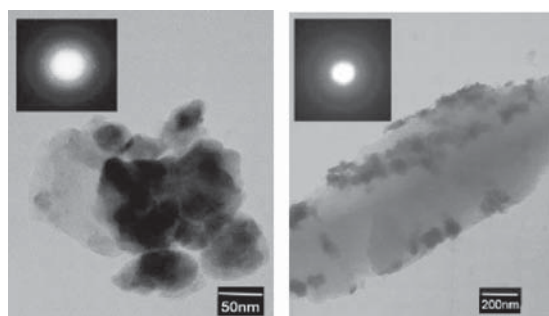


Fig. 10. TEM micrographs of a commercial C-foam

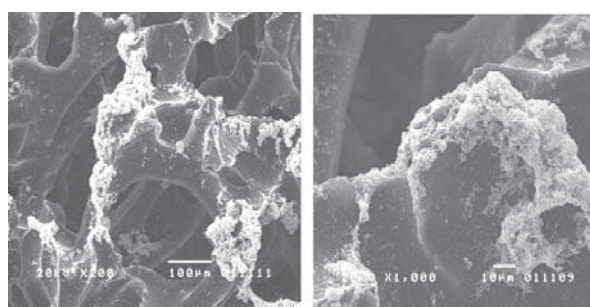


Fig. 11. SEM images of Cu nanoparticles synthesized in C-foam impregnated with 0.2M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$: a - x 200, b - x 1 000

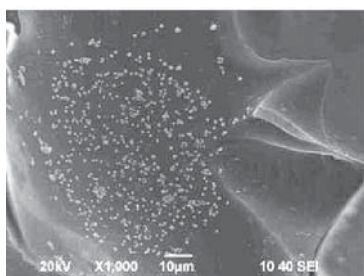


Fig. 12. SEM image of Cu nanoparticles synthesized in C-foam impregnated with 1.0M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, x1000

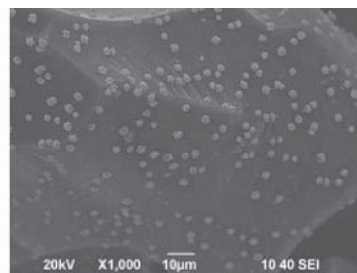


Fig. 13. SEM image of Cu nanoparticles synthesized in C-foam impregnated with 1.5M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, x1000

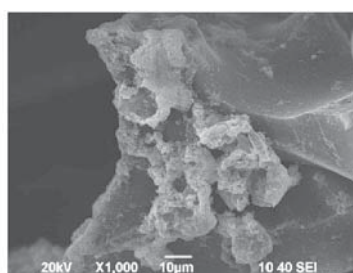
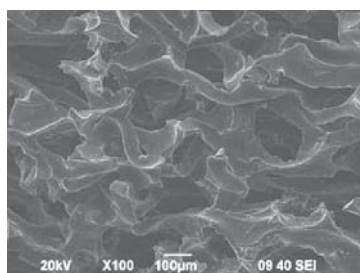


Fig. 14. SEM images of Cu-Sn nanoparticles deposited in C-foam from mixture of 1.0M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 1.0M $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$: a-x 100, b-x 1000

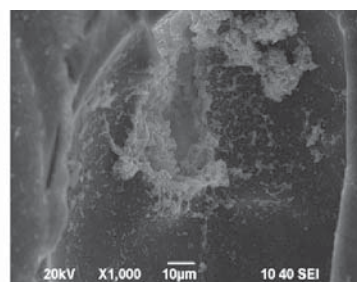
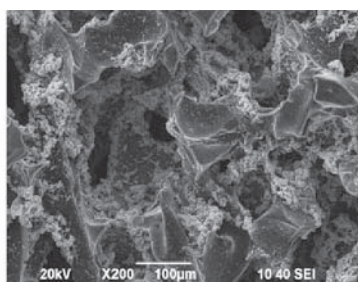
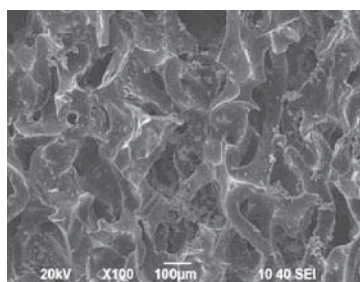


Fig. 15. SEM images of Cu-Sn nanoparticles deposited in C-foam from mixture of 2.0M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 2.0M $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$: a - x 100, b -x 200, c - x 1000

template synthesis of Cu nanoparticles in the C-foam pores. It is observed that Cu nanoparticles have been obtained not only inside the pores formed between the grains, but also on the grain surface. It can be seen that the Cu nanoparticles are aggregated.

SEM image of Cu nanoparticles synthesized from 1.0M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solution using a C-foam is presented in Fig. 12, while in Fig.13 – from 1.5M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solution.

SEM images of Cu-Sn nanoparticles obtained from a mixture of 1.0M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 1.0M $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ solutions, respectively 2.0M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 2.0M $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ solutions at mass ratio Cu:Sn=40:60 are shown in Fig. 14 and 15. It can be seen that the Cu-Sn nanoparticles are deposited inside the C-foam pores and also

on the grain surface.

4. Results from the TEM analysis of the C-foam

In Fig. 16 TEM images of monodisperse Cu nanoparticles synthesized in the C-foam pores treated through impregnation with 0.2M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solution are presented.

The Cu nanoparticles are spherical by shape in size of 10 to 100 nm. From the TEM images (Fig. 16 a) it can be seen that the pores are unsteadily arranged, approximately spherical and interconnected. The SAED photos prove the monocrystalline character of the Cu nanoparticles (Fig. 16 a, c). Figure 17 presents TEM/SAED images of Cu-Sn nanoparticles deposited in the C-

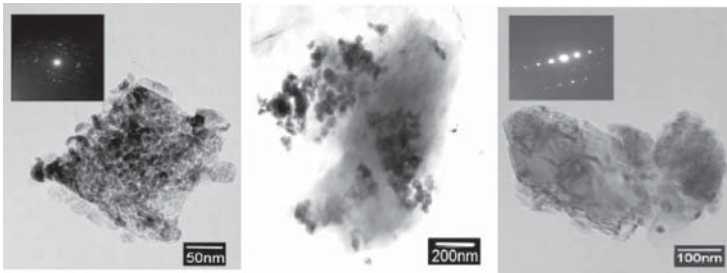


Fig. 16. TEM images of Cu nanoparticles deposited in the C-foam pores at different magnifications

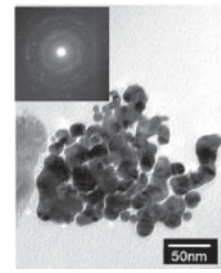


Fig. 17. TEM/SAED images of Cu-Sn nanoparticles deposited in C-foam, x150

foam pores modified with a reaction mixture.

5. Results from XRD analysis of the commercial C-foam and template synthesized nanoparticles

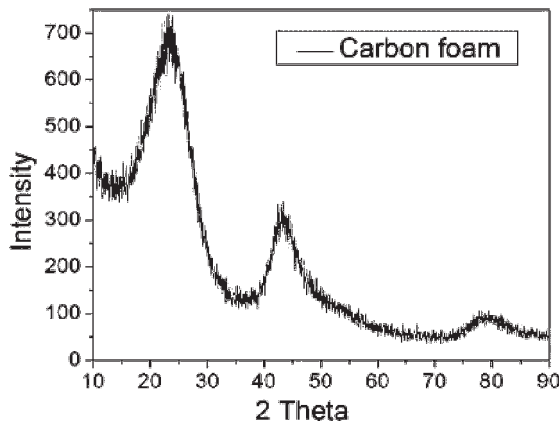


Fig. 18. XRD patterns of commercial C-foam

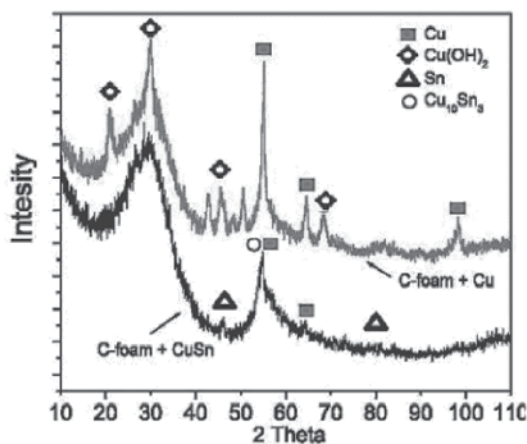


Fig. 19. XRD patterns of Cu and Cu-Sn nanoparticles synthesized with C-foam

Figure 18 shows the XRD patterns of the commercial C-foam. The main broad peaks ($2\theta = 23^\circ, 43^\circ$) correspond to small in size crystallites of the graphite. Figure 19 presents XRD patterns

of Cu and Cu-Sn nanoparticles synthesized using C-foam from 1.5M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, respectively a mixture of 1.5M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 1.5M $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ solutions at a mass ratio Cu:Sn=40:60. Formation of $\text{Cu}_{10}\text{Sn}_3$, Cu, Sn phases is observed.

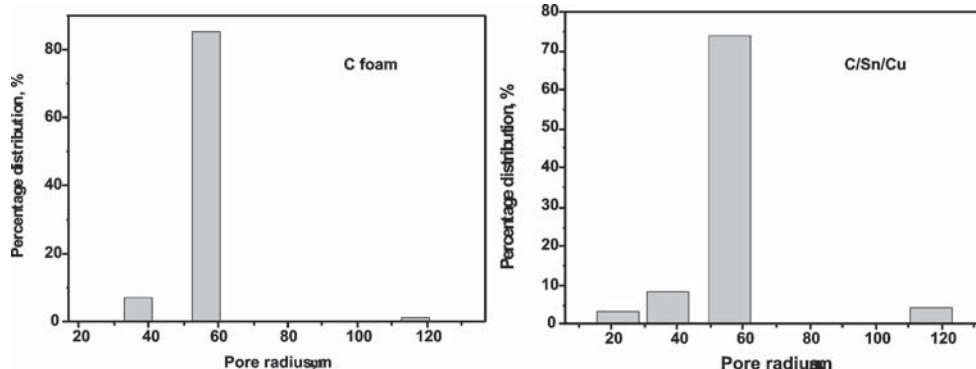
6. Structural characteristics of the samples

The data of the porous characteristics of the investigated samples obtained by the Hg porometry are presented in a Table 1. They show that the modified material is characterized by both higher total volume and average pore radius, respectively higher porosity and lower relative density compared with the initial C-foam. The differential distribution curves of the pore volume vs. pore radius of the C-foam before and after a modification are presented in Fig. 20. It is observed that the curves are identical. It means that the samples are characterized by a macroporous structure with a radius from 34 to 56 μm (92.8 %) for the initial C-foam and from 22 to 117 μm (89.9 %) for the modified material. The pore size distribution in the investigated interval is presented in Fig. 21.

The data show that the modified C-material is characterized by a wider interval of the pore radius. These changes in the structure parameters, as well as higher porosity and total pore volume of the modified material can be explained with the obtaining manner. When the metallic (Cu, Sn) salts solution penetrate at a high pressure, it is possible to occur disruptions in the carbon structure. It could lead to increase of the total pore volume and also to increase the percentage content of the pores with smaller radius at the expense of the pores with a bigger radius.

Table 1. Structural characteristics of the samples

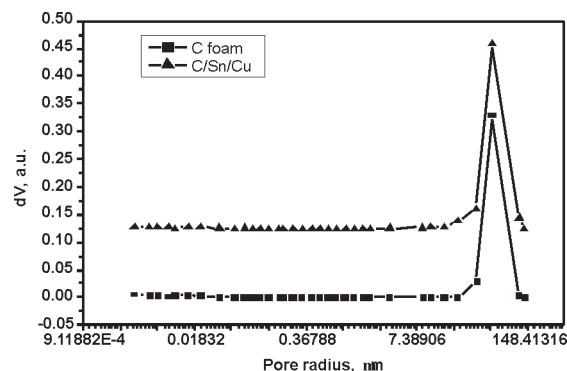
Characteristic	C-foam	C-Cu/Sn
Total pore volume, cm ³ /g	0.3860	0.4540
Apparent density, g/cm ³	1.5826	1.5801
Porosity, %	38	42
Average pore radius, μm	0.1489	0.1561
Bulk density, g/cm ³	0.9824	0.9201
Specific surface area by BET, m ² /g	17.4	15.0

**Fig. 21.** Pore size distribution: a-C foam, b-modified C-foam

CONCLUSION

Cu, Sn and Cu-Sn (Cu:Sn=50:50, 60:40) nanoparticles have been synthesized through a borohydride reduction in water solutions of 0.2M CuCl₂·2H₂O and 0.2M SnCl₂·2H₂O with 0.17M NaBH₄ at room temperature and atmospheric pressure. The Cu, Sn and Cu-Sn nanoparticles are characterized by both regular (tetrahedral) and irregular shape. They are exposed to aggregation, which is typical for nanoparticles.

For the first time a template synthesis of Cu and Cu-Sn nanoparticles using a modified commercial C-foam as a support through a wet borohydride reduction with NBH₄ is executed. The Cu and Cu-Sn nanoparticles are deposited directly in the C-foam pores using water solutions of CuCl₂·2H₂O and SnCl₂·2H₂O with different concentrations or from a mixture of CuCl₂·2H₂O and SnCl₂·2H₂O solutions with the same concentration at three mass ratios Cu: Sn =40:60, 50:50 and 60:40. As a result porous composites based on C-foam matrix and Cu/Cu-Sn nanoparticles have been obtained. These po-

**Fig. 20.** Differential distribution curves of the pore volume vs. pore radius of the C-foam before and after modification

rous nano-composite materials should be a perspective replacement of the graphite anodes in Li-ion batteries. It is expected that the combination of porous C-foam and Cu/ Cu-Sn nanoparticles would reduce mechanical stresses due to Li insertion/removal during the charging/discharging, as well as improve the cycle life.

The Cu nanoparticles are crystalline by structure and have a low dispersion. The Cu and Cu-Sn nanoparticles have been deposited in the C-foam pores and also on the surface of the grains forming the pores. The XRD analysis has proved the existence of Cu, Sn, Cu₆Sn₅, Cu₃Sn, and Cu₁₀Sn₃ phases, which according to the literature data predetermine an application of these synthesized porous composite materials as electrodes in Li-ion batteries.

Based on the results obtained by XRD, SEM/TEM and SAED study of the Cu and Cu-Sn nanoparticles the conclusion follows that the realized direct synthesis of Cu and Cu-Sn nanoparticles in the C-foam pores is a suitable approach to obtain nanocomposites with porous carbon matrix and Cu/Cu-Sn nanoparticles as new electrode

(anode) materials for Li-ion batteries. The morphology, structure and phase composition of the nanoparticles synthesized in the C-foam pores and especially the synthesized intermetallic phase give promise good electrochemical characteristics of these porous C-foam/metallic (intermetallic) nanoparticles composites, the study of which is the subject of investigations during the second stage of the Project DDVU 02/98.

Acknowledgements

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СИНТЕЗ И ФИЗИКО-ХИМИЧНО ИЗСЛЕДВАНЕ НА ПОРЕСТИ НАНОКОМПОЗИТИ НА БАЗАТА НА ВЪГЛЕРОДНА ПЯНА И $\text{Cu}/\text{Cu-Sn}$ НАНОЧАСТИЦИ ЗА Li-ЙОННИ БАТЕРИИ

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Резюме

Представени са резултати, получени през първия етап на Договор ДДВУ 02/98 „Порести нанокomпозитни електроди за ново поколение електрохимични източници на ток на базата на въглеродна пяна и метални наночастици“, финансиран от Фонд „Научни изследвания“ към Министерството на образованието, младежта и науката.

Метални (Cu, Sn) и интерметални (Cu-Sn) наночастици са получени чрез химична редукция във воден разтвор на хлоридни соли ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ и $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ или тяхна смес) с NaBH_4 при стайна температура и атмосферно налягане. Проведен е също "template" синтез на Cu и Cu-Sn наночастици с използване на въглеродна пяна (C-пяна) като подложка. За първи път в тази работа Cu и Cu-Sn наночастици са синтезирани директно в порите на C-пяна чрез борхидридната редукция. Получени са порести нанокomпозити на базата на C-пяна и синтезираните в нейните пори Cu и Cu-Sn наночастици. През втория етап на договора те ще бъдат изследвани като електроди в електро-

химични батерии.

Cu наночастици са получени в порите на С-паяна от разтвор на $CuCl_2 \cdot 2H_2O$ с концентрация от 0.2М до 2.0М, докато *Cu-Sn* наночастици – от смес на $CuCl_2 \cdot 2H_2O$ и $SnCl_2 \cdot 2H_2O$ със същата концентрация при различно масово отношение *Cu:Sn* (*Cu:Sn*=40:60, 50:50 и 60:40).

Морфологията, структурата и фазовия състав

на синтезираните наночастици са изследвани с електронна микроскопия (TEM/СЕМ), вкл. повърхностна електронна дифракция (САЕД) и рентгено-дифракционен анализ (ХРД). СЕМ/ТЕМ снимките показват съществуването на кристални наночастици с правилна и неправилна форма. Установено е наличието на Cu_6Sn_5 , Cu_3Sn , $Cu_{10}Sn_3$ *Cu* и *Sn* фази.

TUNABLE MID-IR LASER SOURCE – A VIABLE ALTERNATIVE TO IR FREE ELECTRON LASERS. TOWARDS NEW METHODS OF MATERIAL SYNTHESIS AND PROCESSING

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Abstract

Since the discovery of lasers, they have been viewed as promising instruments for producing specific material states by selective manipulations that could not be realized by conventional incoherent addition of thermal or electronic energy to the material. Although selective laser chemistry is still a dream, selective control of material processing done by optimization of laser intensity, temporal and spatial coherence is frequently employed to move given contemporary technology beyond its limits. Utilization of the unique mid-infrared (mid-IR) laser radiation in condensed matter and materials research has produced and identified a wealth of high-impact applications and potential technology breakthroughs in these areas. A tunable, ultrashort, pulsed mid-infrared laser system offers a promising new tool for laser-mediated deposition of thermally labile materials, because they can be operated in a regime that largely avoids pathways to electronic excitation and are thus less prone to inducing destructive photochemical processes. Until now, the exclusive mid-IR laser source applicable for the above techniques has been a free-electron laser (FEL), which provides tunable mid-IR radiation with both high-average and high peak power. However, FELs are multi-million dollar facilities with unique pulse characteristics which are not accessible to the general

public. Here we describe the development of a tunable mid-IR table top laser source with an unprecedented pulse energy level (>2 mJ) at kHz repetition rate across the water absorption band at 3 microns. We aim at addressing new technologies for analysis and processing of organic materials based on a large variety of vibrational bonds lying in this spectral region.

INTRODUCTION

Basic concepts and objectives

One of the main goals of the solid state lasers and nonlinear optics laboratory at Sofia University is to develop advanced mid-infrared laser sources for enabling new cutting edge technologies and applications. These include, but are not limited to non-destructive pulsed laser deposition of polymers, small organic molecules, functionalized nanoparticles and laser induced material syntheses. In all of the above applications, unique infra-red radiation is tuned to vibrational modes in the target in order to achieve states of materials that could not be realized by conventional incoherent addition of thermal or electronic energy.

Until now the use of the infrared (IR) radiation generated by free-electron lasers (FELs) in condensed matter and materials research has produced and identified a wealth of high-impact applications in these areas [1]. In particular, the FEL radiation between 2-4 μm has spawned new

technologies for analysis and processing of organic materials. The history of attempts to develop conducting and semiconducting organic and polymeric materials reflects vast potential applications for inexpensive electronic and optoelectronic devices on flexible substrates [2]. Organic light-emitting diodes (OLEDs), polymer light-emitting diodes (PLEDs) and organic and polymer thin-film transistors (OTFTs/PTFTs) are subjects of vigorous world-wide research, development and production programs [3-5]. The recent growth in the OLED and OTFT markets has been fueled by the development of vapor-phase methods for depositing [6] and patterning [7] the complex multi-layer structures needed for maximum electroluminescent efficiency. In contrast, PLEDs, and most other polymer devices, are presently manufactured almost exclusively by solution-phase processes, i.e. ink-jet printing [8] and spin-casting. For significant number of applications, however, solution-phase coating is problematic, due to solvent incompatibilities in multi-layer devices, and non-uniformities introduced by solvent drying effects [9]. ***The future of polymer electronics and opto-electronics will be substantially brighter if the thin-film "tool kit" can be expanded beyond solution phase coating.*** Recently, a new method has been utilized to deposit different polymer thin films through a vacuum-phase, low-temperature process that transports polymers intact from an ablation target to a substrate. This new method (so-called ***resonant infrared pulsed laser deposition (RIR-PLD)*** [10]) employs a powerful mid-infrared free-electron laser (FEL) to selectively excite vibrational modes of polymers.

RIR-PLD requires lasers that are tuned to vibrational modes in the target material. The intense IR laser radiation promotes the solid phase material to highly vibrationally excited states, which leads to vaporization of the material. After condensation on a nearby substrate the material is collected as a thin film. Because of the absence of electronic excitation the complex chemical and physical structure of the organic material is preserved [11]. For numerous organic polymers the absorption of the C-H and O-H stretching modes are being used, which requires a tunable laser source around 3 and 3.4 microns.

The exclusive laser source for this new technique has been the Mark-III FEL at Vanderbilt University in Nashville, Tennessee. Mark-III is broadly tunable between 2.1 and 9.8 μm , pulsed laser sources that provide both high-average power and high peak power. Despite its great advantages the Mark-III FEL system possesses serious drawbacks that are intrinsic to its underlying physical principles. FELs consist of a relativistic electron beam propagating through a periodic magnetic field. The electrons are ejected from a linear accelerator or provided by a storage ring (synchrotron). Hence, FELs are large-scale facilities and their operation requires highly qualified personnel and substantial maintenance costs. The severe costs of such a facility have so far inhibited broad technological usage of RIR-PLD. Moreover, alternative laser sources with similar radiation parameters (energy, average power and tunability in mid-IR) do not exist up to now.

The main strategy in our laser development is a table-top Mid-IR laser system with nanosecond and sub-nanosecond pulse duration, broadly tunable (2.5-4 microns), combining high average power (>1W) and high pulse energy (>1mJ). Hence, the range of potential applications for this laser instrument goes beyond the scope of polymer deposition, e.g. nanoparticle deposition and rapid synthesis of superhard materials by resonant IR decomposition of molecular precursors, medical applications in the water absorption band around 3 microns, etc.

Mid-IR optical parametric oscillator and pump laser development

Presently we have reached two major milestones towards Mid-IR laser system with the above described parameters: one concerning the near IR laser systems used for pumping and one involved with the down-conversion devices.

We have developed a unique laser source at 1064 nm, in which the near diffraction limited pulses of a single-frequency passively Q-switched Nd:YAG laser (240- μJ , 830-ps at 0.5-kHz) are amplified up to 38-mJ in a master oscillator power amplifier system, that consists of a preamplifier and two-stage diode-pumped amplifier, whilst preserving pulse duration, beam quality and linear polarization. Such a laser system on its own is a significant achievement with

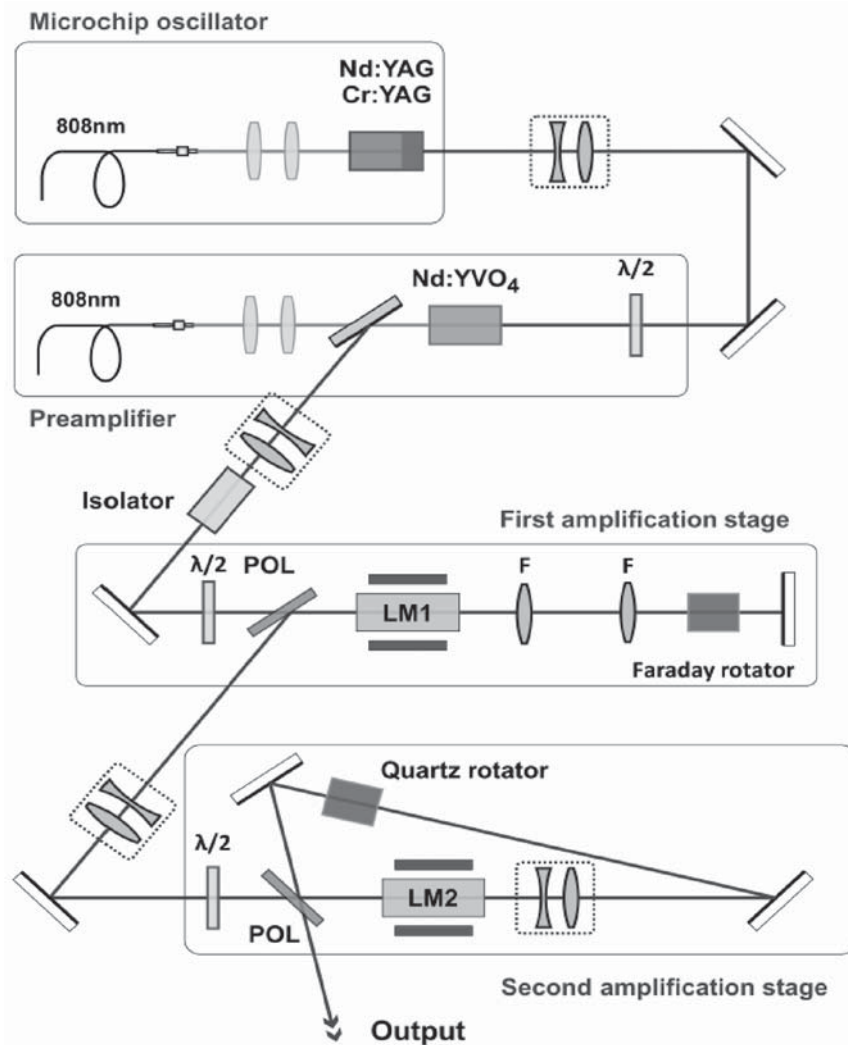


Fig. 1. Schematic layout of the MOPA system, consisting of a preamplifier and two stage diode-pumped amplifiers. Abbreviations are: LM1, LM2 – transversely pumped amplification modules; POL – polarizer.

regard to the laser technique and could potentially have a multitude of technological and scientific applications.

A schematic diagram of the experiment is shown on fig. 1. As a master oscillator, we use a passively Q-switched chip laser with mirror coatings deposited directly on the Cr^{4+} :YAG/Nd:YAG active element. It is longitudinally pumped by a fiber-coupled 70-W quasi-cw diode laser array (Jenoptik Laser GmbH, JOLD70-QPXF-1L) driven with 80- μs 70-A current pulses at 0.5-kHz repetition rate. The pump beam is delivered through a 400- μm core optical fiber and imaged in the active element through an aspheric-lens objective with 1:1 magnification ratio. The single frequency operation of the oscillator is achieved

through the short resonator length (7-mm) and the maximum energy of the polarized output is 240- μJ at 0.5-kHz repetition rate. The signal from the master oscillator is pre-amplified in one pass through an end-pumped, 9-mm long Nd:YVO₄ crystal, with 0.25 at. % doping. The pre-amplifier is longitudinally pumped by a fiber-coupled quasi-cw diode laser (Jenoptik Laser GmbH, JOLD70-QPXF-1L) driven with 120- μs 80-A current pulses (60W peak power) at 0.5-kHz repetition rate. Further amplification is done by utilizing two boost amplification stages operated in double-pass regime with transversely diode-pumped Nd:YAG modules. The first stage employs a 0.6 at. % doped Nd:YAG crystal (dia. 3-mm and 90-mm long), pumped by three linear stacks of laser diode bars in a three-fold geom-

etry; each stack composed of five 100-W quasi-cw laser diode bars. The second stage employs a 0.6 at. % doped Nd:YAG crystal (dia. 4-mm and 90-mm long), pumped by the same diode configuration and each stack is composed of five 40-W quasi-cw laser diode bars.

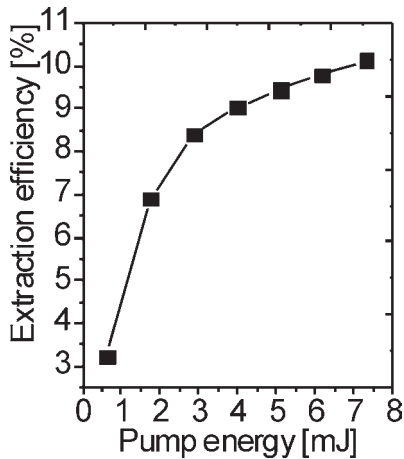


Fig. 2. Saturation of the amplification in the single pass through the Nd:YVO₄ pre-amplifier (solid line is for eye guidance).

By taking advantage of the low saturation density (0.12-J/cm²) of Nd:YVO₄, we are able to achieve high amplification in a single pass through the preamplifier reaching pulse energy of 1-mJ (10% extraction efficiency, fig. 2) at 0.5-kHz repetition rate. With the seed from the preamplifier and a depolarization-compensating scheme [12] the achieved output pulse energy from the first boost amplification stages is 28-mJ (fig. 3a), which corresponds to 9% extraction efficiency. In the second boost amplification stage the double-pass regime was achieved

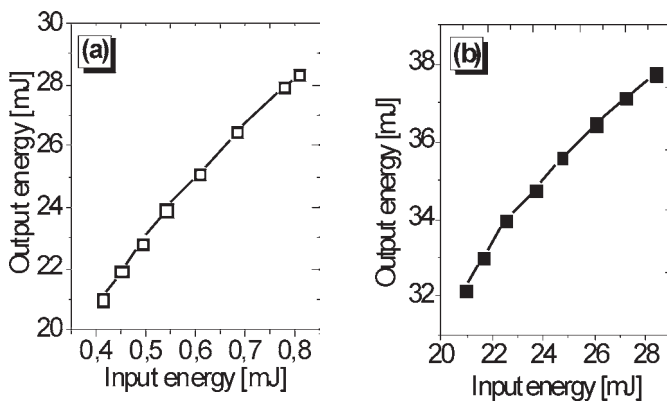


Fig. 3. Output energy vs. input energy for double-pass amplification in the first amplification stage (red curve) and in the second stage (blue curve). Solid lines are for eye guidance.

through a ring configuration with quartz rotator and the output energy is 38-mJ (fig. 3b) with 830-ps pulse duration. The beam quality after the master oscillator is measured to be $M_x^2 \times M_y^2 = 1.2 \times 1.4$ and no significant deterioration is observed until the second amplification stage after which the beam quality is measured to be $M_x^2 \times M_y^2 = 1.35 \times 1.6$ (profile of the laser beam is shown in fig. 4).

This unique laser system was used for pumping a frequency down-conversion stage (OPO), thus resulting in a compact sub-nanosecond, singly resonant mid-IR OPO, based on periodically poled stoichiometric lithium tantalate (PPLST) at a repetition rate of 0.5 kHz that offers high pulse energy and tunability around the peak absorption band of water. We employ a 20 mm long, 10 mm wide, and 3.2 mm (along z axis) thick PPLST crystal (manufactured by Deltronic Crystal Industries (DCI) Inc., NJ) with three different poled zones with domain inversion periods (30.2, 30.3 and 30.4 μm respectively), equally spaced along the width of the crystal. The crystal is antireflection coated for the pump, the signal and idler waves. The OPO cavity length is 27 mm with plane parallel mirrors. As a rear mirror for the OPO we used a silver coated mirror (with reflection of 96-97% at each of the three wavelengths).

The output coupler (OC) is a dielectric mirror with a reflection of >99.9% for the signal wave and transmission >98% for the idler wave. The PPLST crystal is pumped through the OC which transmits >99% at 1064 nm (see fig. 5). The

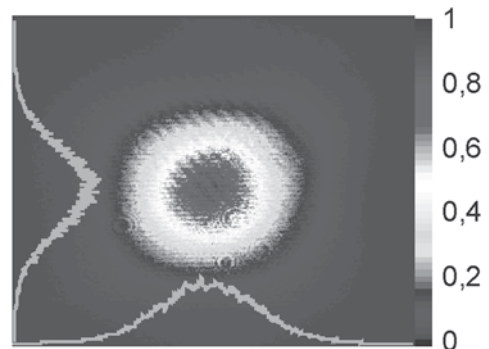


Fig. 4. Laser beam profile at the output of the MOPA system.

pump beam is slightly elliptical and it is focused to a beam size of 2.2x2.3 mm in the position of the PPSLT crystal. The incident pump beam is separated from the idler wave by a dichroic mirror, which has 99% reflection for the pump (p-polarization) and transmits 97% at the idler wavelength, respectively. After the dichroic mirror only the idler wave is measured, the residual pump radiation and the signal are blocked with a filter.

The measured OPO threshold was 1.4 mJ of pump energy (corresponding to 38 MW/cm² av-

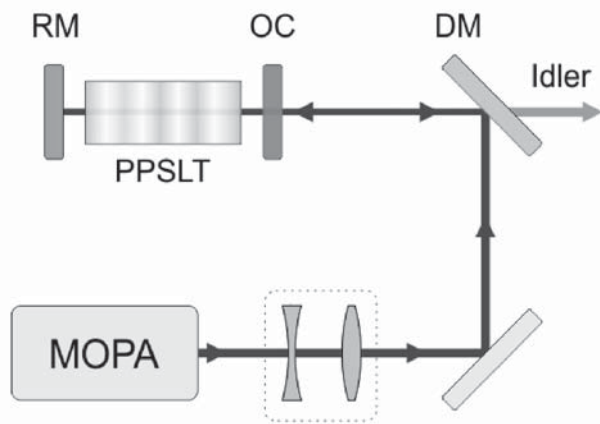


Fig. 5. Schematic of the optical parametric oscillator: RM – rear mirror; OC – output coupler; DM – dichroic mirror.

erage pump intensity). This intensity threshold value is in agreement with the theoretically predicted value of 44 MW/cm² from the Brosnan and Byer theory [13] for the case of a singly resonant OPO with pump reflection. Comparing with CSP OPO employed in a very similar cavity [14] the OPO threshold is over 30 times higher, which should be attributed to the much higher nonlinearity of the CSP crystal. The maximum pump intensity applied in the present work is ~550 MW/cm² (four times below the PPSLT damage threshold). The maximum idler output energy at 3 μm reached 2.2 mJ (see fig. 6), at

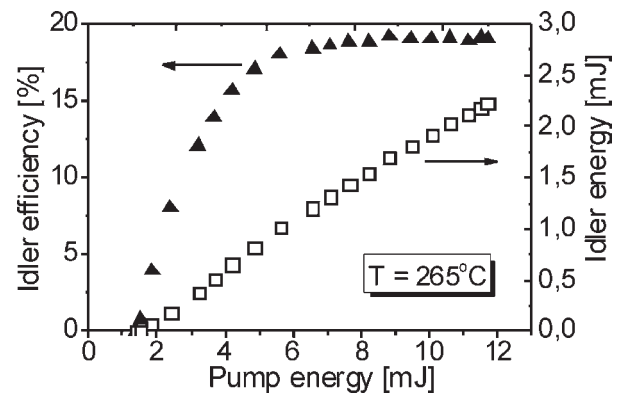


Fig. 6. Idler energy versus pump energy incident on the PPSLT crystal at crystal temperature 265°C (blue rectangles). Idler conversion efficiency (black triangles).

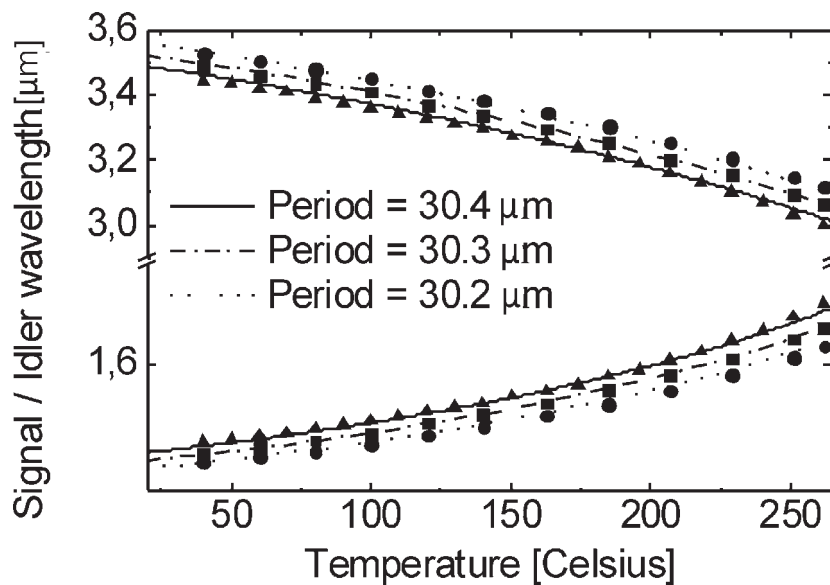


Fig. 7. OPO temperature tuning versus domain inversion period, measured data (dots) and calculated tuning curves (solid curves), see text for details.

pump energy of 11.5 mJ, which corresponds to an idler conversion efficiency of 18.3% and overall quantum conversion efficiency (both idler and resonating signal) of nearly 52 %. At the working pulse repetition rate (0.5 kHz) the generated average power at 3 μm was above 1 W. The average idler output power was 880 mW around 3.4 μm and 970 mW at 3.25 μm , respectively.

Changing the temperature of the PPSLT crystal from room temperature up to 265°C we were able to achieve continuous tuning from 3 to 3.5 μm employing the three domain inversion periods. The experimental results are in very good agreement with the theoretically calculated curves for the domain inversion periods (see Fig. 7). In the above calculations we used the Sellmayer coefficients and the expression for thermal expansion of SLT derived by Dolev et al. [15].

CONCLUSION

We have designed and constructed a laser system with high energy and high average power, which is tunable across the right slope of the water absorption peak. We have also demonstrated operation of a sub-nanosecond, 0.5-kHz OPO, based on PPSLT crystal, tunable between 3-3.5 microns. As a pumping source we utilized an amplified single frequency, passively Q-switched microchip laser and the achieved output energy was 2.2 mJ with above 1 W average power. The output limitation in our frequency conversion stage was determined by the damage threshold of the rear mirror of the OPO. An extension to even higher repetition rates and energies, by utilizing larger aperture nonlinear crystals and second amplification stage, is currently in progress.

Many areas of materials research, medicine and condensed matter sciences, that simply would not have been further developed (because of the lack of access to large-scale laser facilities like the mid-IR FEL), will now become a focus of active studies.

Acknowledgment

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**ПРЕНАСТРОЙВАЕМ ЛАЗЕРЕН ИЗТОЧНИК –
АЛТЕРНАТИВА НА ЛАЗЕРИТЕ НА СВОБОДНИ
ЕЛЕКТРОНИ – В СРЕДНАТА ИНФРАЧЕРВЕНА
СПЕКТРАЛНА ОБЛАСТ, СЪЗДАВАЩ
ВЪЗМОЖНОСТИ ЗА РАЗРАБОТВАНЕ НА НОВИ
МЕТОДИ ЗА СИНТЕЗИРАНЕ И ОБРАБОТКА НА
МАТЕРИАЛИ**

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Резюме

Още от самото си създаване лазерните източници се разглеждат като обещаващ инструмент за реализиране на специфични състояния на материалите чрез селективни манипулации, които не могат да бъдат реализирани чрез конвенционалните източници на енергия. Въпреки че понастоящем селективната химия чрез лазерни източници е все още мечта, селективният контрол при обработката на материали, реализиран чрез оптимизация на интензитета на лазерното лъчение, времевата и пространствената му кохерентност, често се прилага за преодоляване на актуални технологични ограничения. Използването на източници на лазерно лъчение с уникални параметри в средната инфрачервена спектрална област при изследванията в областта на кондензираната материя и материалознанието, непрекъснато

създава и идентифицира потенциални приложения с висока степен на значимост както и върхови постижения в науката и технологиите. В този смисъл лазерна система излъчваща свръхкъси импулси с пренастройваема дължина на вълната в средната инфрачервена спектрална област би била обещаващ нов инструмент за лазерно отлагане на термично лабилни материали, които да бъдат обработвани в режим, при който до голяма степен се избягва електронно възбуждане и съответно е много по-малко вероятно да се развият разрушителни фотохимични процеси. До сега единствените лазерни източници в средната инфрачервена област, приложими за горепосочените техники, бяха лазерите на свободни електрони (ЛСЕ), които осигуряват лъчение с регулируема дължина на вълната с висока средна и пикова мощност. Но ЛСЕ представляват многомилионни по стойност съоръжения с уникални импулсни характеристики, които са трудно достъпни за широк кръг изследователи. В настоящата статия се описва разработването на пренастройваема в средната инфрачервена спектрална област лазерна система, достигаща до безпрецедентно ниво на енергия в импулс (> 2 mJ) около максимума на поглъщане на водата на 3 микрометра при честота на повторение в килохерцовия честотен обхват. Разработената лазерна система ще способства развитието на нови технологии за анализ и обработка на органични материали, въз основа на наличието на характеристични за тези материали вибрационни преходи в тази област на електромагнитния спектър.

**PEPTIDASE ACTIVITIES OF STARTER LACTIC ACID BACTERIA FOR
TRADITIONAL BULGARIAN CHEESES RESULTING IN PRODUCTION
OF PEPTIDES WITH BIOACTIVE EFFECTS**

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Abstract

During the fermentation and digestion of proteins Lactic acid bacteria can release bioactive peptides with antihypertensive function. Accumulation of these peptides is strain dependent; hence, the large number of strains belonging to different species has to be screened in order to get to the best producers. ACE (Angiotensin-converting enzyme) inhibition results mainly in an antihypertensive effect. Epidemiological studies suggest that consumption of fermented milk products is inversely related to the risk for hy-

pertension. In this study we screened a high number of Lactic acid bacteria for their peptidase activities and ability to inhibit ACE. The best producer of ACE inhibitory peptides was strain *L. helveticus* V28, which possessed the highest aminopeptidase activities, too. The objective of the present study was to investigate concentrations of well-known antihypertensive peptides VPP and IPP in milk fermented by *L. helveticus* V28.

INTRODUCTION

Milk proteins are precursors of many biologi-

cally different peptides. These peptides are inactive within the sequence of the precursor proteins but can be released by enzymatic proteolysis during milk fermentation. Milk protein-derived bioactive peptides may function as exogenous regulatory substances with hormone-like activity on different intestinal and peripheral target sites of the mammalian organism. Food hormones such as bioactive peptides may be included in the formulas of physiologically functional foods and in industrial nutraceutical preparations [1]. To date, antihypertensive peptides, together with phosphopeptides and immunomodulating peptides, are the favorite bioactive peptides for application to foodstuffs formulated to prove specific health benefits [6].

The production of fermented dairy products correlates with the main metabolic process of the most common lactic acid bacteria (LAB) during growth in milk and in cheese ripening, i.e. proteolysis of casein. Lysis of LAB and the release of intracellular enzymes are determining factors in the cheese ripening process [4, 5]. The enzymatic pattern of proteolytic systems varies between and within different bacterial species [8].

MATERIALS AND METHODS

Peptidase activities. Aminopeptidase activity was measured by the method of Doi et al. [3]. Dipeptidase activity was measured by the method of Wohlrab and Bockelmann [9]. Tripeptidase PepT and proline-specific peptidase activities were quantified using the modified cadmium-nynhydrin method of Doi et al. [3] in which free amino acids are determined spectrophotometrically (UV Mini 1240, Shimadzu, Japan).

Assay of the total anti-ACE activity. ACE activity was determined by the method of Cushman and Cheung [2] modified by Nakamura et al. [7] with some additional modifications. After the milk fermentation with every evaluated strain the supernatant (5 ml, pH 4.3) was subjected to purification through reverse-phase cartridge (Waters C18ec). Following washing with water the peptides were eluted with 5 ml 60% acetonitrile in 0.1% trifluoroacetic acid (TFA). The eluate was freeze dried and reconstituted in 1 ml 0.1% TFA. The substrate Hip-His-Leu was

dissolved in 100 mM Na-borate buffer (pH 8.3) to concentration in assay mixture of 6 mM. The final concentration of NaCl was 300 mM. To 190 ml of substrate solution 20 ml purified supernatant or peptide fraction were added and the reaction was initiated by 40 ml of ACE enzyme solution (0.1 U/ml). Further, the method of Nakamura et al. was followed [7].

Purification of VPP and IPP peptides. The supernatants were partially purified on reverse-phase cartridges as previously explained and subjected to centrifugal ultrafiltration with membrane 5000 Da. TFA was added to the samples to 0.1% concentration and 1 ml was injected onto RP-HPLC column Nucleosil C18. In parallel, the standard peptides VPP and IPP were run at the same HPLC conditions. The fractions corresponding according to the retention times to the standard peptides were refractionated on HPLC column Nucleodur Sphinx at specific gradient conditions for the respective fractions. The last purification step for VPP and IPP was performed by means of ion-exchange HPLC column Shimadzu SCX in Li mode. The elution was performed through gradient of pH 3.0 to 9.0 in citrate buffers. Finally, VPP and IPP single peaks were collected from the *L. helveticus* V28. The amino acid content of the purified ACE inhibitory peptides was determined after hydrolysis with 4 M methansulphonic acid.

RESULTS AND DISCUSSION

Aminopeptidase and dipeptidase activities of *L. helveticus* V28 are significantly higher than those of other strains. The aminopeptidases Lys-pNa hydrolase and Leu-pNa hydrolase (676.0 U/mg and 1262.3 U/mg) and the proline-specific dipeptidases Leu-Pro hydrolase and Pro-Ile hydrolase (670.4 U/mg and 576.1 U/mg) showed significantly higher specific activity than that of other hydrolases. The same strain showed the best ACE-inhibitory activity. In *L. helveticus* V28 - fermented milk the tripeptides valyl-prolyl-prolyne (VPP) and isoleucyl-prolyl-prolyne (IPP) were identified as the most potent antihypertensive peptides [1]. Important task of this study was to define the ACE-inhibiting peptides produced by *L. helveticus* V28 and to investigate the concentration of VPP and IPP as peptides demonstrated

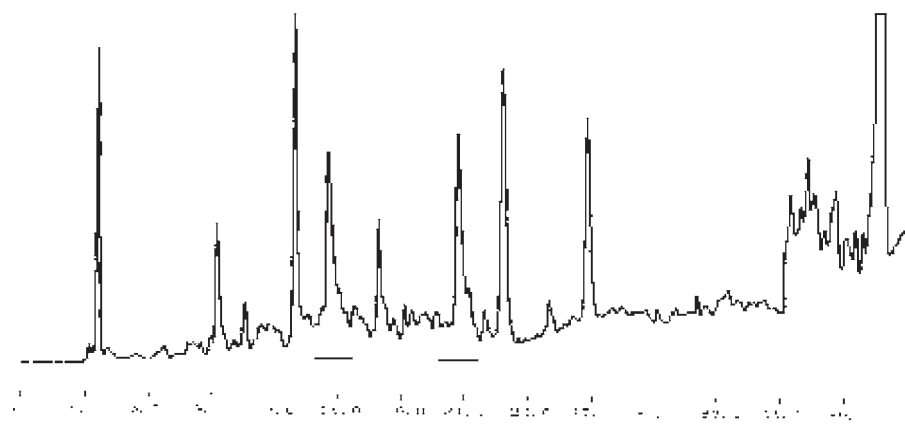


Fig. 1. Crude fractionating of peptides released by strain *L. helveticus* V28. Black line – IPP and VPP peptides; Red line – the fraction with the best ACE-inhibiting effect.

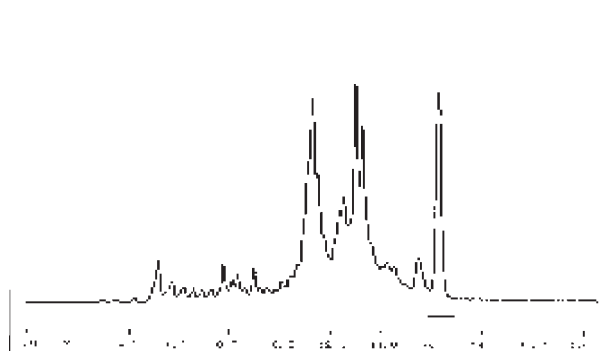


Fig. 2. Reverse phase refractation of VPP and IPP fractions received after the crude fractionating

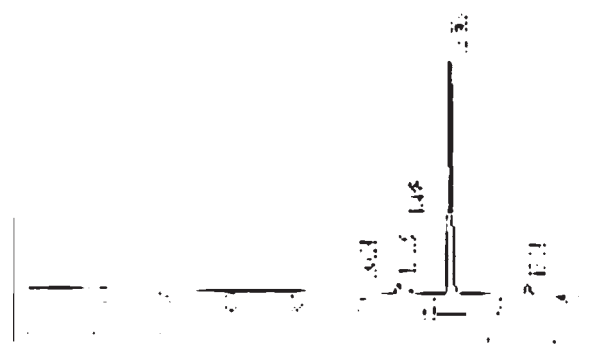


Fig. 3. Ion-exchange purification of the VPP single peptide from *L. helveticus* V28

antihypertensive effect in-vivo. On Figure 1 crude separation of the initially purified peptides is shown as it was explained in the methods. The fraction containing peptides VPP and IPP is underlined in black. The same fraction was subjected to additional fine refractation using again RP-HPLC separation but with specially adjusted gradient program with low gradient rate. The corresponded chromatogram is shown on Figure 2. IPP and VPP peptides show very close retention times and the corresponded fraction is underlined. The final purification step of VPP and IPP fractions was ion-exchange using pH gradient. This different principle of separation comparing with the reverse phase helps to receive well purified single peptides. The chromatogram after ion-exchange separation is shown on Figure 3 and again the fraction (single peptide) with the same retention time to VPP is underlined. Only the fraction corresponding to peptide VPP was obtained which is underlined on the figure. There was not a peptide peak which corre-

sponds to IPP on the base of the retention times. The VPP concentration was estimated by help of calibration with standard peptide VPP, obtained from Invitrogen customer service. The concentration of VPP using the experimental conditions mentioned in the Methods was 12.2 mg/ kg. We prepared solution from standard VPP at the same concentration and the ACE-inhibiting activity was measured. The inhibition percent was 29%. This value is considerably less than the total anti-ACE activity of *L. helveticus* V28 fermented milk (68%). This means that other more potent ACE-inhibiting peptide is produced by *L. helveticus* V28. The probability that this unknown peptide would have stronger ACE inhibitory activity at the same concentration with VPP and IPP is very low. Most likely, the concentration of this peptide is much higher than those of VPP, and that's why the demonstrated ACE-inhibiting activity of this peptide is stronger than from VPP in *L. helveticus* V28 fermented milk. On the figure 1 with red line the most potent

ACE-inhibiting fraction is underlined. It is clear that this is definitely different peptide than VPP and IPP.

CONCLUSIONS

After screening of a large number of Lactic acid bacteria strains the strain demonstrating the highest ACE-inhibitory effect was *L. helveticus* V28. Milk fermented by this strain was investigated for the most potent ACE-inhibiting peptides IPP and VPP. Only VPP was present in the fermented milk.

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ПЕПТИДАЗНИ АКТИВНОСТИ НА ЗАКВАСКИ ЗА ТРАДИЦИОННИ БЪЛГАРСКИ СИРЕНА ВОДЕЩИ ДО ОСВОБОЖДАВАНЕ НА БИОАКТИВНИ ПЕПТИДИ

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Резюме

При ферментацията и усвояването на протеините някои млечнокисели бактерии могат да освободят биоактивни пептиди с антихипертоничен ефект. Продуцирането на тези пептиди е щамово-специфично и затова, за да се открият добри продуценти на биоактивни пептиди, трябва да се изследва голям брой щамове от различни бактериални видове. Инхибирането на АСЕ (Angiotensin-converting enzyme) води до благоприятен ефект при повишено кръвно налягане. Научни изследвания сочат, че консумацията на ферментирани млека рефлектира благоприятно върху риска от повишено кръвно налягане. В настоящото проучване бяха изследвани голям брой млечнокисели бактерии за техните пептидазни активности и способността да инхибират АСЕ. Щамът, който демонстрира най-силно инхибиране на АСЕ и същевременно най-висока аминокпептидазна активност е *L. helveticus* V28. Една от целите на изследването е да се определи концентрацията на антихипертоничните пептиди VPP и IPP в млека, ферментирани от *L. helveticus* V28

DROUGHT AS A CHALLENGE FOR IMPROVED SCREENING OF CEREAL GENOTYPES FOR SUSTAINABLE PLANT PRODUCTION

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Abstract

A bilateral project between the Institute of Plant Physiology and Genetics at the Bulgarian Academy of Sciences and The Slovak University of Agriculture in Nitra entitled 'Drought as a challenge for improved screening of cereal genotypes for sustainable plant production' was funded by the Bulgarian Ministry of Education, Youth and Science and the Slovak Research and Development Agency. The main goal of the Project is to study drought tolerance mechanisms in wheat and barley as important crops and to offer confident criteria for evaluation and screening of genetic resources under unfavorable climate conditions. The relationship between leaf water deficit, structural changes in leaves, cell membrane stability, osmolytes accumulation, development of oxidative stress and photosystem II efficiency in some of the most widely used Bulgarian and Slovak wheat and barley genotypes under drought conditions will be investigated. On the basis of the obtained new data, a model for drought resistance in cereals would be established. It might facilitate breeders in their pursuit of drought tolerance and sustainable plant production.

INTRODUCTION

Climate change evokes a need for better characterization of plant responses to stress and deeper understanding of physiological mechanisms related to adaptation and productivity under adverse conditions. Soil drought is the abiotic factor which most seriously limits growth and development of crop plants and negatively affects their yield. Clarification of physiological and biochemical mechanisms of stress adaptation is a basic approach towards breeding for higher drought tolerance in crops. Metabolic reactions such as osmotic adjustment, cell mem-

brane stability, plant water status under stress, and their relation to the activity of the photosynthetic apparatus are among the most common parameters for selection of tolerant plant genotypes (Zivcak et al., 2008; Chipilski et al., 2012). In order to better identify the aspects of drought tolerance, an integration of methodological approaches and investigation of plant responses to stress on multiple levels of organization (from molecular to organ and whole-plant level) is necessary. Laboratory screening techniques for evaluation of physiological mechanisms of plant resistance have certain advantages compared to field studies. They allow precise regulation of the degree of stress treatment and avoid interaction between stress factors, which often occurs in natural conditions.

Wheat and barley are the most important cereal crops in many countries. In this regard, a bilateral project between the Institute of Plant Physiology and Genetics at the Bulgarian Academy of Sciences and The Slovak University of Agriculture in Nitra entitled 'Drought as a challenge for improved screening of cereal genotypes for sustainable plant production' has been funded by the Bulgarian Ministry of Education, Youth and Science and the Slovak Research and Development Agency. The main goal of the Project is to study drought tolerance mechanisms in cereals and to offer confident criteria for evaluation and screening of genetic resources under unfavorable climate conditions. Some of the most widely distributed Bulgarian and Slovak wheat and barley genotypes will be used for scanning the phenotypic variation in response to drought stress. An interdisciplinary approach will be applied and new methods and innovative technologies will be implemented. The research will be of particular importance to breeding practice and will render better understanding of

drought tolerance in cereals, which will facilitate farmers in their pursuit to improve and stabilize yield.

MATERIAL AND METHODS

In the present project, a selection of the most widely distributed Bulgarian and Slovak wheat (*Triticum aestivum* L.) and barley (*Hordeum vulgare* L.) genotypes will be screened for phenotypic variation at seedling stage in response to dehydration. Water stress will be induced by treating the roots with polyethylene glycol (PEG) and by growing seedlings on drying soil. The physiological response to stress will be characterized by measuring relative water content, transpiration and total water potential of stressed leaves (Turner, 1981). Morphometric data of leaf tissue from control and stressed samples will be compared by measuring leaf thickness, area of mesophyll cells and stomatal density (Mehri et al., 2009). For assessment of cell membrane stability of stressed samples, injury index and kinetics of electrolyte leakage will be employed (Kocheva et al., 2005). Additionally, the quantities of some compatible metabolites in cells such as soluble proteins (Bradford, 1976), reducing sugars (Ashwell, 1966), free amino acids (Yemm & Cocking, 1955) and proline (Bates et al., 1973) will be determined as a measure of osmoregulation capacity of samples under stress conditions. Common parameters of developing oxidative stress such as malonildialdehyde and hydrogen peroxide content in leaves will be determined as well (Alexieva et al., 2001). The functional activity of photosystem II will be assessed on the basis of chlorophyll fluorescence measurements. The results will be fitted to chlorophyll content, stomatal conductance and water and CO₂ exchange rate. On the basis of the obtained results, a simulation model for the evaluation of physiological drought tolerance of cereal genotypes will be developed and its applicability for breeding practice will be tested.

EXPECTED RESULTS

The relationship between leaf water deficit, membrane stability, development of oxidative stress, and photosystem II efficiency in different wheat and barley genotypes under drought conditions will be investigated. This holistic approach has the advantage of being fast and indicative

for early diagnostics of physiological disorders in plants under stress (Lawlor & Cornic, 2002; Strasser et al., 2007). The ion leakage kinetics model offers excellent interpretation of the changes in cell membrane stability and relates them to the magnitude of stress (Kocheva et al., 2005). PEG simulates fast dehydration by reducing the osmotic potential of the medium, while soil desiccation reduces water availability for plants more slowly. Using the comparative approach, the adaptive mechanisms of wheat and barley genotypes with different degree of tolerance will be revealed under conditions of osmotic stress and soil dehydration. The results will enrich the knowledge on the reaction of Bulgarian and Slovak wheat and barley genotypes to drought. On this ground, a model for drought resistance in cereals would be established that could be used in breeding and cultivation practices.

The study of the reactions of various wheat and barley genotypes in relation to their susceptibility to drought is of significant importance to agronomy and selection practice and will facilitate breeders in their pursuit of drought tolerance and high yield.

The Project is in accordance with the Action Plan on Food Price Volatility and Agriculture affirmed by the Agricultural Ministers from the G20 group of nations in June, 2011 in Paris regarding the establishment of an International Research Initiative for Wheat Improvement. The initiative aims at reinforcing synergies between national and international wheat research programmes and developing scientific collaborations to accelerate progress in wheat yield and stress tolerance, and thereby increase food security, nutritional value and safety as a part of sustainable agricultural production practices and systems.

The results of the Project will also feed into training and development of young professionals such as agronomists, physiologists and geneticists (students, PhD students) in predicting the drought resistance of wheat and barley varieties.

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ИЗУЧАВАНЕ РЕАКЦИЯТА НА ЖИТНИ РАСТЕНИЯ КЪМ ЗАСУШАВАНЕ И СЪЗДАВАНЕ НА СКРИНИНГ МОДЕЛ ЗА ТЯХНАТА СУХОУСТОЙЧИВОСТ

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Резюме

Необходимостта да се изучават физиологичните основи на адаптацията на растенията и тяхната продуктивност в неблагоприятни условия е продиктувана от непрекъснато променящите се климатични условия и нарастването на световната популация, изискващо по-високи добиви от зърнени култури. С изследванията по проекта се цели да се установи ефекта на засушаването при млади пшенични и ечемични растения от важни български и словашки сортове върху основни биохимични, физиологични и морфологични показатели, като активност на ключови ензими, синтез на метаболити, регулация на водния обмен, функционална активност на фотосинтетичния апарат. Изясняването на механизмите на толерантност ще спомогне за постигането на по-добра ефективност при подбора на генотипи и оптимизиране на отглеждането им в условия на засушаване. Ще бъде приложен интердисциплинарен подход за изучаване на корелацията между нивото на стреса и степента на запазване на продуктивността на генотипа. Настоящият проект ще допринесе за изясняване на връзката между механизмите, способстващи за адаптацията на клетъчно ниво (осмотично приспособяване, антиоксидантна система, състояние на клетъчните мембрани) и оценка на въздействието на засушаването върху цялото растение (активност на фотосинтетичния апарат, морфо-анатомични промени в структурата на листа) и значението на тяхната координация за способността на житните растения да преживяват периоди на засушаване. Използването на редица съвременни методи ще позволи изграждането на интегрална представа за поведението на важни физиологични, биофизични и анатомични показатели в условия на стрес. Крайната цел на поставените задачи е да се създаде модел за бърз скрининг (подбор) на сортове и/или линии пшеница и ечемик, притежаващи такава комбинация от признаци, която да способства за преживяемостта в условия на засушаване при запазен оптимален продуктивен потенциал. Последното ще има съществен икономически ефект за селскостопанската практика.



BULGARIAN ADDED VALUE TO ERA

STUDIES AND ACHIEVEMENTS AT THE UNIVERSITY OF FORESTRY'S LABORATORY OF BIOTECHNOLOGY AND MOLECULAR GENETICS

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Abstract

The present survey presents briefly the University laboratory of biotechnology and molecular genetics at the University of Forestry, Sofia, established with the support by the National Science Fund of Bulgaria. Major achievements of the Lab are in two main fields of research: 1) applying of modern methods for micropropagation and cloning in vitro of ornamental plants and forest tree species and 2) genetic studies of populations mainly of forest tree species. A large part of the studies was performed within the framework of international research projects.

The laboratory of Biotechnology and Molecular Genetics at the University of Forestry (Sofia) is equipped with new and modern technique and its main goal is to develop technologies in the field of biotechnology and genetics of ornamental plants and forest tree species. The laboratory had been established with the support of the National Science Fund of Bulgaria through a national research project within the framework of a call "Establishment of integrated research centres in the universities" (Fig. 1). Even though the full equipping was achieved after completing the above mentioned project, the lab was functioning before, albeit less equipped. Activities of the lab could be summarized as directed to two main reserearch areas: plant propagation using modern methods and technologies, and popula-

tion and evolutionary genetics, mostly of plants, with emphasis on forest tree species.

1. Tissue cultures of ornamental and forest species.

One of the most interesting areas of biotechnology is tissue culture and micropropagation. The technique of plant tissue culture is used for growing isolated cells, protoplasts, tissues, and organs under aseptic laboratory conditions (*in vitro*). Micropropagation is a form of tissue culture used to regenerate (propagate) entire plants. Different techniques of culturing plants *in vitro* may offer certain advantages over traditional methods of propagation. Growing plants *in vitro* in a controlled environment, with in-depth knowledge of the culture conditions and the nature of the plant material, ensures effective clonal propagation of genetically superior genotypes of economically important plants. Tissue cultures represent the major experimental systems used for plant genetic engineering, as well as for studying the regulation of growth and organized development through examination of structural, physiological, biochemical and molecular bases underlying developmental processes. Micropropagation has become an important part of commercial propagation of many plants (George and Sherrington 1984, Zimmerman et al. 1986, Hartmann et al. 2002) because of its advantages as a system for cloning and multiplication (Iliev 1990, Pierik 1997, Iliev et al. 1998, Iliev and Borisova 2002, Razdan 2003, Iliev et al.

2010) and additional method for inducing of variability in the plants (Iliev 1991).

The studies in the field of plant tissue cultures are orientated to investigation of peculiarities of generative and vegetative propagation *in vitro* of economically valuable ornamental and forest tree species.

The earliest investigation in the field of biotechnology of the forest and ornamental tree species in Bulgaria started with the successful cloning of *Betula pendula* through callus cultures, introduced from apical and leaf segments (Iliev and Chavdarov 1988). Later the researches were aimed to study disinfection, culture establishment, and multiplication; morphological and anatomical studies of the root formation and the variability *in vitro*; biochemical and karyological studies, and acclimatization of *in vitro* propagated plants.

Investigations of the peculiarities of generative propagation *in vitro*

These studies are related with determination of quality of the seeds of some introduced broadleaved tree species. Comparative investigations of scarified seeds from *Albizia julibrissin* from different origins did not show statistical differences in the germination *in vitro* and *in vivo* (Iliev and Alexandrov 1996). However it was demonstrated that the conditions *in vitro* are more suitable for the germination of *Metasequoia gliptostroboides* and *Robinia pseudoacacia* seeds in comparison with the conditions *in vivo* (Iliev and Tsvetkov 1995, Iliev and Chavdarov 1996). The results proved that the low germination of *Sequoiadendron giganteum* and *Metasequoia gliptostroboides* could be considered as physiological peculiarity of the seeds (Iliev 1994, 1997, Iliev and Tsvetkov 1995). The determined appearance of polyembryony and mono- and threecotyledonary seedlings during the germination process of *Robinia pseudoacacia* seeds are with scientific and theoretical contribution because we are not familiar with similar findings with this species. Appearance of "twin" seedlings could be regarded as the result of formation of two ovums in the ovary. The peculiarities of their appearance, growth, and size support the hypothesis that one of them could be result of apomixis (Iliev and Chavdarov 1996).

Investigation of the *in vitro* propagation of conifer and broadleaved tree species

Disinfection, culture establishment, and multiplication

The disinfection of explants before culture is essential to remove surface contaminations with minimal damage to plant cells. It was demonstrated that different disinfection is necessary, depending of the type, age, and physiological stage of initial explant (Iliev and Chavdarov 1988, Karanikas et al. 2005, Mitras et al. 2005, Dancheva 2012).

Physiological stage, order of the bud, level of plant growth regulators, genotype, and the nutritive medium are key factors for the development of the buds on the dormant apical and nodal segments from *Betula pendula*. However, formation and elongation of the axillary shoots is not significant and have not practical significance. It was proved that the induction of callus and multiplication of adventitious shoots from dormant and green nodal segments is with higher effect (Iliev 1996, Iliev et al. 2010a). It was demonstrated that the using of leave explants is more effective for the induction of adventitious shoots in comparison with nodal and apical segments from mature trees. It was proved that regeneration capacity of the organs is different (Iliev 1996, Iliev et al 2002). Evidences for rejuvenation were demonstrated. Black-bark silver birch was cloned for a first time by this method (Iliev et al. 2003a). This method gives possibility for cloning of mature individuals without application of techniques for rejuvenation of mature stock plants (Iliev and Zhelev 1994, Iliev et al. 2001).

Application of red light and GA₃ during cultivation of *Morus alba* 'Pendula' and *Sorbus domestica* supported the elongation of the shoots (Karanikas et al. 2005, Nikolaou et al. 2008).

Method for overcoming the seed dormancy in *Fraxinus excelsior* was developed by cultivation of isolated embryos (Dancheva et al. 2010, Dancheva 2012) and the cultivated epicotils and hypocotyls showed high multiplication effect (Mitras et al. 2005, 2009, Dancheva 2012).

It was found that the ontogenetical age of the stock plant is the main factor for successful cloning of *Sequoiadendron giganteum* and *Se-*

sequoia sempervirens (Iliev and Iliev 1996, Iliev and Trifonov 1996). A specific method for rejuvenation of *Sequoia sempervirens* was elaborated and it could serve as a model system for rejuvenation *in vitro* (Iliev and Trifonov 1996).

It was showed that genotype is a key factor for realization of the establishment and multiplication phase during the *in vitro* propagation of *Prunus avium*. The using of combinations of auxins and cytokinins (Scaltsoyiannes et al. 1998, Kitin et al. 2005), half strength concentration of NH_4NO_3 in the Murashige and Skoog (1962) medium and decreased photosynthetic photon flux density during the cultivation support the multiplication effect (Scaltsoyiannes et al. 2009b). However, the elongation of the shoots could be realized on a medium, free of plant growth regulators, enriched with high concentration of gibberellic acid (Scaltsoyiannes et al. 1998), and red light additionally stimulates this process (Scaltsoyiannes et al. 2009b). The using of jars with bacteriological filters additionally stimulates this process and prevents the hyperhydricity (Scaltsoyiannes et al. 2009b).

On the base of personal experience the application of the most commonly used *in vitro* propagation techniques for trees, shrubs and herbaceous species that can be implemented on a continuous basis throughout the year are summarized. This information focuses on the explants that could be used as initial plant material for cultivation *in vitro*, the essential methods for surface disinfection, culture media and their preparation, stages of micropropagation, techniques of micropropagation (cultures of apical and axillary buds, meristem and single- or multiple-node cultures, adventitious shoot formation, somatic embryogenesis), difficulties and problems, arising during the cultivation of plants *in vitro* and the technics for their overcoming (Iliev et al. 2010b).

Morphological and anatomical studies of root formation

The obtained results demonstrate that the type and concentration of auxin are key factors for the induction of root formation of shoots in *Sequoia sempervirens*, *Sequoiaderndon giganteum*, *Fraxinus excelsior*, *Morus alba* 'Pendula' and *Robinia pseudoacacia* (Iliev 1992, Tzvetkova

et al. 1995, Iliev and Iliev 1996, Iliev and Trifonov 1996, Mitras et al. 2005, 2009, Karanikas et al. 2007). They are different for explants from individuals of *Sequoiaderndon giganteum* and *Sequoia sempervirens* with different ontogenetical age (Tzvetkova et al. 1995, Iliev and Iliev 1996, Iliev and Trifonov 1996) and the genotype is an important factor for the rhizogenesis potential *in vitro* of axillary shoots of *Prunus avium* (Scaltsoyiannes et al. 2009b). However, the type and concentration of the auxin do not influence the percentage of the rooted adventitious shoots in *Betula pendula*, but are significant factors for passing of the rooting process and quality of the formed root system *in vitro* (Iliev and Tomita 2003, Iliev et al. 2003). Key factors for the rooting, quality, and morphological peculiarities of the formed root system in *Sequoia sempervirens*, *Sequoiaderndon giganteum*, and *Fraxinus excelsior* are the duration of cultivation of axillary shoots on inductive and their transfer to expressive medium (Tzvetkova et al. 1995, Iliev and Iliev 1996, Iliev and Trifonov 1996, Mitras et al. 2005, 2009, Dancheva 2012). High percentage of rooted explants including controls, suggests a high ontogenetical rejuvenation rate (Iliev et al. 1998, 2001, 2002, 2003, Iliev and Tomita 2003, Iliev and Zhelev 1994).

An anatomical study of the *in vitro* rooting adventitious shoots in *Betula pendula* established that the auxin induced increased cambial activity resulting in new xylem and callus formation. Iso-diametric meristematic cells appeared in the cambial zone or adjacent to it in the cortex. These cells gave rise to adventitious root primordia, which grew radially outwards between the sclerenchyma bundles of the cortex. Tracheid-like cells were formed at the base of the developing adventitious roots to provide a vascular connection between the root and the shoot (Iliev et al. 2001).

Morphological and anatomical studies of variability

Hyperhydricity (vitrification), i.e appearance of transparent and eatery structures, is physiological disorder occurring in plant tissue cultures (Iliev et al. 2010). In the most cases it can be caused by a high cytokinin concentration. Our

investigations demonstrated that this phenomenon appears during the rooting of shoots on rich nutritive medium with high concentration of auxin and vitamin D₂ (Iliev et al. 1996, Iliev and Iliev 1996) and its frequency is on opposite dependence with the age of the stock plants (Iliev and Iliev 1996). Anatomical investigation of the hyperhydric explants demonstrates low degree of tissues differentiation, pathogenous increasing of the bark parenchyma and pith, and thin cell membrane of the epidermal cells (Iliev et al. 1996).

The appearance of fasciated shoots was observed during the differentiation of leaf callus of *Betula pendula* (Iliev 1996, Iliev and Tomita 2003, Iliev and Zhelev 1994, Iliev et al. 2009) and induction of axillary shoots of *Fraxinus excelsior* (Mirtas et al. 2009, Dancheva 2012) and *Prunus avium* (Kitin et al. 2005). Our results showed that appearance and frequency of the formed fasciated shoots depend on the genotype of the stock plants (Iliev and Tomita 2003, Kitin et al. 2005, Iliev et al. 2009, Mitras et al. 2009), the type and concentration of cytokinin (Iliev et al. 2002, 2003b, 2009, Iliev and Tomita 2003, Kitin et al. 2005, Mitras et al. 2009).

Anatomical study of the induced fasciated shoots in *Betula pendula* and *Prunus avium* showed that the tissues were ordered correctly and subordinate to the same structural peculiarities as in normal shoots. However, the cross-sectional area of stem of the fasciations was apparently greater than that of the normal shoots (Iliev et al. 2003b, Kitin et al. 2005, Mitras et al. 2009, Dancheva 2012). The most striking difference between normal and fasciated stems of *Betula pendula* is in the shape of the vascular cylinder and the pattern of development of the vascular tissues. It was demonstrated that the differentiation of the xylem of the fasciated shoots is slow in comparison with the normals (Iliev et al. 2003b). In particular, the volume of vascular tissues, of pith and of some individual parenchyma cells in the cortex and pith of the fasciated shoots in *Prunus avium* was apparently greater in fasciated shoots than in normal shoots. Increases in cytokinesis and morphogenetic activity, such as development of callus-like regions and formation of adventitious

shoot, were observed in the cortex and pith throughout the fasciations. The fasciated shoots had numerous buds and initiating new shoots at their apices, while normal shoots had a single dominant axial bud (Kitin et al. 2005). Compared to normal stems, the cortex in fasciated stems in *Fraxinus excelsior* appeared less differentiated. Phloem fibers were frequently observed in normal stems but were not seen in fasciated stems, which suggests that cortex differentiation occurs later in fasciated than in normal stems (Mitras et al. 2009, Dancheva 2012).

Hypotheses for the reasons, caused appearance of fasciated shoots *in vivo* and *in vitro* are suggested (Iliev et al. 2003b, Kitin et al. 2005, Mitras et al. 2009, Iliev and Kitin 2011).

Biochemical and karyological studies

Quantitative changes of peroxidase and leucineaminopeptidase in the process of rooting of adventitious shoots of *Betula pendula* do not show changes during the 10-day's period of investigation in all variants of the medium, although rooting was visible in this period (Iliev and Zhelev 1994). However, the beginning of the rooting process is related with increasing of isozyme activity (Iliev and Tzvetkova 1995a). The demonstrated dependence between accumulation of protein and passing of rhizogenesis could be used as biochemical marker for the rhizogenesis process (Iliev and Tzvetkova 1995b). The lack of new isozyme peroxidase fractions and the keeping of permanent maximal level of the peroxidase activity is an indicator that for successful rooting an obligatory transfer of the explants from inductive to expressive rooting medium is necessary (Iliev and Tzvetkova 1995a). Comparative biochemical studies of stock and *in vitro* produced plants demonstrated that the investigated 7 isozyme systems (GOT, IDH, LAP, MDH, PGI, PGM, 6-PGD) are ontogenetically and physiologically stable and do not undergo changes in the process of micropropagation (Iliev et al. 2002).

The total peroxidase activity reached its maximum value on the 21st day after the beginning of the experiment for the rooting of axillary shoots from *Sequoia sempervirens*. Then, second isozyme peroxidase fraction appeared and accumulation of the total protein reached maximal

values. For this reason this deadline could be determined as final for induction of root primordia and the shoots should be transferred from the inductive to an expressive medium (Tzvetkova et al. 1995).

The comparison of the *in vitro* propagated plants of *Betula pendula* showed that there is no change in their karyotype (Iliev 1996, Iliev et al. 1998). The higher mitotic index was found for the *in vitro* propagated plants as a result of the faster growth of the regenerants during the multiplication phase, result of the induced rejuvenilisation. The lower mitotic index of the *in vivo* propagated plants proved that the deviation of the cells decrease with the increasing of the ontogenetical age, which explains low percentage of development and elongation of the cultured nodal segments *in vitro* (Iliev et al. 1998).

Acclimatization of micropropagated plants

It is demonstrated that key factors for the acclimatization of *in vitro* produced plants of *Betula pendula*, *Sequoiadendron giganteum*, and *Fraxinus excelsior* are high air humidity and type of soil substrate (Iliev et al. 2001, Iliev et al. 2003, Rohr et al. 2003, Iliev and Tzvetkova 1995a, Iliev and Iliev 1996, Dancheva 2012).

The elaborated methods for *in vitro* propagation of ornamental and forest tree species give an opportunity for enlargement of the season's and ontogenetical possibilities for successful propagation and cloning, i.e. to overcome the limiting mature ontogenetical phase and autumn-winter period are overcome.

2. Population and evolutionary genetics

The second major direction of the lab's work is in the field of (mostly) population genetics of forest trees, with a few exceptions. Two classes of markers were applied for solving population genetic problems and for describing variation in natural and artificial populations – isozyme gene markers and DNA-based markers.

Isozyme gene markers

The lab staff has a long experience in applying isozyme gene markers for revealing population genetic structure in different tree species, like *Pinus sylvestris* (Zhelev et al. 1994, Scaltsoyiannes et al. 2009a), *Pinus nigra* (Scaltsoyiannes et al. 2009a), *Pinus peuce* (Scaltsoyiannes et al. 2008, Zhelev and Tsarska

2009), *Pinus mugo* (Slavov and Zhelev 2004), *Fagus sylvatica* (Gömöry et al. 1999), Oaks (Zhelev et al. 2002, Tsavkov and Zhelev 2010), *Platanus orientalis* (Grueva and Zhelev 2011), *Betula pendula* (Zhelev and Angelov 2012) and in some other species (unpubl.).

The study of Zhelev et al. (1994) on Scots Pine was among the first studies on the genetic variation in natural populations of forest trees in Bulgaria. Results obtained concurred with the trends revealed on the basis of extensive reviews (e.g. Hamrick et al. 1992). It was found that major part of variation (96%) was due to within-population diversity. Heterozygosity estimates were rather high, outlining the level of genetic diversity in Scots Pine in its marginal area of distribution. Individual heterozygosity distribution in natural populations of Scots Pine matched the distribution expected under random mating and Hardy-Weinberg equilibrium. No significant deviations were detected in 15 Bulgarian populations (Doncheva et al. 2003).

Scots pine, as an economically and environmentally important tree species was subjected to additional studies in an international perspective. An extensive study covering a significant part of the European distribution of *P. sylvestris* and *P. nigra* revealed that Black Pine populations were more differentiated (Fig. 2) expressing clear separation of "Eastern" and "Western" groups of populations, representing subspecies *nigra* and *salzmannii* (Scaltsoyiannes et al. 2009a).

Small share of among population diversity was found also in *Pinus mugo*, and the fact that coniferous species are at least partly self-fertile has been proven in this species by means of allozyme markers (Slavov and Zhelev 2004).

Allozyme gene markers were applied to *Platanus orientalis* – a species whose northernmost marginal populations are in Southern Bulgaria (Grueva and Zhelev 2011). Relatively high level of diversity was found within populations and about 7% of the total diversity was due to among-population variation.

Zhelev et al. (2002) studied the inheritance and linkage of allozyme variants in a Balkan endemic, *Pinus peuce*, which was a pioneer study with this species. Eight polymorphic loci were identified with segregation ratio consistent with

a Mendelian mode of inheritance. Two significant linkage groups were found in *P. peuce*: FEST-2:LAP-2 and 6PG-1:6PG-2, which correspond to the results obtained for other pine species. The results obtained allowed using the markers in a population genetic study (Zhelev and Tsarska 2009, Scaltsoyannes et al. 2008) and in the analysis of the reproductive process of the species.

Plant mating systems is another issue of interest and has been within the topics of the lab. Wind-pollinated forest trees usually display mixed mating model with some amount of the progeny resulting from self-fertilization. The comparison between the reproductive process in a natural population and in a seed orchard of Black Pine (*P. nigra*) showed that there were no considerable differences in outcrossing rates and the level of inbreeding, although outcrossing rate was slightly higher in the natural population.

Mating system parameters of *P. peuce* (Zhelev et al. 2008) did not differ significantly between a natural stand and a seed orchard. Multilocus estimates of outcrossing rate were within the range 0.77-0.79, while mean single-locus estimates were lower (0.69-0.73). The results indicate that at least 20% of the progeny of *P. peuce* result from self-fertilization.

DNA-based markers

The rise of DNA-based markers in the last two decades of the 20th century after introducing PCR led to rapid development of different genetic markers: RFLP, RAPD, mini- and microsatellites, SNPs, etc. Cytoplasmic DNA (chloroplast and mitochondrial) is of particular interest for the evolutionary studies in plants. Being maternally inherited, cpDNA could reveal the migration routes of the species after the last glaciation, i.e. during Holocene. Since the Balkan Peninsula was one of the most important refugia, genetic diversity here is higher than in the other parts of Europe. For example, Grivet and Petit (2003) found only one haplotype of European Hornbeam (*Carpinus betulus*) in Central and Western Europe, while in Carpathians haplotype diversity was higher. Our preliminary results within the framework of a bilateral project between Bulgaria and Romania confirmed the high level of diversity (Postolache et al., 2009). A

clear geographical pattern revealed by found haplotypes was in agreement with glacial refugia located on the Balkan Peninsula (Fig. 3).

Preliminary results of a study on *Quercus cer-ris* revealed high haplotypic diversity within the Balkan area and presence of unique Balkan haplotypes (Bagnoli et al. 2009), thus pointing out the importance of the Balkans as glacial refugium.

Species with different life-history characteristics could differ in level and distribution of genetic diversity. A study on *Sorbus torminalis* (L.) Crantz genetic diversity performed within the framework of bilateral project Bulgaria - Slovakia showed that the differentiation level was relatively high (Kučerová et al. 2010), which reflects the fragmented range of the species. Also, the species is insect-pollinated and with scattered distribution, and this could be also a factor differentiating it from the widespread and wind-pollinated species.

Population differentiation of *Platanus orientalis* in the Eastern Mediterranean region was studied by means of six polymorphic microsatellite regions of the chloroplast genome. High divergence among groups of populations was detected and also high haplotypic diversity and private haplotypes were found within some areas (e.g. Crete).

Within the framework of a bilateral project Bulgaria-Slovakia entitled "Gene conservation of rare plant and animal species" the Lab contributed, albeit modestly, to the studies of Chamois (*Rupicapra rupicapra*) and Capercaillie (*Tetrao urogallus*). Genetic diversity and differentiation of Chamois were characterized by using 24 nuclear microsatellites. The study proved genetic proximity of Slovenian and Northern Croatian populations together with Slovakian populations to Alpine populations while Bulgarian formed a separate group.

The study on Capercaillie showed that the Bulgarian populations are genetically distinct from Alpine and Dinaric populations (Bajc et al. 2011).

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Fig. 1. Part of the Lab - general view

chard of *Pinus peuce*. Annals of Forest Research, 51, 159.

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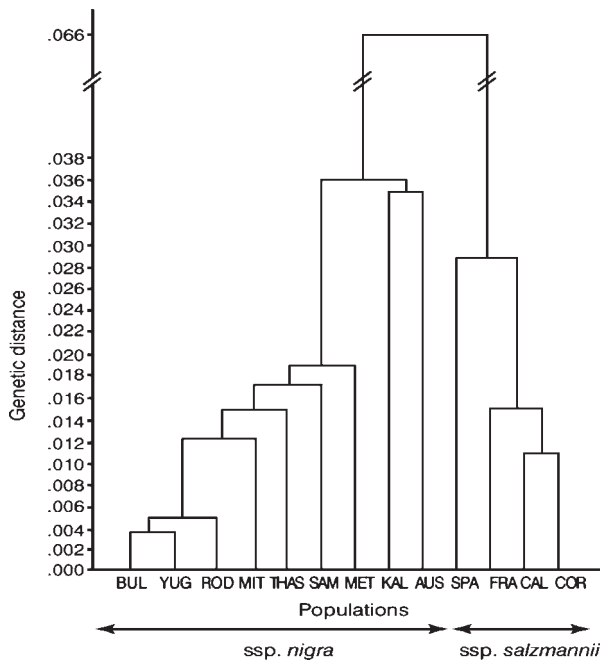


Fig. 2. Cluster analysis based on genetic distances among populations showing the grouping of populations studied in *Pinus nigra*. The eastern and western groups of populations are well differentiated. Abbreviations: BUL – Bulgaria, YUG – former Yugoslavia, ROD – Rhodopes (Greece), MIT – Mitilini Island, THAS – Thassos Island, SAM – Samos Island, MET – Central Greece, KAL – Kalamata, AUS – Austria, SPA – Spain, FRA – France, CAL – Calabria, COR – Corsica (for details, see Scaltsoyiannes et al. 2009a)

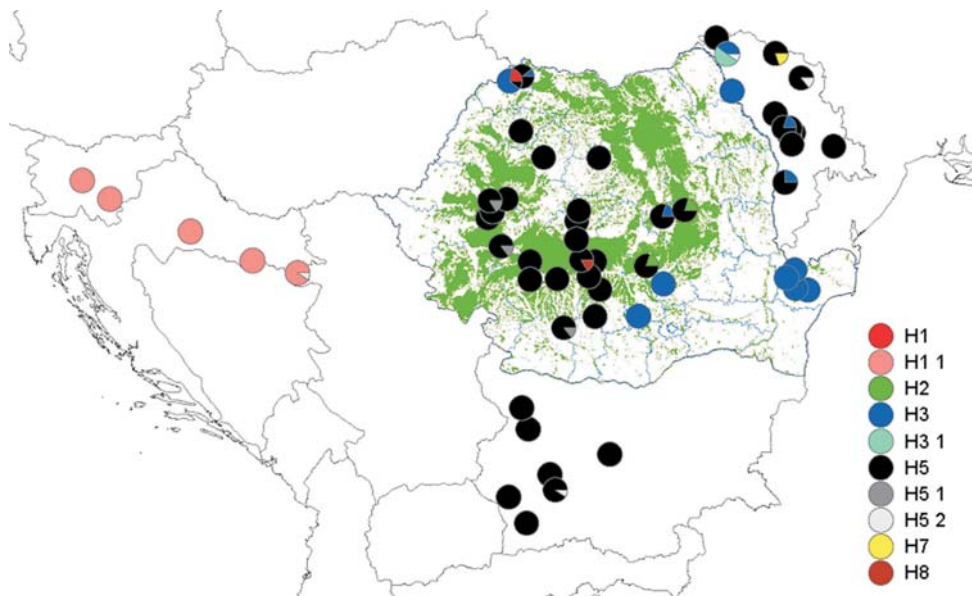


Fig. 3. Distribution of haplotypes and microsatellites of European Hornbeam (*Carpinus betulus* L.) on a part of Balkan Peninsula (Postolache et al. 2009)

**ИЗСЛЕДВАНИЯ И ПОСТИЖЕНИЯ НА
УНИВЕРСИТЕТСКАТА ЛАБОРАТОРИЯ ПО
БИОТЕХНОЛОГИЯ И МОЛЕКУЛЯРНА ГЕНЕТИКА
В ЛЕСОТЕХНИЧЕСКИЯ УНИВЕРСИТЕТ**

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Резюме

*В настоящия преглед представяме накратко Университетската лаборатория по биотехнология и молекулярна генетика в Лесотехническият университет. Лабораторията е създадена в рамките на проект с финансовата подкрепа на Националния фонд "Научни изследвания". Основите на лабораторията са поставени много по-рано, но пълноценното ѝ оборудване стана възможно с помощта на цитирания проект. Главните направления на научните изследвания на лабораторията са две: 1) прилагане на съвременни методи за микроразмножаване и клониране *in vitro* на декоративни растения и дървесни видове и 2) генетични изследвания на популациите главно на дървесни видове. В първата част са представени накратко постигнатите резултати по редица про-*

*блеми, като генеративно размножаване на растенията, *in vitro* методи за размножаване на иглолистни и широколистни видове, морфологични и анатомични изследвания на формирането на корените при микроразмножаването, морфологични и анатомични изследвания на варирането при микроразмножените растения, биохимични и кариологични изследвания на клонираните генотипове и постигнатите резултати при аклиматизацията на микроразмножените растения. Втората част представя постигнатите резултати в изследването на генетиката на популациите при редица дървесни видове с приложение на изоензимни генетични маркери и ДНК-маркери – хлоропластна ДНК, хлоропласти и ядрени микросателити и др. Основните насоки на изследванията са следните: 1) характеризиране на генетичното разнообразие в и между популациите; 2) изследване на репродуктивния процес и системата на кръстосване при дървесните видове и 3) изследвания на следледниковите миграционни процеси при някои дървесни видове. Голяма част от изследванията са извършени в рамките на международни изследователски проекти. Лабораторията има скромни приноси в рамките на по-мощни международни изследвания и в проучването на генетичното разнообразие на популациите на два редки животински вида – дива коза и глухар.*

LABORATORY FOR ENVIRONMENTAL CONTROL

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INTRODUCTION

The shortage of raw materials and environmental problems because of pollution require developing new green technologies utilizing some of the wastes and transforming them to secondary raw materials [1-4]. At the same time the use of wastes needs preliminary studies on the way to determine properties and the content of useful elements, because legal requirements are getting stronger and stronger [5-12]. It could be done if best available techniques for analysis are available and in use in certified laboratories [13-22].

The aim of this work is to present information for the project development, related to establishment of new Laboratory for environmental control at the University of Chemical Tech-

nology and Metallurgy (UCTM) in Sofia on the base of co-operation with existing Laboratory of Applied Physics, branch of the Bulgarian Academy of Sciences (CLAP_BAS) in the city of Plovdiv and the Research Laboratory for Radio-management and Environmental Control at Technical University (SRL-RMEC-TU) in Sofia.

SHORT PROJECT PRESENTATION

Integrated team proposal includes interdisciplinary partners from the UCTM, TU and BAS with long-term experience in the area of research and analysis. Team leader of the project is prof. Y. Pelovski from UCTM and the partner's project leaders are prof. R. Kakanakov for CLAP_BAS and prof. E. Altimirski for SRL-RMEC-TU. The main objectives for partners are as follows: physical-chemical analysis and control

of solid, gas and liquid products and wastes in the UCTM; purification and control of waste waters in CLAP_BAS and distance control of waste gases in the SRL-RMEC-TU. During the first stage of the project development new equipment was supplied, installed and put in operation. As a result the capacity and quality of analysis in the new established laboratory for environmental control has been developed. As a result only in UCTM new apparatus for Liquid (HPLC) and Gas-Chromatography (HPGC) with automatic sampler, TG-DTA/DSC (STA Simultaneous Thermal Analysis) and Automatic Element's Analyzer were installed and put in operation. The total cost of the new equipment installed is 432000 BGN. The new equipment was installed and put in operation only few months after training the new staff involved in the project development. The new equipment was combined with the existing spectroscopic apparatus ICP, FTIR and AAS and thus more than 70 elements and different ion groups could be determined in solid and liquid wastes and products.

Some of the PhD students, members of the project team, start to use the facilities for development of their doctor's thesis and 3 of them have already completed needed studies. Only during the first stage of the project 221 samples for element organic analysis, 243 - for TG-DTA/DSC and 193 - for chromatographic studies were performed. About 68 % of the samples were solid and liquid wastes and the other 32% - new products developed at the University. The view of the STA PT1600 TG-DTA/DSC (STA Simultaneous Thermal Analysis), production of LINSEIS Messgeräte GmbH, Germany, is shown on fig. 1.

RESULTS

Data obtained during the study of thermal stability and the rate of decomposition of some metallurgical wastes in the temperature interval $20 \div 1550^{\circ}\text{C}$ at heating rate $10^{\circ}\text{C}/\text{min}$ is given in fig. 2-5.

Data from the studies were used to determine temperature ranges of stability and weight



Fig. 1. Photos of STA Simultaneous Thermal Analysis

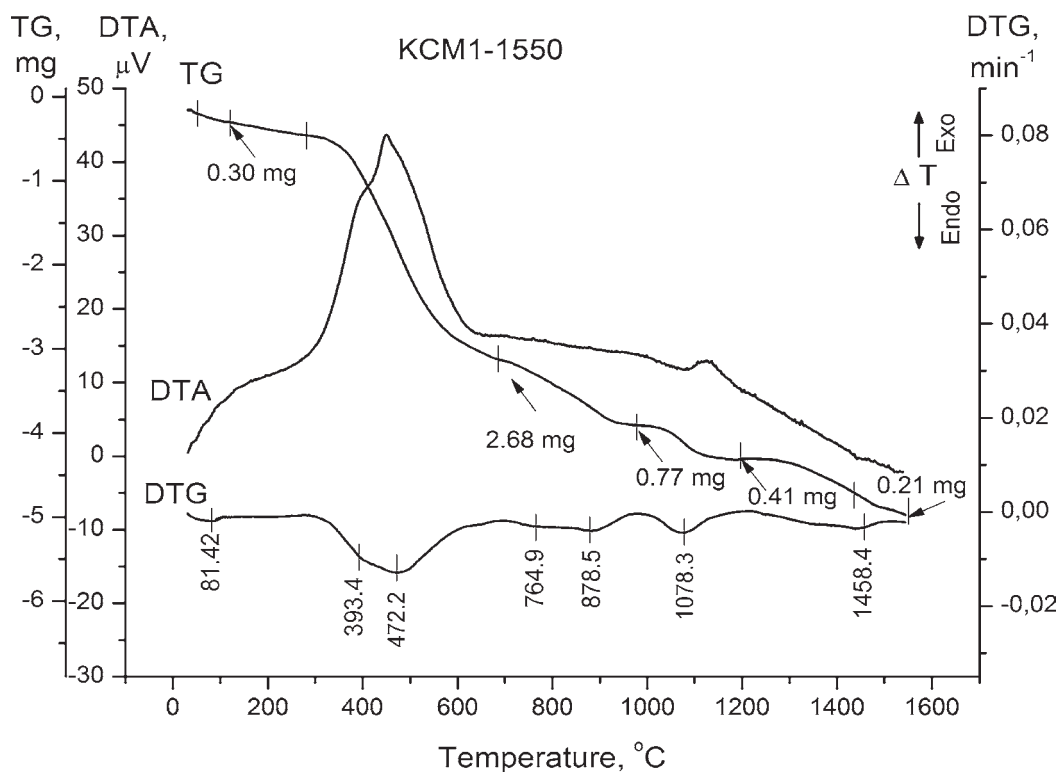


Fig. 2. TG-DTG-DTA curves for metallurgical wastes 1 – KCM 1-1550

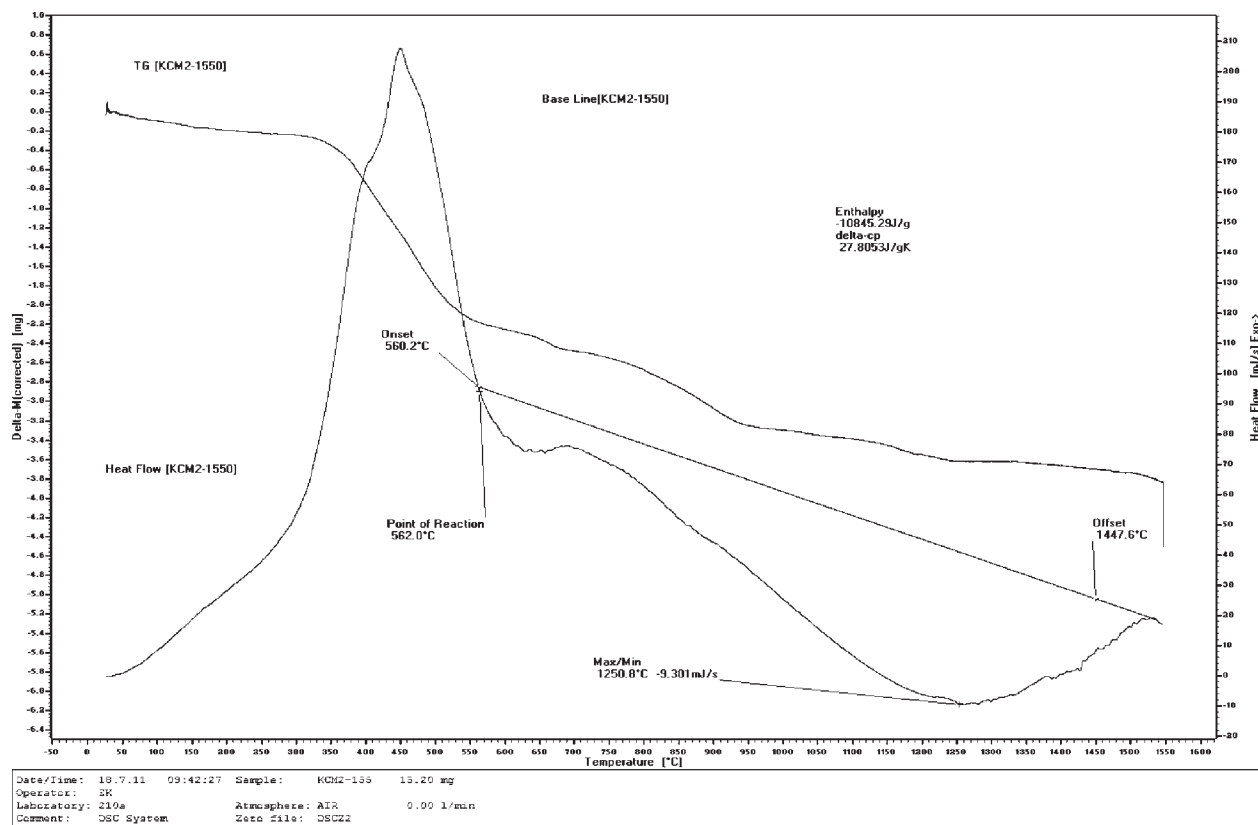


Fig. 3. DSC curves for metallurgical wastes 1 – KCM 1-1550

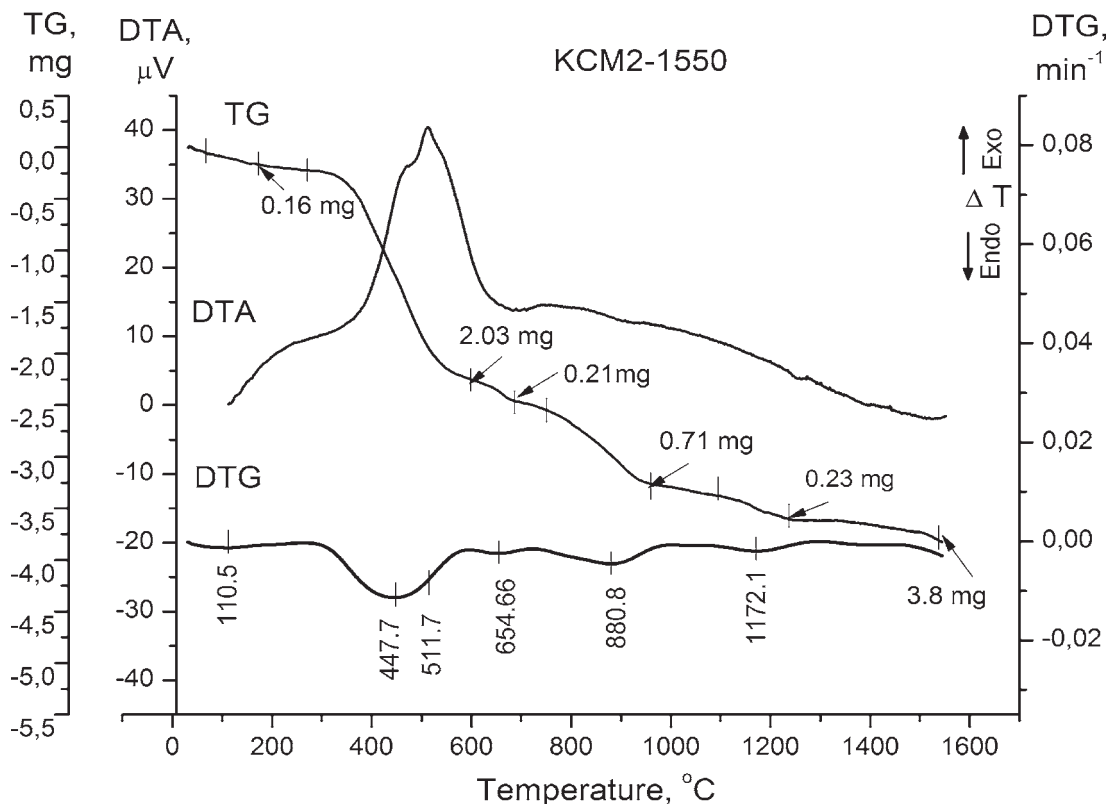


Fig. 4. TG-DTG-DTA curves for metallurgical wastes 2 – KCM 2-1550

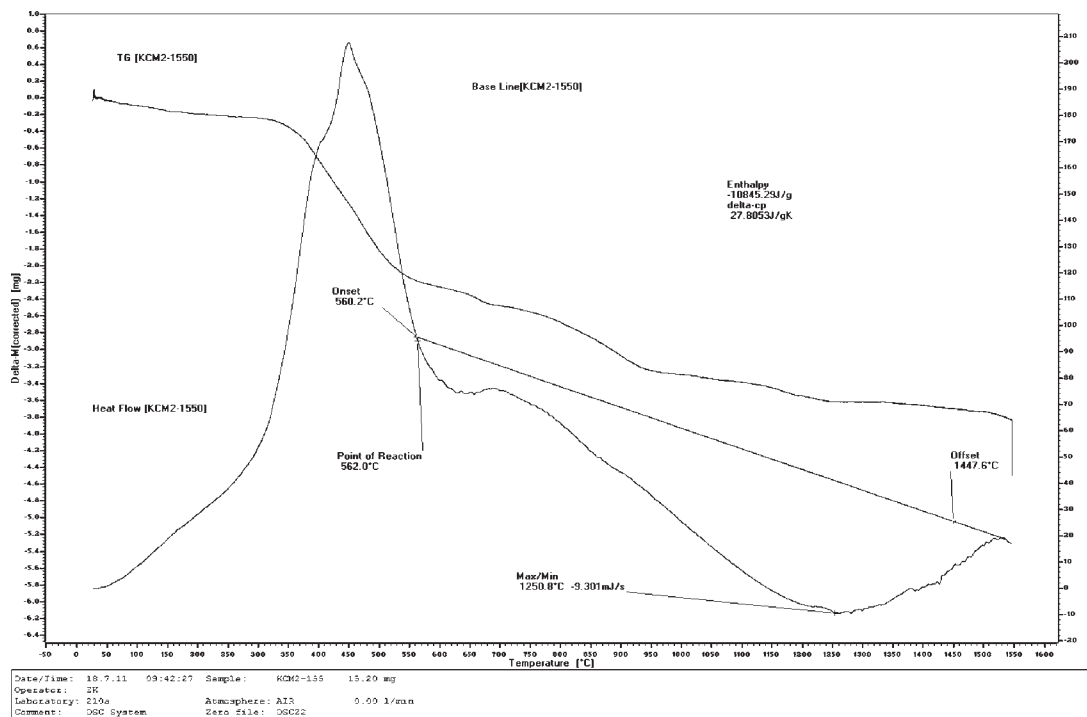


Fig. 5. DSC curve for metallurgical wastes 2 – KCM 2-1550

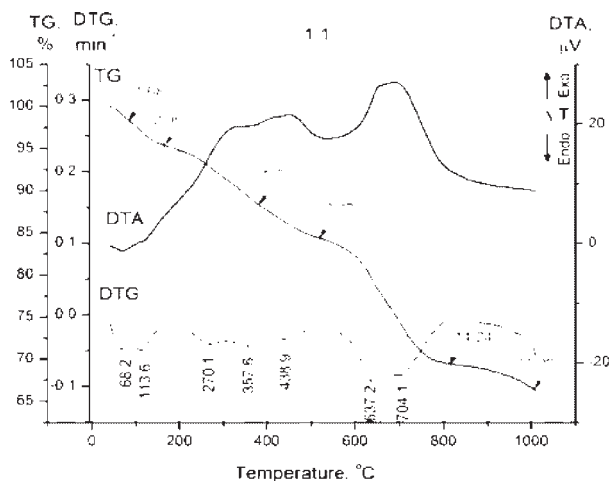


Fig. 6. TG-DTG-DTA of soil conditioner1

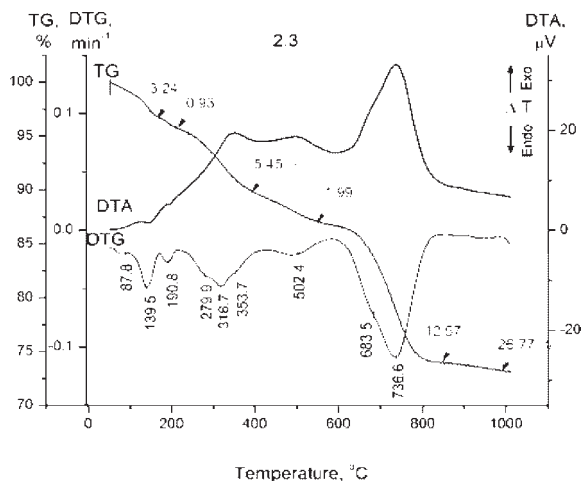


Fig. 7. TG-DTG-DTA of soil conditioner 2

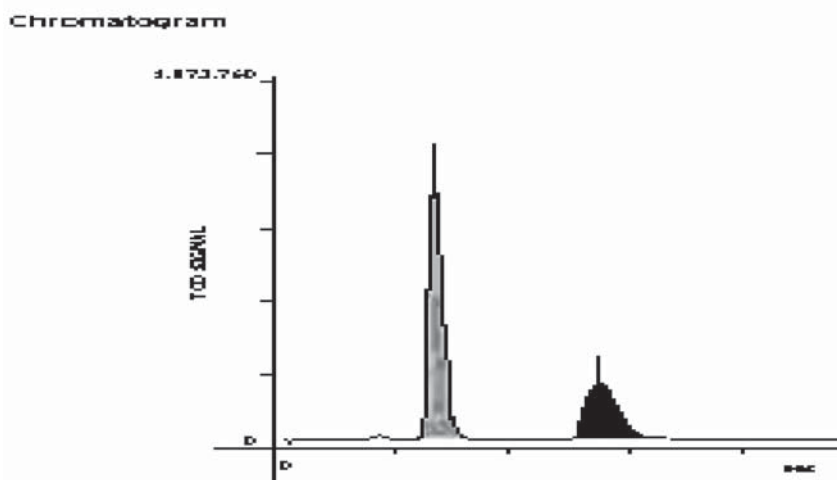


Fig. 8. Chromatogram of soil conditioner 1P

losses during thermal treatment. DSC curve gives information about Cp values and enthalpy changes in the system.

All new techniques were applied in the study of new soil conditioners, produced on the base of chicken litter and wood ash. The results are given in fig. 6-8 and the organic elements content in weight % is as follows: 42.002%C, 1.7006%N and 6.341%H.

CONCLUSIONS

From the investigations made it was found that the new techniques operate with very high sensitivity and accuracy and it is suitable for a number of research studies in the future.

Acknowledgement

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2009.

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MADE IN BULGARIA WITH EUROPEAN SUPPORT

NEW NANO-COMPOSITE COATINGS FOR CORROSION PROTECTION

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Abstract

The aim of the present work is to synthesize, deposit, investigate, (structure, properties and performance) and to accomplish a total validation in terms of technology and application of new nano-composite coatings for corrosion protection, covering EU directives. New additional functions, as self-healing and/or selective absorption ability to electromagnetic radiation (sun light) into the respective important bands of the optical (UV-, Vis- and IR) region are also expected. To analyze the patents state-of-art and to present an expert analysis for innovations aspects and market needs.

Experiments carried out are focused on preliminary surface treatment of the substrates, sol-gel synthesis, application of different Ce(III)- and Ce (IV)-salts inhibitors, structural (OM, AFM, SEM, EDX, XPS and PAS) and electrochemical (LSV, EIS) studies of these new nano-composite coatings for corrosion protection. On the base of the results obtained adequate conclusions are presented.

INTRODUCTION

According to the statistical data up to 1995, annual economic losses from corrosion reach almost \$350 million. Annual losses in European Union (EU), caused by corrosion, enhanced €100 million. Giving the higher degree of relevance to

the topic for corrosion protection during the FP6, EC funded two large integrated projects MULTIPROTECT and MUST [1, 2]. LAMAR, as a part of UCTM, was an effective partner in MULTIPROTECT with coordinator- Leibniz Institute for New Materials, Saarbrücken, Germany. The basic idea for these advanced projects was to develop an innovative technology for corrosion protection via nano-structural coatings with new effects, definite structure and properties aiming at a vanguard practical use, generally in transport and aerospace. It is necessary to underline, that there is a big blank space in our knowledge, for example, how the nano-powdered materials can be introduced in a polymeric or inorganic matrix in such a way as to avoid their destruction or not to change their new function. This fact, in parallel with MULTIPROTECT, initiates a new project development [3].

It is not known how the nano-materials can be effectively used against a number of corrosive and deformation processes, processes of aging or fatigue, etc., in parallel with existence of new effects, such as self-healing, self-assembling, self-strengthening or other effects that are not inherent in traditional materials and coatings. Undoubtedly, the study of this new class of nano-structural multi-material systems is a challenge for scientists referring high-tech industrial applications in the future. In short, there

are three innovative technologies for preparation of protective coatings based on nano-composites, namely: (1) Hybrid nano-composite coatings containing an inhibitor [4]; (2) Coatings with self-healing effect [5] and (3) Coatings, containing microcapsules [6]. These three technologies are very broad from a scientific and industrial point of view and have been an object of intensive RTD activities, in different aspects of the above integrated projects with European dimension.

It is necessary to underline, that the use of chromates and compounds of other heavy metals in EU has been banned since 2007 under a directive: "End of Live Vehicles"(ELV), preceded in 2004 and 2002 by the Directive "Restriction of Hazardous Substances"(RoHS), concerned for electrical and electronic industries [7, 8]. The main legislative rules (EU Directives) regarding the coatings relate not only to Cr (VI) compounds and Cr-plating technology [9]. Much of the atmospheric pollution is due to the volatile organic compounds (VOCs). In this aspect we mark the project funded by the EC, where UCTM-LAMAR has been an active partner [10] as well.

The aim of the present work is to synthesize, deposit, investigate (structure, properties and performance) and to accomplish a total validation in terms of technology and application of new nanocomposite coatings for corrosion protection, covering EU directives. New additional functions, such as self-healing and/or selective absorption ability to electromagnetic radiation (sun- light) in the respective important bands of the optical (UV-, Vis- and IR) region are highly appreciated. In addition, we had the aim to analyze the patents state-of-the-art and to perform an expert analysis of innovation aspects and market needs.

INNOVATION ASPECTS AND MOTIVATION

The innovative idea concerns effective corrosion protection in combination with additional features of the coatings. It can be treated as borrowed from the biological matter that is currently not typical for inorganic and organic/inorganic and inorganic/organic hybrid matter. In order to improve operational properties, (e.g. in terms of corrosion protection) and impart to

other desirable features (eventually self-restoration, selective absorption, color, etc.), it provides some suitable nanoparticles with or without inhibitors, added in the composition, which together with high corrosion protection have the effect of self-restoration and other desired by us properties for multifunctional use. For example, only the new concept of corrosion protection is based on three key motivation aspects: (i) to obtain the thermodynamic stable interphase boundary between the protective coating (primer) and metal, which is important for adhesion and mechanical stability of the coatings; (ii) to evaluate the impact of surface quality and surface modification of chemical immobilization or tie it on the surface of the metal substrate (alloy AA2024) and (iii) to study the effect of nanoparticles actions by PAS method.

Hybrid nano-composite coatings may be produced by reinforcement of the main polymer sol-gel matrix with nano-particles. Sol-gel route is a cheaper and industrial attractive technology. Nano-particles should have a diameter less than 30 nm, since otherwise the corresponding suspensions are unstable. It is known [11, 12] that nano-particles lead to a further improvement of the barrier properties, due to low tendency to cracking of the composites.

Yasakau et al. [5] have classified hybrid nanocomposite coatings into three groups, depending on the relationship between the organic and the inorganic part of them. Namely, (a) without chemical bonds between the organic and inorganic part (b) with the presence of chemical bonds between the organic and inorganic components and (c) available chemical bonds between the inorganic part and some non-polymerized organic sections. They combine properties for which these organic polymers and ceramics used are indicative. Thus, the organic component imparts flexibility, density, and organic functional compatibility, for example, with polyurethane paint. The inorganic part of the hybrid coating gives mechanical and heat resistance and improved adhesion to metal substrate. Following these self-complementary effects hybrid materials exhibit improved behavior as protective coatings and a really high level of motivation exists.

Patents status

It is known that the patents issue activities have direct influence on the innovation status. In this context the patent state-of-art of the problem discussed was studied for the period from 2003 to 2012. The following procedure was selected as a searching methodology in the respective four thematic groups: (1) Patents for corrosion protection inhibitors, including rare and cerium; (2) Patents for nano-composite coatings for corrosion protection; (3) Patents about coating having self-healing effect and (4) Patents for corrosion resistance and protection. It was done via the respective websites to access to the relevant patent database. In short, in the four fields marked above we found 22 patents. For 2003 it was established that no issued patents are registered.

After a classification of the patents in the above 4 thematic subgroups the following distribution exists: (1) regarding corrosion inhibition - 10 patents, and in group (4) anticorrosion stability – 6 patents are found, respectively. Two patents about nano-particles are registered in (2) group, and 4 patents have a self-healing effect, i.e. group (3) after classification. This indicates that there exists a gap in the innovative ideas and we may expect progress in the future.

EXPERIMENT AND DISCUSSION

Experimental conditions, selection and synthesis

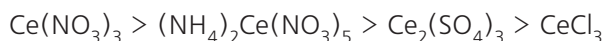
On the base of a wide range of available and tested aluminum alloys, the most important from industrial point of view is the aluminum alloy AA2024. We would only like to mention that the main components of the alloy are Al, Cu, and Mg. Nevertheless, the alloy was subjected to chemical analysis by ICP- OES spectroscopy. Its composition in wt.% is: Cu - 3.716, Fe - 0.404, Mg - 1.259, Mn - 0.537, Ni - 0.055, and Si <0.01; Al - residue to 100 wt.%. According to the East European standards this alloy is classified as a motorway D16 alloy.

The following main studies stages (A, B, C) have been selected as effective. Namely, (A)- study the effects of preconditioning on corrosion behaviour and the behaviour of cerium salts as corrosion inhibitors; (B)- Synthesis and characterization of hybrid composite coatings, and

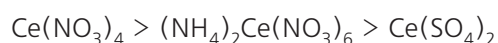
(C)- study of hybrid-nano-composite coatings. After surface pre-treatment of the samples by skimming, mechanical and chemical processing, they were tested by two model corrosion media: 3.5% NaCl and 0.01M NaCl solution, respectively. The following Ce(III) salts: $\text{Ce}(\text{NO}_3)_3$, $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_5$, $\text{Ce}_2(\text{SO}_4)_3$, CeCl_3 and Ce(IV) salts: $\text{Ce}(\text{NO}_3)_4$, $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, $\text{Ce}(\text{SO}_4)_2$, were used as inhibitors. As a method of deposition the sol-gel route was applied, which has a number of advantages. Syntheses of coatings were carried out with different variations of one basic procedure - to explore various conditions on the properties of the coatings.

The research, technological and development (RTD) aspects involved in the present project are multidisciplinary in conception. Multi- and interdisciplinary character of the work covers a well balanced approach between fundamental study and applied research. Since the compositions and experiments are too broad, in the present short report it is not possible to discuss the obtained results in detail. There are only selected compositions and some experiments as illustrations of the work in progress.

In short, in stage A the influence of preconditioning treatment on the corrosion behaviour was investigated as a function of selected Ce salts. Different kinds of inhibitors were an object of precise study and report [13]. On the base of OMM, SEM and EDX experiments carried out it was established that the inhibition effect of Ce (III) salts is in the order, as follows:



Regarding the inhibition effect of Ce (IV) salts used it was established that they can be arranged in the order as follows:



After correlation of the results obtained for both families of Ce(III)- and Ce(IV)-salts it was established that Ce(IV)-salts possess a lower level of inhibition in comparison to that of the Ce(III)-salts.

The next two stages (B and C) of research are focused on synthesis and characterization of

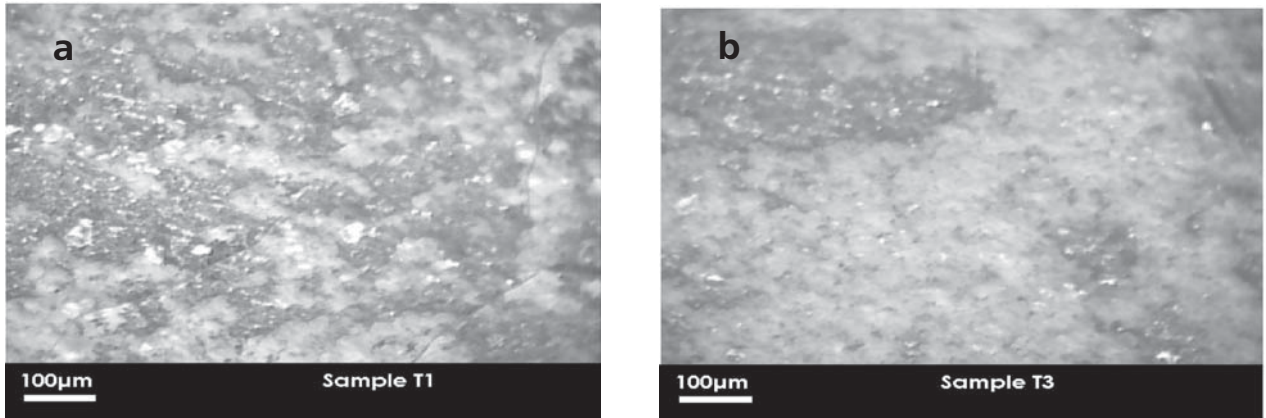


Fig. 1. Optical microscope surface morphology of samples T1(a) and T3(b)

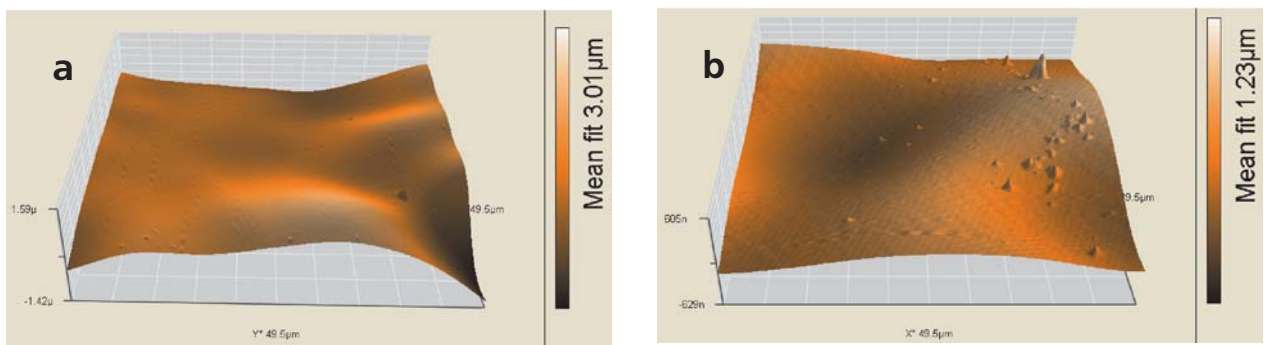


Fig. 2. AFM 3D images of the surface morphology of samples N6(a) and N3Ce4(b)

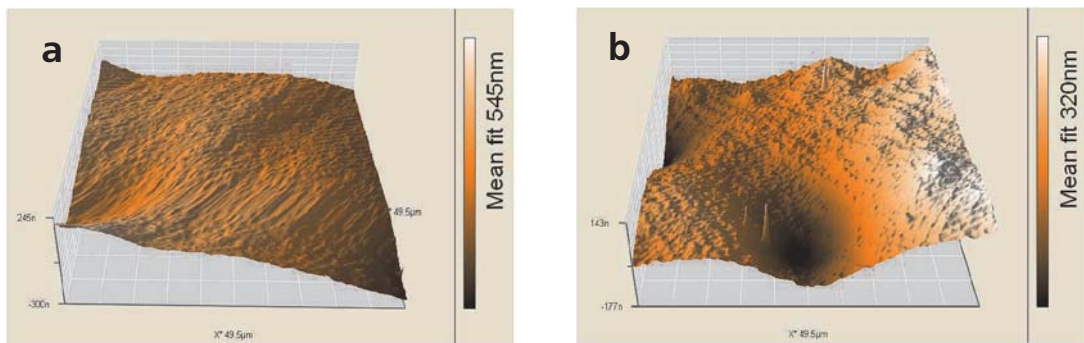


Fig. 3. AFM 3D images of the surface morphology of samples A6 , (a)- outside and (b)- inside the area of electrochemical test

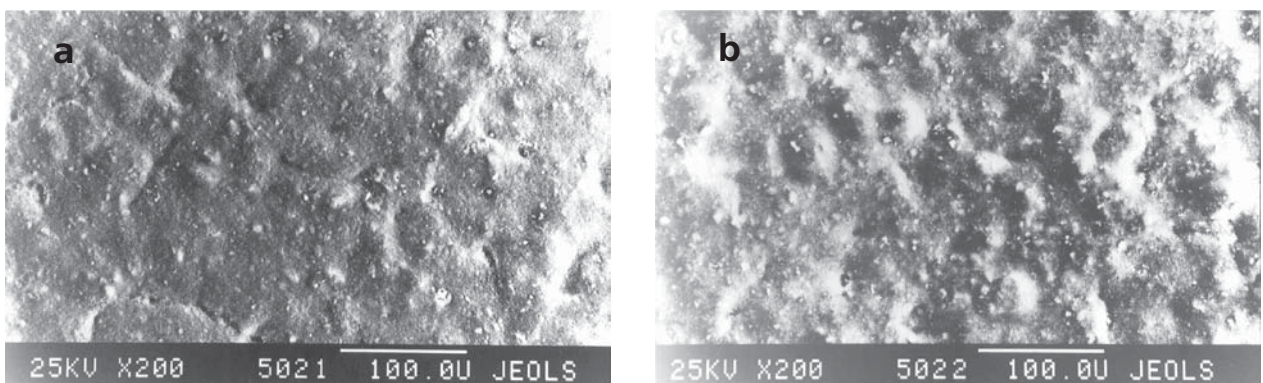


Fig. 4. SEM surface picture of samples F9, (a)- outside and (b)- inside the area of electrochemical test

hybrid composite coatings and hybrid nanocomposite coatings, respectively. After synthesis and sol-gel coating deposition, the samples obtained were an object of morphological studies by OMM, AFM and SEM- EDX analyses. Fig. 1 shows an OMM surface view of hybrid composite coatings with index T1 and T3. It is obvious that on the surface TiO_2 white agglomerates are distributed.

AFM study of the samples shows that after deposition process the coatings surface topology does not follow the substrate topology. The coating surface is relatively smoother than that of the metal substrate. The addition of cerium compounds to the sol-gel systems during the hybrid matrix synthesis does not lead to significant changes in the surface morphology of the coatings. This is well illustrated in Fig. 2 (b) for CeIV-coating with index N3Ce4.

Electrochemical corrosion tests were accomplished for all of the samples. After electrochemical tests, AFM studies were executed in order to check the difference of the surface morphology inside and outside the area of electrochemical treatment. Fig. 3 shows 3D surface morphology of electrochemical non-treated and treated zones, respectively.

Complex SEM and EDX analysis was per-

formed, as well. Fig. 4 shows SEM- correlation of the surface outside and inside the area of electrochemical experiment. EDX chemical analysis of the composition in details of the coatings was executed, too. As an object of analysis were Al, Si, Cl and Ce elements, in both treated surface areas (outside and inside) of the electrochemical tests. Fig.5 shows a correlation of the Ce content in untreated and treated zones of selected samples, respectively.

Precise electrochemical research (Linear Sweep Voltammetry-LSV and Impedance Spectroscopy- EIS) was accomplished on the protective coatings. In fact, these experiments give us the most detailed information and analysis on the corrosion behavior of inhibitors, hybrid- and nano-composite coatings. The measurements were executed in three aspects: polarization measurements (cathode and anode polarization curves), impedance spectroscopy studies (Bode and Nyquist graphs) and electrochemical impedance modeling. The measurements were performed as a function of the Ce-valence state in the inhibitors used and the time of treatment. pH value and temperature treatment were under control, as well. A correlation analysis was done regarding the effective inhibition behaviour of Ce(III)- and Ce(IV)- salts, as an object of the investigation. As an illustration Fig. 6 shows the change in resistance in the pores of the

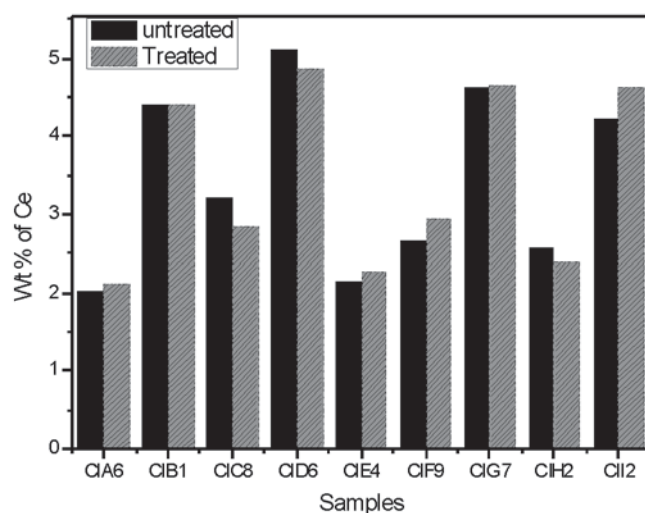


Fig. 5. EDX histograms after analysis of Ce elements in correlation of both treated and untreated surfaces for the investigated samples

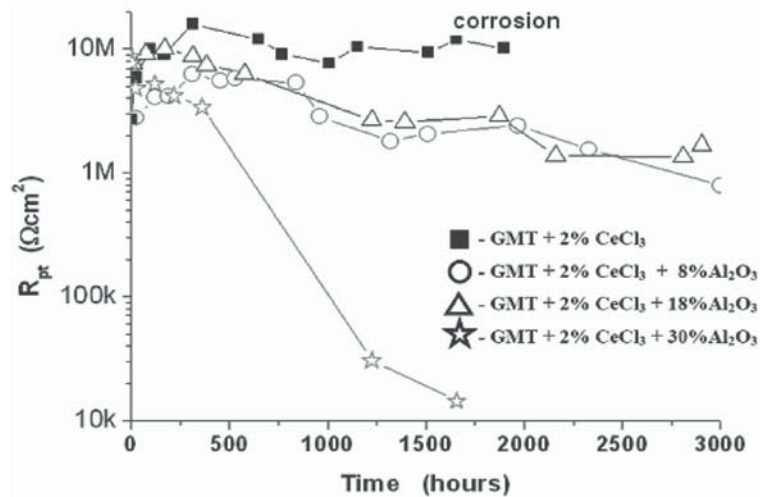


Fig. 6. Influence of the resistance (R_{pt}) values in the pores of the coating-primers with 2% $CeCl_3$ and different content of the nano-particles

coating- R_{pt} (a value characterizing the barrier properties of the coating) for the sample primers, containing the same quantity of $CeCl_3$ inhibitor (2%), but with different quantities impregnated Al_2O_3 nano-particles (0, 8, 18 and 30%), respectively.

From the electrochemical experiments carried out the following conclusions can be drawn: (i)- The primers containing direct inhibitor in the sol-gel matrix (without incorporation of nano-particles), show the highest R_{pt} values, but the sample-primers are unstable during a long exposure into the corrosion media; (2)- Corrosive ulcers regions on primer occur much earlier, when the inhibitor content in the matrix is higher. For sample I2, (4% $CeCl_3$ directly imported into the matrix), pitting occurs after about 1500h. of exposure, in comparison to sample index H2 (2% $CeCl_3$), where pitting is not observed even after 2000h. treatment procedure into corrosion media. Recently, part of the electrochemical results obtained is published in ref. [14-16].

Parallel to the electrochemical experiments a structural study was carried out. The attention was focused on an adequate micro- nano- and sub-nano level analyses and their interpretation. Namely, the structural study of the samples was performed by OMMs (surface optical micro analysis, low resolutions), by SEM (microanalysis), by AFM and EDX analysis (nano- and micro-2D- and 3D-analysis). For the subnano level X-ray photoelectron spectroscopy (XPS) and Posi-

tron- Annihilation Spectroscopy (PAS) methods were applied successfully.

After a process of deconvolution, the XPS spectra show that the deposits analyzed formed a mixture of Ce(III) and Ce(IV) ions on the surface, when Ce (III)- containing inhibitors are used. Well resolved XPS peaks were checked (marked v , v^{III} and u , u^{III}) that correspond to the $3d_{5/2}$ and $3d_{3/2}$ electronic states, due to Ce(IV)-ions contribution. Another peaks were detected from the contribution from Ce (III) ions, namely of $3d_{5/2}$ and $3d_{3/2}$ Ce (III)-electron states detection. For Ce (IV)- inhibitors used XPS spectra show that on the sample surface only a Ce(III)-oxidation product is detected. Therefore, they form precipitates in the case of Ce (III) salts and are more stable in comparison to those, formed in the case of Ce (IV) salts. It was established that formation or non-forming of Ce(IV)- oxidation product during the corrosion inhibition process is going on and it strongly depends of the pH- value of the solution used.

The aim of PAS analysis was to examine the electronic and defect structure in the selected hybrid nano-composite coatings and to get information on super fine, sub-nano level. By the positron spectroscopy method we can measure extremely small defects and voids in the film, which is important for the next exploitation period of the coatings. Very useful information can be received regarding the nano-porosity level of Al_2O_3 nano-particles, used before and after Ce (III) and Ce(IV)- inhibitor impregnation process.

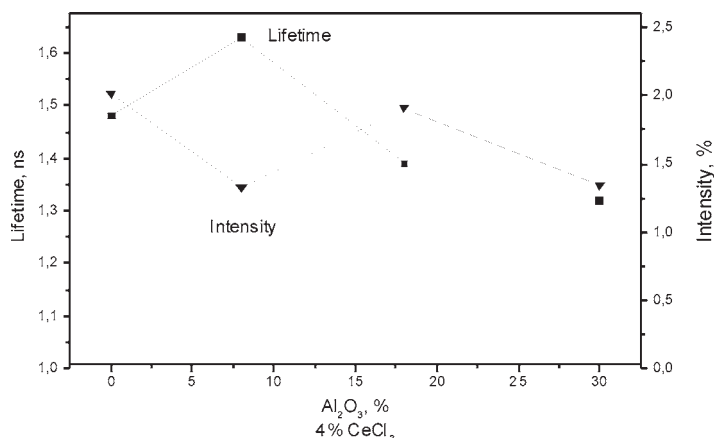


Fig. 7. Correlation between ortho-positronium lifetime and corresponding intensity of 4% Ce(III)-salt, impregnated into Al₂O₃ nano-particles

As outcome information it will be useful for the efficient storage of corrosion inhibitors inside the film.

The PAS experimental data were an object of processing with the program LT9. This was applied mainly to the annihilation process of positrons in the interatomic spaces with lower electron density. When the spectra were an object of processing for four components it was found that the fourth component of the long lifetime of positrons in the model does not exist and therefore there is no information about them.

It was established that by increasing the percentage of alumina, ortho-positronium lifetime of positrons decreases i.e. a reduction of the amount of free volume can be accepted. When the concentration of the inhibitor in the samples increases, as for sample with 4% CeCl₃ (see Fig. 7), dependence of the amount of free volume on the concentration of alumina decreases. In both cases the inflection occurs at about 15% Al₂O₃-nanoparticles, judging of the curves behavior. This concentration can be considered as an optimal one.

CONCLUSIONS

On the base of the experiments carried out the following conclusions can be extracted:

1. Preliminary surface treatment of the samples has a great impact both on their behavior in corrosive environments and on their operating characteristics.

2. Experiments carried out in details, covering preliminary surface treatment of the substrates, sol-gel synthesis, application of Ce(III)-

and Ce (IV)-salts inhibitors, structural and electrochemical tests served us to evaluate both scientific and industrial contribution. An assessment is accomplished for the future practical application of the studied nano-composite coatings for corrosion protection. It is appropriate to seek innovative and more effective inhibitors based on Ce (III) ions, but with different anionic components.

3. It was established that the studied hybrid coatings with 8% Al₂O₃ porous nano-particles and 2% CeCl₃ inhibitor possess a high protective effect and remarkable corrosion resistance in 0,05 M NaCl solution treatment. Coatings are stable in the corrosion medium more than 4500 hours treatment without any visible signs of corrosion.

4. The adverse effects of the high content of nano-particles on the R_{pt} value are offset by the positive effect of the nano-particles. According to PAS data we can accept that up to 15% Al₂O₃ nano-particles are the optimal concentrations for introduction into sol-gel coatings. It was established that indirect inhibitor introduction into the sol-gel matrix via impregnation of nano-particles into nano-porous Al₂O₃ carriers stimulates the lowering of the R_{pt} values. Eventually this is due to the easier penetration of the electrolyte through the porous aggregates, thus creating paths that are more conductive.

5. On the base of the electrochemical measurements it is established that pitting was observed over intermetallic inclusions, which are not well covered by the oxide film. These intermetallic inclusions are described as cathodic

sites.

6. According to AFM study it is established that at the presence of nano-particles higher concentrations of inhibitors reduce the roughness of the coatings. When the nano-particles are absent, the opposite effect was observed i.e. increasing the roughness of the coatings.

7. XPS study confirmed that corrosion deposits on the surface are a form from a mixture of Ce^{3+} and Ce^{4+} deposited products when Ce (III) ions are used for the inhibition of the alloy.

8. PAS measurements of nano-composite coatings show that about 80% of the positrons are directed to the porous nano-particles of aluminum oxide and only about 1% to $CeCl_3$. It was established that the micropores in depth do not change significantly. This result indicates that the homogeneity of the layers in depth exists. It is also found that with increasing of the $CeCl_3$ concentration a reduction effect of the pore size is established. This is a logical consequence, since the inhibitor, in this case $CeCl_3$, is impregnated into the Al_2O_3 nano-particles.

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**НОВИ НАНОКОМПОЗИТНИ ПОКРИТИЯ ЗА
КОРОЗИОННА ЗАЩИТА**

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Резюме

Целта на настоящата разработка е да се синтезират, отложат и изследват (структура, свойства и характеристики), както и да се направи

технологична оценка относно приложението на нови нанокomпозитни покрития за корозионна защита, съгласно директивите на ЕС. Очаква се също наличието на нови допълнителни функции като самовъзстановяване и/или селективна абсорбция по отношение на електромагнитно лъчение (слънчевата светлина) в съответните области (UV-Vis, IR) на оптичния диапазон. Анализира се съвременното патентно състояние и се представя експертен анализ за иновационните аспекти и нуждите на пазара.

Проведените експерименти са фокусирани върху предварителната повърхностна обработка на подложките, зол-гелен синтез, прилагане на различни Ce (III)- и Ce (IV) соли като инхибитори, структурни (ОМ, АСМ, СЕМ, ЕДА, РФС и ПАС) и електрохимични (ЛВА, ЕИС) изследвания върху тези нови нанокomпозитни покрития за корозионна защита. На базата на получените резултати са представени адекватни заключения.

VARROA CONTROL IN THE REPUBLIC OF BULGARIA

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INTRODUCTION

In Bulgaria, Varroa destructor was first detected in 1967-1968, in bee families with queen bees imported from the USSR, and varroasis was officially registered as a disease in 1971 (Kanchev, 1986).

Destruction of Varroa is a very difficult and complicated task and its fulfillment has required the creation of a program designed for prevention and bee pest extermination; this program has been included in veterinary services' normative documents. The program comprises schemes proposing continual (throughout the year) extermination of the Varroa through a combination of different fight methods and efficient organization of their realization.

A spring (March-April) and autumn (basic) treatment is performed, using chemical agents (in the beginning of August - after the removal of goods from the shops) and applying mechanic-biological methods (during the receiving of goods).

Acaricides from different chemical groups

(flumetrin, fluvalinat, amitraz, coumaphos, etc.) are applied, showing different levels of effectiveness. (Gurgulova, K. et al., 2006).

The natural-climatic conditions and the technology of bee keeping in the Republic of Bulgaria allow successful use of alternative control methods against varroosis as well (Gurgulova, K. et al, 2004).

The aim of the present work is to perform a comparative examination of the acaricide effectiveness of the preparations Varostop (3.6 mg flumetrin per strip) and Ecostop (5.0 g thymol and 2.0 ml mint oil per plate), products of «Primavet-Sofia» Ltd, Sofia, developed for Varroa control in a spring treatment in the conditions of the Republic of Bulgaria.

MATERIALS AND METHODS

The investigations were carried out on 30 bee colonies at a test apiary in the region of the city of Stara Zagora. The bee colonies were treated with Ecostop /active substance containing 5.0 g of thymol and 2.0 ml of mint oil per plate/, that was offered as solid aerosol with prolonged re-

lease of active substances and Varostop - strips (3,6 mg flumetrin strip).

Control and trial groups were set up. In the trial group Ecostop was applied according to the manufacturer's instructions, and the results obtained were compared to the results obtained from a trial group that was treated with Varostop, as well as to the results obtained from a control group that remained untreated. Observations looking for manifestations of adverse side effects of Ecostop and Varostop upon the bee colonies, such as death among the queen-bees, bees, and brood, as well as "robberies", have been carried out.

The treatment was conducted in the following way:

Group I: 10 bee colonies with strength of 1,72+0,04 kg were treated with 2 plates of Ecostop for 45 days.

Group II: 10 bee colonies with strength of 1,82+0,05 kg were treated with 2 strips of Varostop (3.6 mg of flumetrin in a single strip) for

45 days.

Group III: 10 bee colonies with strength of 1,77+0,06 kg remained untreated.

The changes in the numbers of the mites fallen were determined within the trial groups on the 7th, 14th, 21st, 28th, 35th, 42nd, and 45th days.

In order to obtain a more comprehensive and complex evaluation of the effectiveness of Ecostop and Varostop the EI /Extensinvasion/ of trials and control groups before and after the treatment was determined.

The acaricidal activity of the preparation was established via control treatment of the trial and control groups with Varrostat - R /Rodovarr/ by determination of the number of the mites fallen. The preparation contained Amitraz 12,5%, and was applied on the 45-th day for all Groups -1, II, and III respectively.

The results represented undergone variation - statistical work-up via the routine methods with the help of a computer program.

RESULTS

Table 1. Condition of Bee Colonies

Groups	Beginning - April 21st				End - June 5th			
	Strength - kg		Brood- number of cells		Strength - kg		Brood- number of cells	
	x ± Sx	C	x ± Sx	C	x ± Sx	C	x ± Sx	C
Group I (2 plates of Ecostop)**	1.72 ± 0.04	8,23	8310±514.34	19.57	2.32 ± 0.07	10.20	10620±729.96	21.74
Group II (2 strips of Varostop)**	1.82 ± 0.05	9.25	7650±308.13	12.74	2.42 ± 0.05	6.96	10760±474.50	13.94
Group III(K) (untreated)**	1.77 ± 0.06	10.39	8860±453.19	16.17	2.60 ± 0.07	8.11	12080±509.86	13.35
Reliability			III-K (P < 0.05)				I-K (P < 0.05)	

Table 2. Extensinvasion among Bee Colonies

Signs	Groups		
	1-2 plates of Ecostop	II - 2 strips of Varostop	III(K) untreated
	x ± Sx	x ± Sx	x ± Sx
1. Extensinvasion among bees - Beginning (April 21st) % - End (June 5th) %	4.98 ± 1.40 0.90 ± 0.11	1.47 ± 0.14 0.80 ± 0.56	1.59 ± 0.18 5.94 ± 1.42
Reliability Beginning End	I - II (P≤0.05) II - III (K) (P≤0.001) I - III (K) (P≤0.05) I - III (K) (P≤0.01)		
2. Extensinvasion among brood - Beginning (April 21st) % - End (June 5th) %	46.80 ± 1.17 2.80 ± 0.90	10.00±2.00 0.00 ± 0.00	11.20±2.21 14.40±1.43
Reliability Beginning End	I - III (K) (P≤0.001) II - III (K) (P≤0.001)		

After the plates had stayed in the beehives for 45 days, the EI of the mite in the trial group (I) that was treated with two plates of Ecostop was $0.90 \pm 0.11\%$ among bees and $2.80 \pm 0.90\%$ among larvae.

The group that was treated with Varrostop (II) showed the lowest EI rate - $0.80 \pm 0.56\%$ among bees and $0.00 \pm 0.00\%$ among brood.

In the control (untreated) group (III) EI rate was increased from $1.59 \pm 0.18\%$ to $5.94 \pm 1.42\%$ among bees and from $11.20 \pm 2.21\%$ to $14.40 \pm 1.43\%$ among larvae $/p \leq 0.001/$.

This was due to the breeding of the mite and pointed out that the parasite was still found in a higher percentage within the sealed brood-cells.

When monitoring the number of the mites fallen the following data were obtained in the trial groups.

In Group I /treatment with Ecostop lasted for 45 days/ 820.2 ± 216.32 mites have fallen.

In the group II that was treated with Varrostop 311.7 ± 68.52 mites have fallen.

The number of mites fallen after the control treatment in the trial groups was 62.60 ± 8.95 in

the I group (that was treated with 2 plates of Ecostop for 45 days) respectively $/p \leq 0.001/$. In the II group (that was treated with Varrostop) 1.3 ± 0.27 mites fell and in the control group III (that remained untreated), a reliably greater amount of mites fell, i.e. 259.89 ± 33.45 mites in comparison with Group I and II $-p \leq 0.001$ (Fig. 1).

The established effectiveness of Ecostop manifested (Fig. 2) that the preparation possessed a relatively high acaricidal activity during spring treatment with 2 plates for 45 days of colonies with strength of $1.72 \pm 0.04 - 90.59 \pm 1.83\%$.

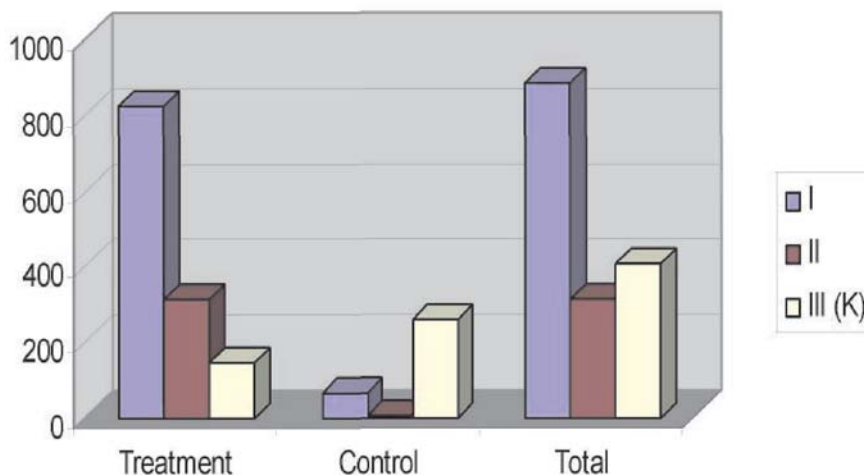
In the II group (that was treated with Varrostop) very high acaricidal effect was established $-99.15 \pm 0.39\%$.

DISCUSSION

The new requirements for production of pure bee products, including honey, direct the investigators to test acaricidal agents based on natural substances.

The effectiveness of Ecostop ($90.59 \pm 1.83\%$)

Mites fallen due to the Treatment with Ecostop and Varrostop (number)



Groups	Treatment	Control treatment	Total
I	820.2	62.6	882.8
II	311.7	1.3	313
III (K)	142.6	259.89	406.11

Fig. 1.

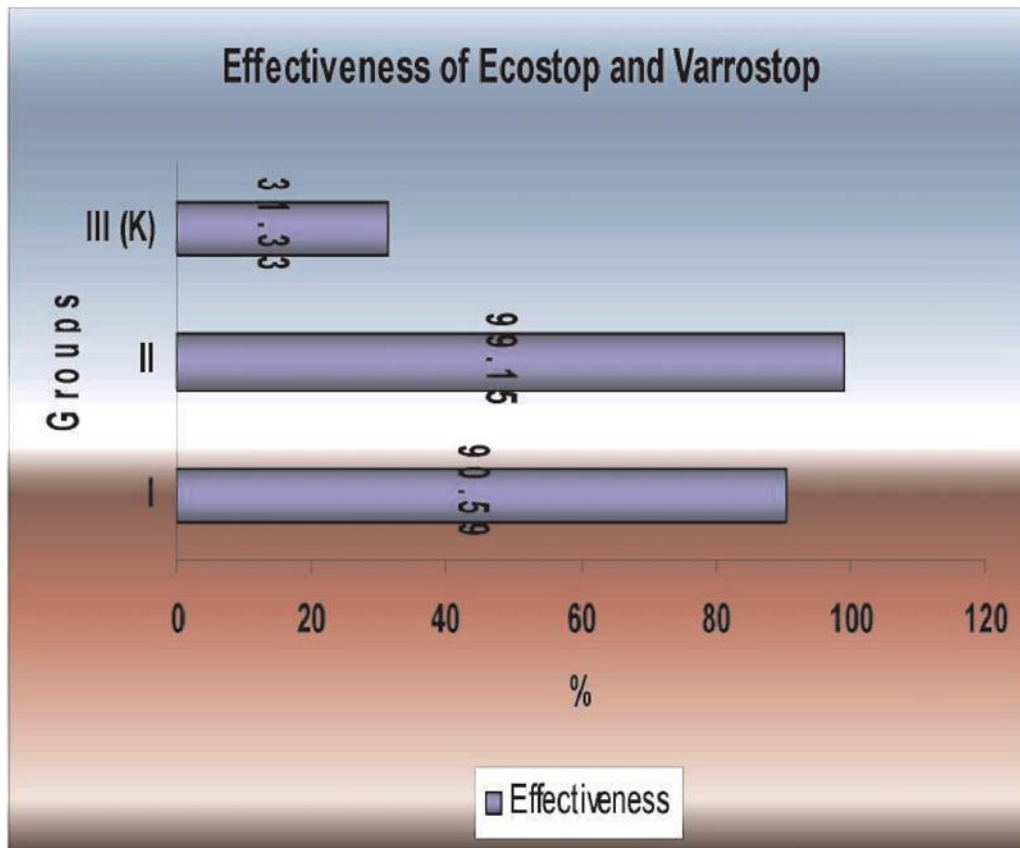


Fig. 2.

that was observed confirmed our statement that the treatment should continue for 45 days in order to eliminate a sufficient percentage of the mites so they could not cause harm to bee colonies.

These results confirm the data of other authors who got 95-98% effectiveness during treatment with Api-Life-Var (Abou-Zaid et al. 1993; Imdorf et al. 1994, 1995; Moosbeckhofer 1993).

The observation showed that Ecostop did not have any adverse side effects upon the bee colonies, such as death of queens, bees and brood, and no robberies were observed during the treatment.

The results obtained by us provide good reasons to consider this preparation as a suitable means for control of Varroa under the conditions in the Republic of Bulgaria, due to its proven effectiveness when applied during fall and spring treatments. **Ecostop** will supplement the limited spectrum of preparations for fighting against varroa at apiaries with organic apiculture and it will provide the apiarists the opportunity to produce bee honey without remnants of

chemically based acaricidal agents that are harmful to humans.

The good acaricidal effect in the group that was treated with Varostop ($99.15 \pm 0.39\%$) proved that in the Republic of Bulgaria no resistance to flumethrin has been created yet.

CONCLUSION

- Ecostop manifested its effect ($90.59 \pm 1.83\%$) against Varroa in a dose of 2 plates to colonies with strength of 1.72 ± 0.04 kg and parasite infestation rate of $4.98 \pm 1.40\%$ among the bees and $46.80 \pm 21.17\%$ among the brood.
- Varostop in a dose of 2 strips applied in colonies with strength 1.82 ± 0.05 kg manifested $99.15 \pm 0.39\%$ effectiveness. No resistance to flumethrin has been created in Bulgaria yet.
- By means of utilizing highly effective substances which are synthetic pyrethroids (flumethrin) and thymol combined with menthol oil, successful prophylaxis and treatment of varroosis in Bulgaria was achieved.

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Vice-head of the Department, leader of research projects in the field of New Materials and Nanotechnologies, New porous nanocomposites for electrode materials. Author of 4 books in Material Science in Microelectronics, 1 monographic

book in Nanomaterials, author and co-author of more than 100 research papers published in International and Bulgarian scientific journals, and 1 BG Patent.

Ivania Markova-Deneva was born in 1948 in Teteven. She is a professor in Material Science at the University of Chemical Technology and Metallurgy (UCTM), Sofia, Department of Metallurgy of non-Ferrous Metals and Semiconductor Technologies. She graduated from UCTM in 1971 and received her MSc degree in the Faculty of Inorganic Chemistry at the same University. In 1976 she defended her PhD thesis at UCTM in the area of transparent conductive SnO₂ thin films. From 1976 till 1989 she was scientific researcher in the Research sector at UCTM-Sofia, partnership in the elaboration of more than 40 contract topics, 4 technologies realized in the industry and 3 author's certificates; from 1989 till 2011 she is a lecturer (associate professor) at UCTM-Sofia; tutor of more than 50 diploma

works, 15 students scientific works, 5 training specialists, 3 Bulgarian PhD students, 3 AUF cotutell PhD students, supervisor of 1 specialist related to the World Federation of Scientists Planetary Emergency "Medicine and Biotechnology" (Geneva, Switzerland), and 1 specialist from the Tashkent University (Uzbekistan) in the frame of Erasmus Programme. In 2011 she became full professor based on her monographic book.

Scientific interests: in the area of semiconductor materials and thin films for microelectronics (transparent SnO₂, ferromagnetic Fe-Ni-P, wear resistant TiC and TiN), synthesis and IR spectroscopy investigations of metallic nanomaterials (nanoparticles and nanowires) obtained through a borohydride chemical reduction method and nanocomposites bases on porous matrix (carbon foam) and intermetallic (Cu-Sn, Ni-Sn, Co-Sn) nanoparticles. She participated with oral presentations in more than 15 international conferences and congresses published as contributions in Proceedings.

Specializations: in Moscow University of Chemical Technology, Loughborough Technical University - UK, National Polytechnical Institute

in Toulouse - France, Institute of Materials in Nantes - France.

Prof. Ivania Markova-Deneva delivers lecture courses for bachelor and master degree students on Materials Science in Microelectronics, Deep Purification of Substances for Microelectronics, Membrane Technologies for deep Purification of Substances for Microelectronics, Chemistry and Physicochemistry of Semiconductor Materials, Magnetic Materials, Technologies for Electronic components, Chemistry of Solid State, Nanomaterials, IR spectroscopy as investigation method of nanomaterials.

From 2004 till 2008 prof. I. Markova-Deneva was a head of Department of Metallurgy of non-Ferrous Metals and Semiconductor Technologies – UCTM, and from 2008 till now she is vice-head of the same department. She is a member of the National Coordination Center on Nanotechnologies in Bulgaria, Chemists Union – Bulgaria, Faculty Council at Metallurgy and Materials Science Faculty – UCTM, Sofia, Scientific Councils of the Universities in Toulouse, Montpellier and Nantes – France.

Assoc. Prof. PENKA STEFANOVA-PEEVA, MD, PhD

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Head of the Department of Pediatric surgery - Medical University of Plovdiv. Author of more than 91 articles in scientific journals, textbooks, educational textbooks and monographs.

Assoc. Prof. Penka Stefanova was born in 1958 in Stara Zagora. After finishing English Language School in 1977, she graduates in medicine in 1983 from Higher Medical Institute, Plov-

div. The same year she becomes an assistant professor in the Department of Pediatric surgery, where she works at the moment. She defended successfully her PhD theses in 1995, acquiring DM. In 2008 she becomes an Assoc. professor and chief of the Department of Pediatric surgery.

Assoc. Prof. Stefanova specialized in many elite Pediatric surgical centers all over the world, such as Harvard Medical School, Children's Hospital of Philadelphia, Cornell Medical center – New York, Winston- Salem – USA, also in EU centers of Pediatric surgery. She is an active member of many scientific organizations. Assoc. Prof. Stefanova delivers lectures for bachelor

and master course students in General and Pediatric surgery in English.

Assoc. Prof. Stefanova has participated in scientific and educational projects financed by the European research fund, Tempus, Erasmus, Bulgarian Ministry of Education, Youth and Science, Medical University of Plovdiv and in many clinical investigations.

Her scientific interests are in the field of surgical treatment of congenital diseases, in congenital vascular disease, in pediatric oncology,

pediatric urology and pediatric abdominal surgery.

Assoc. Prof. Stefanova has published more than 91 articles in peer-reviewed journals and took part in writing of textbooks and monographs and in constructing of national guidelines in the field of Pediatric surgery. She has been cited in foreign and Bulgarian journals. At the moment she is a PhD advisor of three PhD students.

AWARDS

MINISTRY OF EDUCATION, YOUTH AND SCIENCE BESTOWED PYTHAGORAS AWARD TO BEST BULGARIAN SCIENTISTS

The fourth annual ceremony for handing the Pythagoras award for science took place in Sofia on June 26, 2012. The ceremony was hosted by Mr. Sergey Ignatov, Minister of education, youth and science.

Pythagoras awards for science have gained recognition as a prestigious annual event distinguishing best Bulgarian researchers. This year 16 researchers were nominated for the award in 7 categories. The winners were determined by a prestigious seven-member jury of outstanding representatives of the academic community.

As a host of the event Mr. Ignatov handed the **Grand Prize for successful manager of international projects**, Pythagoras statuette created by the Minister of Culture Vezhdi Rashidov, and 10 000 BGN prize money to **Prof. DSc Ovanes Mekenyan** from Laboratory of Mathematical Chemistry at Asen Zlatarov University – Burgas.

Grand Pythagoras Prize for young scientist and 10 000 BGN prize money were handed to **Assoc. Prof. PhD Ekaterina Borisova** from the Institute of Electronics at the Bulgarian Academy of Sciences (BAS) by Prof. Valeria Fol.

On behalf of the management of BAS prizes were awarded **for established scientist in the field of natural and mathematical sciences** to **Prof. DSc Nicolai Vitanov** from Faculty of Physics at Sofia University St. Kliment Ohridski, and **in the field of technical sciences** – to

Corresponding member Prof. DSc Chavdar Rumenin from the Institute of System Engineering and Robotics at BAS. The winners received crystal Pythagoras plaquettes and 5000 BGN prize money.

Prof. Vanyo Mitev, Chairman of the Board of Rectors, distinguished **Assoc. Prof. DSc Andrei Chorbanov** from the Institute of Microbiology at BAS in the category **“established researcher in the field of biomedical sciences”**.

The prize **for established researcher in the field of social and humanitarian sciences** was given to **Prof. DSc Dimitar Popov** from Faculty of History at Sofia University St. Kliment Ohridski. The prize was handed by the Minister of education, youth and science Mr. Sergey Ignatov.

Honors for a research team with implemented developments in business were awarded to **Assoc. Prof. DSc Dimitrina Yotova Ilchovska** from the Institute of Maize in the town of Knezha. Mrs. Ilchovska received her award from Mr. Ognyan Stoichkov, Chairman of the Commission on education, science and problems of children, youth and sports at the National Assembly.

Ministry of Education, Youth and Science, as an institution encouraging development of young talents, singled out graduate students from the National Musical Academy “Prof. Pancho Vladigerov” to perform music before selected audience at the Annual Pythagoras awards for science.

JOHN ATANASOFF AWARDS FOR THE YEAR 2012

President of the Republic of Bulgaria Mr. Rosen Plevneliev continues the tradition for the established in 2003 John Atanasoff award for significant achievements in the field of information and communication technologies. The award is established and named after a renowned scientist of Bulgarian descent John Atanasoff –

the creator of the first digital computer. Its aim is to encourage young Bulgarian researchers working in the field of informatics and communication technologies and to create a favorable and supportive environment for the development of young talents in these spheres, as well as to support the development of information and

communication technologies in Bulgaria.

This year President Rosen Plevneliev handed in one John Atanasoff Grand Award and four new honor certificates – for implementation of research achievements in practice, for projects with high social importance, and two certificates “John Atanasoff – for students and their teachers”. The recipients of the John Atanasoff awards were announced on October 04, 2012 – John Atanasoff’s 109-th birthday.

This year’s recipient of **John Atanasoff Grand Award** for fostering of young researchers’ personal achievements in the field of information technologies is **PhD Dimitar Zhechev**. Dimitar Zhechev works in the sphere of cryptography and information security and is a lecturer at a prestigious university in Switzerland. He got his PhD in mathematics from University of California, Berkeley, and his BA in mathematics from Harvard University.

He is co-author of two patents in the field of cryptography, laureate of numerous international prizes and grants, supervisor of PhD students and chief coordinator of one of the large projects under the VII Framework program of the European Commission in the field of informatics.

The award was handed personally by President Rosen Plevneliev. The head of state mentioned that there was an unprecedented compe-

tion among the candidates for the 2012 award, which made him optimistic about the future of the native science.

For the first time in the 10-year history of the John Atanasoff awards two awards are provided for students and their teachers. **Yordan Chaparov** from Mathematical High School Atanas Radev from the town of Yambol and **Dimitar Vuldzhev** from National High School of Mathematical and Natural Sciences in Sofia, together with their teaching teams, got from the head of state **“John Atanasoff – for students and their teachers” honor certificates** for their achievements in the field of information technologies and informatics.

Another new John Atanasoff category is connected **with implementation of research discoveries in practice and socially important projects**. **PhD Ivelina Stoyanova**, MSc in computer sciences and mathematics of University of Bath and PhD in the field of computer linguistics, as well as PhD Ivan Dimov, MSc in electrical engineering of Stanford University and PhD in applied biophysics, were distinguished in this area.

After closing of the awards ceremony young researchers hold the first meeting of the newly-established **John Atanasoff Award Winners Club**.

ARTICLES

RECENT PUBLICATIONS OF BULGARIAN SCIENTISTS

Title: **Environmetrics as a tool for sustainability assessment**
Authors: Simeonov, Vasil
Source: International Journal of Technology Management, Vol. 60, 1-2, Special Issue, (2012), 83-95
Author Affiliations: Sofia University "St. Kliment Ohridski", Fac. Chem., Dept. Analyt. Chem., 1164 Sofia, Bulgaria
ISSN: 0267-5730

Title: **Compact complex surfaces with geometric structures related to split quaternions**
Authors: Davidov, Johann^{2,3}, Grantcharov, Gueo¹, Mushkarov, Oleg², Yotov, Miroslav¹
Source: Nuclear Physics B, Vol. 865, 2, (11 Dec 2012), 330-352
Author Affiliations: ¹Florida Int. Univ., Dept. Math. & Stat., Miami, FL 33199 USA;
²Bulgarian Academy of Science, Inst. Math. & Informat., BU-1113 Sofia, Bulgaria;
³L. Karavelov Civil. Engn. Higher Sch., 1373 Sofia, Bulgaria.
ISSN: 0550-3213

Title: **Synthesis and In Vitro Study of the Anticancer Activity of New Analogs of Octreotide**
Authors: Staykova, S.¹, Naydenova, E.¹, Wesselinova, D.², Kalistratova, A.¹, Vezenkov, L.¹
Source: Protein and Peptide Letters, Vol. 19, 12, (Dec 2012), 1257-1262
Author Affiliations: ¹University of Chemical Technology and Metallurgy, Dept. Organ. Chem., 1756 Sofia, Bulgaria;
²Bulgarian Academy of Science, Inst. Expt. Morphol. Pathol. & Anthropol. Muzeum, BU-1113 Sofia, Bulgaria.
ISSN: 0929-8665

Title: **Tacrine-induced tachyphylaxis in gastric smooth muscles**
Authors: Prissadova, N. A.¹, Kristev, A. D.¹, Getova, D. P.², Argirova, M. D.³, Turiiski, V. I.¹, Ardasheva, R. I.¹
Source: Central European Journal of Biology, Vol. 7, 6, (Dec 2012), 1013-1020
Author Affiliations: ¹Medical University, Dept. Biophys., 4002 Plovdiv, Bulgaria;
²Medical University, Dept. Pharmacol. Clin. Pharmacol. & Drug. Toxicol., 4002 Plovdiv, Bulgaria;
³Medical University, Dept. Chem. & Biochem., 4002 Plovdiv, Bulgaria.
ISSN: 1895-104X

Title: **Surface tension of concentrated electrolyte solutions**
Authors: Slavchov, Radomir I., Novev, Javor K.
Source: Journal of Colloid and Interface Science, Vol. 387, (Dec 2012), 234-243
Author Affiliations: Sofia University "St. Kliment Ohridski", Dept. Phys. Chem., Sofia, Bulgaria
ISSN: 0021-9797

Title: Thermo-mechanical study of rapidly solidified amorphous alloys Al85Ni5Co2RE8
Authors: Stojanova, L.², Russew, K.², Fazakas, E.¹, Varga, L. K.¹
Source: Journal of Alloys and Compounds, Vol. 540, (5 Nov 2012), 192-197
Author Affiliations: ¹Wigner Res. Ctr. Phys. HAS, Inst. Solid State Phys. & Opt., H-1539 Budapest, Hungary;
²Bulgarian Academy of Science, Inst. Met. Sci. Acad. A. Balevski, 1574 Sofia, Bulgaria.
ISSN: 0925-8388

Title: Monte Carlo sensitivity analysis of an Eulerian large-scale air pollution model
Authors: Dimov, I., Georgieva, R., Ostromsky, Tz.
Source: Reliability Engineering & System Safety, Vol. 107, Special Issue, (Nov 2012), 23-28
Author Affiliations: Bulgarian Academy of Science, Dept. Parallel Algorithms, Inst. Informat. & Commun. Technol., BU-1113 Sofia, Bulgaria.
ISSN: 0951-8320

Title: On the column apparatuses modeling
Authors: Doichinova, M., Boyadjiev, Chr.
Source: International Journal of Heat and Mass Transfer, Vol. 55, 23-24, (Nov. 2012), 6705-6715
Author Affiliations: Bulgarian Academy of Science, Inst. Chem. Engn., 1113 Sofia, Bulgaria.
ISSN: 0017-9310

Title: Planetary wave coupling of the atmosphere-ionosphere system during the Northern winter of 2008/2009
Authors: Pancheva, D., Mukhtarov, P.
Source: Advances in Space Research, Vol. 50, 9, (1 Nov. 2012), 1189-1203
Author Affiliations: Bulgarian Academy of Science, Natl. Inst. Geophys. Geodesy & Geog., BU-1113 Sofia, Bulgaria
ISSN: 0273-1177

Title: The Importance of Rhamnolipid-Biosurfactant-Induced Changes in Bacterial Membrane Lipids of *Bacillus subtilis* for the Antimicrobial Activity of Thiosulfonates
Authors: Sotirova, A.¹, Avramova, T.¹, Stoitsova, S.¹, Lazarkevich, I.¹, Lubenets, V.², Karpenko, E.², Galabova, D.¹
Source: Current Microbiology, Vol. 65, 5, (Nov. 2012), 534-541
Author Affiliations: ¹Bulgarian Academy of Science, Stephan Angeloff Inst. Microbiol., BU-1113 Sofia, Bulgaria;
²Ukrainian Acad. Sci., Inst. Phys. Chem., Lvov, Ukraine.
ISSN: 0343-8651

Title: **Two Anderson impurities in a two-dimensional host with Rashba spin-orbit interaction**
Authors: Ivanov, T. I.
Source: Physical Review B, Vol. 86, 15, (16 Oct. 2012), Article Number: 155429
Author Affiliations: Sofia University "St. Kliment Ohridski", Dept. Phys., 1164 Sofia, Bulgaria.
ISSN: 1098-0121

Title: **Electromagnetic shock wave in nonlinear vacuum: exact solution**
Authors: Kovachev, L. M.¹, Georgieva, D. A.², Kovachev, K. L.¹
Source: Optics Letters, Vol. 37, 19, (1 Oct. 2012), 4047-4049
Author Affiliations: ¹Bulgarian Academy of Science, Inst. Elect., BU-1784 Sofia, Bulgaria; ²Technical University of Sofia, Fac. Appl. Math. & Comp. Sci., 1000 Sofia, Bulgaria.
ISSN: 0146-9592

Title: **Real-time GPS track simplification algorithm for outdoor navigation of visually impaired**
Authors: Ivanov, Rosen
Source: Journal of Network and Computer Applications, Vol. 35, 5, (Sep. 2012), 1559-1567
Author Affiliations: Technical University, Dept. Comp. Syst. & Technol. 5300 Gabrovo, Bulgaria.
ISSN: 1084-8045

Title: **Surface modification of polymeric ultrafiltration membranes I. Effect of atmospheric pressure barrier discharge in air onto some characteristics of polyacrylonitrile ultrafiltration membranes**
Authors: Petrov, S.¹, Atanasova, P.², Dineff, P.³, Vladkova, T.²
Source: High Energy Chemistry, Vol. 46, 4, (Jul. 2012), 283-291
Author Affiliations: ¹University Prof Dr. Asen Zlatarov, 8008 Burgas, Bulgaria; ²University of Chemical Technology and Metallurgy, BU-1756 Sofia, Bulgaria; ³Technical University of Sofia, 1756 Sofia, Bulgaria.
ISSN: 0018-1439

Title: **Third party application control on quality of service in IP based multimedia networks**
Authors: Pencheva, E., Atanasov, I.
Source: Information Systems Frontiers, Vol. 14, 3, (Jul. 2012), 555-569
Author Affiliations: Technical University of Sofia, Dept. Commun. Networks, Fac. Telecommun., 1000 Sofia, Bulgaria.
ISSN: 1387-3326

Title: **Antibacterial activity of SiO₂/hydroxypropyl cellulose hybrid materials containing silver nanoparticles**
Authors: Angelova, T.¹, Rangelova, N.², Yuryev, R.³, Georgieva, N.¹, Muller, R.³
Source: Materials Science & Engineering C-Materials for Biological Applications, Vol. 32, 5, (1 Jul. 2012), 1241-1246
Author Affiliations: ¹University of Chemical Technology and Metallurgy, Dept. Biotechnol., BU-1756 Sofia, Bulgaria;

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²University of Chemical Technology and Metallurgy, Dept. Fundamentals
Chem. Technol., BU-1756 Sofia, Bulgaria;
³Hamburg Univ. Technol., Inst. Tech. Biocatalysis, D-21071 Hamburg,
Germany.
ISSN: 0928-4931

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Title: **Periodic solutions of the non-integrable convective fluid equation**
Authors: Kamenov, Ognyan Y.
Source: Journal of Mathematical Physics, Vol. 53, 6, (Jun. 2012), Article
Number 063705
Author Affiliations: Technical University of Sofia, Dept. Appl. Math. & Informat.,
Sofia 1000, Bulgaria.
ISSN: 0022-2488

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Title: **A new model of cosmogenic production of radiocarbon C-14 in
the atmosphere**
Authors: Kovaltsov, G. A.², Mishev, A.^{1,3}, Usoskin, I. G.^{1,4}
Source: Earth and Planetary Science Letters, Vol. 337, (1 Jul. 2012), 114-120
Author Affiliations: ¹University Oulu, Sodankyla Geophys. Observ., Oulu Unit, Oulu, Finland;
²Ioffe Phys. Tech. Inst., St Petersburg, Russia;
³Bulgarian Academy of Science, Inst. Nucl. Res. & Nucl. Energy,
BU-1784 Sofia, Bulgaria;
⁴University Oulu, Dept. Phys. Sci., Oulu, Finland.
ISSN: 0012-821X

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Title: **Global Response of the Ionosphere to Atmospheric Tides Forced
from Below: Recent Progress Based on Satellite Measurements Global
Tidal Response of the Ionosphere**
Authors: Pancheva, D., Mukhtarov, P.
Source: Space Science Reviews, Vol. 168, 1-4, (Jun. 2012), 175-209
Author Affiliations: Bulgarian Academy of Science, Inst. Geophys., BU-1113 Sofia, Bulgaria.
ISSN: 0038-6308

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Title: **Cross-Layer QoS Provisioning in Cognitive Radio Networks**
Authors: Mihov, Yakim Y.
Source: IEEE Communications Letters, Vol. 16, 5, (May 2012), 678-681
Author Affiliations: Technical University of Sofia, 1000 Sofia, Bulgaria.
ISSN: 1089-7798

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Title: **Column solid phase extraction and determination of ultra-trace Au,
Pd and Pt in environmental and geological samples**
Authors: Mladenova, E.¹, Dakova, I.¹, Karadjova, I.¹, Karadjov, M.²
Source: Microchemical Journal, Vol. 101, (Mar. 2012), 59-64
Author Affiliations: ¹Sofia University "St. Kliment Ohridski", Fac. Chem., 1164 Sofia, Bulgaria;
²Bulgarian Academy of Science, Inst. Geol., BU-1113 Sofia, Bulgaria.
ISSN: 0026-265X

Title: **Molecular cytogenetic identification of a wheat-Aegilops geniculata Roth spontaneous chromosome substitution and its effects on the growth and physiological responses of seedlings to osmotic stress**

Authors: Landjeva, S.¹, Kocheva, K.¹; Karceva, T.¹, Sepsi, A.², Molnar, I.², Schneider, A.², Ganeva, G.¹, Georgiev, G.¹, Molnar-Lang, M.²

Source: Plant Breeding, Vol. 131, 1, (Feb. 2012), 81-87

Author Affiliations: ¹Bulgarian Academy of Science, Inst. Plant Physiol. & Genet., BU-1113 Sofia, Bulgaria;
²Hungarian Acad. Sci., Agr. Res. Inst., H-2462 Martonvasar, Hungary.

ISSN: 0179-9541

Title: **Subsistence farming, incomes, and agricultural livelihoods in the new member states of the European Union**

Authors: Davidova, S.¹, Fredriksson, L.¹, Gorton, M.², Mishev, P.³, Petrovici, D.⁴

Source: Environment and Planning C-Government and Policy, Vol. 30, 2, (2012), 209-227

Author Affiliations: ¹Univ. Kent, Cg Keynes Coll 3, Sch. Econ., Canterbury CT2 7NP, Kent, England;
²Newcastle Univ., Sch. Business, Newcastle Upon Tyne NE1 4SE, Tyne & Wear, England;
³University of National and World Economy, 1700 Sofia, Bulgaria;
⁴Univ. Kent, Kent Business Sch., Canterbury CT2 7PE, Kent, England.

ISSN: 0263-774X



EVENTS

EUROPEAN RESEARCHERS' NIGHT IN BULGARIA

European Researchers' Night was held for the eighth in succession year in the whole Europe, with the support from the European Commission, within the framework of the largest program for financing of scientific research and technological development – the 7-th Framework program. Its goal is to direct public attention to the role of researchers and science as a whole in our everyday life, economic development, social wellbeing and further integration in the common European home, as well as to encourage young Europeans to take the path of scientific career and to turn Europe in the leading research power.

In Bulgaria the project dedicated to Researchers' Night 2012 - INClose (Innovations: New Competence and Leading Opportunities for Sustainability and Endurance) is realized by a consortium with participants: Unified Center for Innovations at the Bulgarian Academy of Sciences (coordinator), Technical University – Sofia, Young Talents Club, Trakia University – Stara Zagora, Plovdiv University Paisii Hilendarski, Medical University – Plovdiv, and with partnership on national and local levels with the Union of Scientists in Bulgaria, Union of Physicists in Bulgaria, "Osem" Magazine, VIVACOM Art Hall and many other organizations.

European Year for Active Ageing and Solidarity between Generations is in the focus of the initiative. Public interest was attracted to innovations in medicine, reproductive health, electronic services in healthcare, robotics and active ageing, new materials and quality of life, as well as participation of researchers from other spheres of science. One of the accents of the activities is 100-th anniversary from discovery of the roentgen rays diffraction and X-ray diffraction analysis – a method for studying the struc-

ture of matter with numerous applications.

On September 28, 2012 Bulgarian participation in the all-European initiative comprised universities and municipalities from Sofia, Plovdiv, Burgas, Stara Zagora, Haskovo, Varna and Pleven.

In Sofia the event started at 17.00 in the central management of the Bulgarian Academy of Sciences. The night of researchers talents at BAS started with special research café dedicated to the 100-th anniversary from the discovery of the X-ray diffraction analysis. The program continued with opening of two exhibitions, presentation of books, etc. Young paleobotanist Boris Tsenov told a "fairytale" about history, climate and plants; the chairman of the Union of Scientists in Bulgaria (USB), corresponding member Damyan Damyanov, introduced the doyenne of Bulgarian medicine Prof. Dr. Alexander Monov. One of the youngest members of USB – Dr. Georgi Maksimov made a short walk through different factors in different periods of our lives, which are responsible for a better health.

The partner of BAS was a "living laboratory" – "Digital spaces". It presents an online platform for sharing photos and texts of what happens in the city. "The idea is researchers to be able to show their inventions and discoveries there in the nearest future", explained the project leader Stavri Nikolov.

During the European Researchers' Night in the Institute of Information and Communication Technologies at the Bulgarian Academy of Sciences there were demonstrated modern electronic infrastructures for scientific computations.

Visitors at Sofia Technical University had the opportunity for several hours to get into research laboratories and see unique inventions.

Over 20 laboratories were a part of the initiative. In the laboratory of the Chair of Modern Systems and Management the guests could take a closer view of how robots, systems of connected tanks and even miniaturized helicopters are being made. In the Laboratory of Virtual Reality the team of Assoc. Prof. Stoyan Maleshkov demonstrated a unique technology allowing seeing definite object in simulated environment before being brought in use.

Guests of universities, BAS and Telephone Chamber in the capital had an opportunity to view an exhibition of innovative products in cosmetics, bioproducts and nutritional supplements.

Researchers presented application of modern medical technologies for achievement of a better quality of life and how one can preserve beauty and keep youthfulness as long as possible.

Presentations of specialists from medical universities in Plovdiv, Varna and Pleven put emphasis on innovations and new technologies in the sphere of health care and medicine.

The idea of the Researchers' Night – 2012 was to popularize science as a significant part of the economy and social life of the society, and first of all to present it as an opportunity for career development of young people.

EIGHTH NATIONAL INNOVATION FORUM

On December 18th, 2012, the Applied Research and Communications Fund, Enterprise Europe Network – Bulgaria and the Ministry of Economy, Energy and Tourism with the support of the Representation of the European Commission in Bulgaria organised **the Eighth National Innovation Forum "Innovation and Competitiveness"**.

Mr. Ognian Shentov, *Chairman of the Applied Research and Communications Fund*, opened the Eighth National Innovation Forum and provided a brief summary of the main results of the Innovation Forum achieved over the eight years of its existence. In the first place, he praised the efforts of ARC Fund in assembling valuable information, analyses and recommendations related to the innovation landscape, system and policies in the country. In cooperation with the public administration, scientific institutions and innovative firms, ARC Fund has managed to develop an analytical capacity that is being highly valued both within the country and by the European Commission. Secondly, Mr. Shentov underlined the significance of the collated information about a few hundred innovative Bulgarian enterprises, which have undergone a thorough evaluation process conducted jointly by internal experts, representatives of ministerial departments as well as World Bank professionals. In conclusion, it was emphasized that successful innovation development cannot happen without active and proper government support.

The President of Republic of Bulgaria, Mr. Rossen Plevneliev reassured that the creation and nurturing of the country's innovation ecosystem is among the priorities of the presidential institution. Mr. Plevneliev underlined that the rising entrepreneurship and innovative culture contribute to a faster and more integrated implementation of the necessary reforms. He mentioned the on-going discussions on the Law on Innovations, the amendment of the Law on Investment Promotion, the creation of a separate Operational Program for science and innovations. Finally, the President noted that the Bulgarian ICT sector has managed to become a regional hub and that the automobile industry has also shown potential to further gain importance for the national economy.

Ms. Zinaida Zlatanova, *Head of EC Representation in Bulgaria*, commenced her statement by reminding the indisputable role of innovations as a tool for overcoming economic downturns. In this relation, Ms. Zlatanova pointed out that this is among the reasons why the European Commission plans to increase its spending for science and innovation in the next programming period by 50% in a budget that is about to remain constant in terms of size.

The President of the Republic of Bulgaria, Mr. Rosen Plevneliev awarded the winners in the **Innovative Enterprise of the Year national contest**.