6. Applications of newly developed nanostructural and microporous materials in biomedical, tissue and mechanical engineering

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Abstract

Purpose: The purpose of the paper is to present the main results of own research in 3 principal aspects indicating that the research is up to date and modern. This relates to nanotechnologies, modern biomedical materials and rapid manufacturing techniques used for the production of, in particular, microporous materials applied for medical and dental purposes. The paper comprises the explanation of structural mechanisms and phase transformations taking place in newly created engineering nanostructural and microporous materials under the influence of the applied, advanced technological processes newly developed, and especially nanotechnological processes, using the most modern scientific and research equipment being at disposal of modern materials engineering, in particular with the common use of high-resolution transmission electron microscopy (HRTEM). The results of investigations into the formation of the structure and surface properties results according to a different thickness scale of coatings or surface zone, from several hundred nanometres to several millimetres, are presented in the paper, including PVD and CVD coatings and laser treated surface on the steels and light alloys substrates. The paper also describes the nanostructural effects in solid materials, and especially the counteraction of cracking of new-developed high-manganese austenite steels Fe-Mn-Si-Al by twinning or/and martensitic transformation induced by the cold plastic deformation. The paper also outlines the results of research of the development of special micro and nanocomposite materials designed mainly for use in regenerative medicine and regenerative dentistry. The studies of the structure and the properties of newly obtained
materials and originally developed technologies are included to present the author’s contribution into materials science, nanotechnology, surface engineering and biomedical engineering including the usefulness of the newly developed nanoengineering materials and their applicability, in particular, in regenerative medicine, as well as tissue engineering. The described outcomes of the research constitute a basis for creating, apart from rigid porous implant-scaffolds, an innovative generation of rigid and elastic biological-engineering composite materials for regenerative medicine.

**The content and scope of the paper:** The paper discusses the key aspects of own research performed over the last decade in scope of nanotechnologies, modern biomedical materials and rapid manufacturing techniques used for the fabrication of, in particular, microporous materials applied for medical and dental purposes. The conditions for the performance of the research according to the scope mentioned were ensured by implementation of investment projects for constructing and equipping research and didactic laboratories in scope of nanotechnology, technologies of material processes and computational materials science, including LANAMATE (2010-2014) and MERMFLEG (2010-2013), and also BIO-FARMA (2010-2012).

The obtained materials and technologies are of high practical importance, which was confirmed in many cases with the results of laboratory tests and investigations at a semi-technical scale, and in some cases with the initiation of implementation works. The results of research in scope of bioengineering and dental engineering may find their applications in tissue engineering, in bone surgery, for three-dimensional tissue scaffolds and in dentistry or oncology, to replace the natural tissue removed because of a cancer with the possibility of applying a therapeutic agent.

The present paper is the original report from a personal own research and explains the concept, scope and results of own research of a new obtained microporous and nanostructural materials and coatings, including hybrid solid-porous products and newly obtained materials processing and additive technologies. Some of the mentioned research results are protected by patents or patent applications, and many of them were awarded over 60 prizes and medals at international fairs of innovation, invention and rationalisation in many countries.

**Additional information:** Selected issues related to this paper were presented in the opening lecture on “Electron microscopy as a synergic tool of the nanotechnology development” at the

It is the reprint of the original paper which was published as follow:

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6.1. Introduction

The paper includes three aspects indicating that the investigations performed together with the Team of the closest Co-workers during last years, are up to date and modern. It is related to nanotechnologies, modern biomedical materials and rapid manufacturing techniques used for the production of microporous materials applied for medical and dental purposes. Although the paper was published a few months ago, it contains a lot of interesting research results also for the participants of the Session held in Miskolc, Hungary, on the occasion of this great event of granting me the Dignity and the Title Doctor Honoris Causa by the University of Miskolc, Hungary which are worth re-disseminating. That is why the text is given to this Issue. I hope I will have a chance to give a lecture on “Nanotechnology as the advanced part of the contemporary materials engineering” in the Session time.

6.1.1. Nanotechnology as a modern branch of science and technology

N. Taniguchi (1912-1999), who was a professor of Tokyo University of Science and who, as the first person in the history, used in 1974 the term “nanotechnology” to describe semiconductor processes connected with the deposition of thin layers and processing with a beam of ions with the nanometric accuracy [1], would have been very surprised had he then knew how great advancements in this field would be witnessed today. The following was the justification of the 1st Lifetime Achievement Award, granted to him in May 1999 in Bremen, Germany by the European Society for Precision Engineering and Nano-technology [2]: “Through his vision, writings and example of total dedication to his field of endeavor he has stimulated the development of what will be one of the dominant technologies of the 21st Century”. R. Feynman (1918-1988), a Noble Prize winner in Physics in 1965, is, however, commonly thought to be a father of nanotechnology. He delivered a lecture on 29th December 1959 at the American Physical Society meeting at CalTech in Pasadena, titled "There's Plenty of Room at the Bottom", which forecast the future of nanotechnology in remarkable detail, describing among other marvels of the future machinery capable of encoding and reading the Encyclopaedia Britannica on the head of a pin [3, 4]. The term "nanotechnology" was applied by K.E. Drexler in 1986 in his book [5], thus popularising the term and promoting the technological significance of nanoscale phenomena and devices, also in his another book [6], which received the Association of American Publishers award for Best Computer Science
Book of 1992. It should be noted, however, that the earliest available description of nanotechnology [5, 6] refers to a detailed technological aim related to the accurate manipulation of atoms and particles for manufacturing products at a macro scale, also referred to as molecular nanotechnology. A more general description of nanotechnology was then defined by the National Nanotechnology Initiative (NNI) as a United States federal government program for the science, engineering, and technology research and development for nanoscale projects, initiated on 3rd December, 2003 when the President of the USA signed into law the 21st Century Nanotechnology Research and Development Act (Public Law 108-153). “The NNI serves as the central point of communication, cooperation, and collaboration for all Federal agencies engaged in nanotechnology research, bringing together the expertise needed to advance this broad and complex field.” The documents provide that “Nanotechnology is science, engineering, and technology conducted at the nanoscale, which is about 1-100 nm” [7]. This definition reflects the fact that quantum mechanical effects are important at this scale, so the definition was shifted from a particular technological aim to a category of research, taking into account all types of research and technologies concerning special properties of the matter which exist below the agreed threshold value of sizes. Nanometric dimensions are not unequivocally defined. The broadest adopted definition is thought to be a recommendation of the European Commission, in which nanomaterials are defined similar as at the NNI in the USA: “Nanomaterial means a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1-100 nm. In specific cases and where warranted by concerns for the environment, health, safety or competitiveness the number size distribution threshold of 50% may be replaced by a threshold between 1 and 50%” [8]. A compliance with this definition may be determined on the basis of the specific surface area by volume. A material should be considered as falling under the definition where the specific surface area by volume of the material is greater than 60 m²/cm³. However, a material which, based on its number size distribution, is a nanomaterial should be considered as complying with this definition even if the material has a specific surface area lower than 60 m²/cm³ [8]. “Manufacturing at the nanoscale is known as nanomanufacturing. Nanomanufacturing involves scaled-up, reliable, and cost-effective manufacturing of nanoscale materials, structures, devices, and systems. It also includes research, development, and integration of top-down processes and increasingly complex
bottom-up or self-assembly processes” [9]. At present, nanotechnology determines the whole array of techniques and methods of manufacturing various objects and their elements with nanometric sizes, i.e. at the level of single atoms or particles in scope of linear sizes, although in one direction 1-100 nm. Since the establishment of the NNI in 2001 in the USA, considering the President’s 2015 Budget ensuring more than USD 1.5 billion for activities concerning nanotechnology under the NNI, nearly USD 21 billion was earmarked, incrementally, for further investments to support innovation priorities and strategy for nanotechnology [10]. This support reflects the potential of nanotechnology to substantially improve the basic understanding and control of the matter at nanoscale and to translate this knowledge into application solutions based on nanotechnology and currently with the pressure on accelerated transition from elementary and development investigations to innovations, while continuing the basic scientific research, to ensure the development of future innovations. On the other hand, for instance, the European Union invested USD 1.2 billion in nanotechnology research in 2012, while Japan over US 750 million. Research in this field has also been pursued by me with my Co-operators and much of it is reported in this article.

6.1.2. Bionic implants, scaffolds and tissue engineering

The dynamic growth of cases of organ or tissue loss or damage in the human population due to post-injury losses, post-resection losses, as well as those originating from operative treatment of cancerous tumours or inflammation processes and as a result of other disorders and the related necessity to replace or supplement such organs or tissues aimed at the prevention of biological and social degradation of patients and restoration of their living functions, either normal functions or such acceptably similar to normal, constitutes a significant and costly problem of modern medicine. It is hard to overestimate, nowadays, the achievements of modern implantology, where courage, imagination and knowledge of doctors supported by accomplishments of engineers have, on a global scale, given many people an opportunity to return to their normal or quasi-normal conditions of functioning, and very often to have their health restored after experiencing severe injuries or losses, and also other disorders. One of the challenges for regenerative medicine is to reconstruct sections of bone losses in maxillofacial surgery, restorative dentistry, laryngology, including otolaryngology, orthopaedics and traumatology, and to supplement soft tissues, e.g. in case of esophagus and blood vessels prosthetics/implantation, where in particular bone or organ stumps are not in
contact. This refers to post-injury losses, postresection losses, as well as those originating from operative treatment of cancerous tumours or inflammation processes. Implantable biomedical devices are currently aggregately considered to be medical bionic implants where bionics is understood as production and investigation of biological systems to prepare and implement artificial engineering systems which can restore the lost functions of biological systems [11].

A market potential analysis indicates clear development trends of the global medical product markets, and directly relevant are, most of all, development tendencies of the biomaterials market, medical bionic implant/artificial organs market, orthopaedic devices market, orthopaedic soft tissue repair market, orthopaedic trauma fixation devices market, orthopaedic soft tissue repair market, and 3D Printing in Medical Applications Market. The development of a complementary market should also be expected. In general, medical bionic implants encompass numerous solutions eliminating various dysfunctions of a human organism, among others orthopaedic prostheses (bone grafts, bone plates, fins and connecting and stabilising devices, including screws applied in the area of ankles, knees and hands, bars and pins for stabilising fractured limbs), screws and plates in skull-jaw-face reconstructions, dental implants, and also scaffolds of bones and tissues in tissue engineering [11]. The undertaken foresight research shows that the global the medical bionic implant and artificial organs market is a potentially growing one with a global market of USD 12.67 billion in 2012 as it is expected to grow at a CAGR of 7.1% to reach USD 17.82 billion in 2017 [12], and the market of tissue engineering and regenerative medicine will grow in the USA only from USD 6.9 billion in 2009 to USD 32 billion in 2018 [13]. This constitutes a real and tangible reason for the intensification of research and implementation works, which inevitably leads to higher industrial spendings for investments associated with know-how acquisition and expansion of manufacturing capacities in this field. The current methods of organ and tissue replacement employ primarily autographs, allografts or metal devices or such made of other engineering materials [14]. Tissue scaffolds have been intensively developed for several years apart from transplantable implants, and in fact instead of them. Tissue engineering seeks innovative methods of restoring a natural tissue and provides an alternative solution to the currently used conventional methods [15]. Tissue engineering, as a field of technical sciences using medical knowledge and materials engineering methods [16, 17], has been involved in construction and fabrication of scaffolds, maintaining the developing tissues, in manipulation of somatic and stem cells, in influencing the tissues growth conditions and their structure and in maintaining...
the physiochemical conditions of the environment supporting this growth, in order to produce functional substitutes of damaged tissues or entire organs. Research in the field of application of various engineering materials and diverse manufacturing and processing technologies for production of bionic and classical implants have also been performed for years by me together with Co-operators, and a large part of results of the research is reported in this article.

### 6.1.3. Additive manufacturing technologies

In 1981, H. Kodama of Nagoya Municipal Industrial Research Institute, discovered two alternative fabricating methods of a three-dimensional plastic model with photohardening polymer, where the UV exposure area is controlled by a mask pattern or the scanning fibre transmitter [18]. It also seems that he did not think then that this discovery would contribute to the development of one of the most development-oriented technologies of additive manufacturing in the 21st century. The general term additive manufacturing was popularised in the 2000s and additive manufacturing now consists of production of three-dimensional, physical objects based on a computer model, and – along with advancements in production accuracy of objects by 3D printers – it has become a method of producing ready objects. Additive manufacturing systems were on the market that ranged from USD 2,000 to USD 500,000 in price and were employed in industries including aerospace, architecture, automotive, defense, and medical replacements, among many others. The methods are used for obtaining final products and serve to sinter a wide range of metallic powders, including, among others, light metal alloys, titanium alloys, steel, cobalt and chromium alloys and superalloys, and also polymer materials (e.g. polyamide) or ceramics and composite materials. Due to the application of this innovative technology, the quality of products made of polymer materials do not differ from those produced conventionally by injection. The technology allows to produce single elements or elements in small series, according to individual market demand, ensuring hollows, cuts and internal channels which it is difficult or even impossible to achieve conventionally. They are also employed for applications in medicine, implantology, e.g. titanium or ceramics, for fabrication of highly specialised medical tools, although had been initially employed almost only for rapid prototyping and fast production of tools, known as Rapid Tooling (RT), for producing steel moulds for injection moulding or for pressure casting, for metal stamp dies, and also for machine parts. The first technique of 3D printing having real practical importance was developed in 1984 by C. Hull as StereoLithography (SLA or SL), in
which layers are added by curing photopolymers with ultraviolet light lasers, as in H. Kodama’s idea, where his significant input consisted in the design of the STL (STereoLithography) file format widely accepted by 3D printing software as well as the digital slicing and infill strategies common to many processes today and the launch of production of the first stereolithography devices [19, 20]. S. Crump developed in 1988 a method of Fused Deposition Modeling (FDM), which derives from automatic polymeric foil hot air welding system, hot-melt glueing and automatic gasket deposition. He later founded Stratasys company which in 1992 launched into the market its first 3D Modeler machine [21]. The first printer employing Selective Laser Sintering was created in 1988. This technique is more accurate and gives more freedom than FDM. In Selective Laser Sintering (SLS) or Direct Metal Laser Sintering (DMLS), layers of powder are bonded using an infrared laser radiation beam, a source of which is a CO₂ or Nd:YAG laser. A double, and even triple system of lasers can also be applied. No additional supporting elements have to be used here, as the material subjected to sintering supports the projecting parts and the bent or closing sur-faces of the element produced. The process is controlled by a computer, after designing and modelling the manufactured product using relevant Computer Aided Design (CAD) software. In order to execute an entire manufacturing cycle of any part by one of the technologies mentioned, the subsequent thin layers of powder or a mixture of powder have to be spread across the working table surface with appropriate roughness and temperature, placed on a working table with automatic position adjustment, and then on the surface of the layers bonded in advance. Each layer of powder is levelled each time with a scraper. A computer-controlled laser beam is guided across the powder surface with CAD software in subsequent layers (corresponding to the cross section of a virtual 3D model of an item recorded using CAD 3D digital recording), causing the sintering of powder particles in a strictly defined manner and in selectively chosen places on the powder surface. A table with another layer of powder is lowered to the set height according to automatic virtual division of a 3D model of an object onto layers with the set thickness, and the powder distribution and laser sintering cycle is repeated until a fully bonded item is achieved, which can be put into use after cooling down and cleaning off the excess powder. The system ensures temperature monitoring of the item produced and laser sintering conditions of the item with mechanical properties reproducible in the whole volume. It is possible to melt powder with a laser beam and then the material transits into the solid state in form of powder via the liquid state to the solid state in the form of the item produced, and the
method is called Selective Laser Melting (SLM) [22]. The mentioned methods can also be used for producing microporous materials containing a skeleton sintered by SLS/SLM methods with open micropores with the size of not less than approx. 100 μm. The size of the pores in nanoporous materials is generally 100 nm or smaller. Most nanoporous materials can be classified as bulk materials or membranes. SLS/SLM methods, due to the size of the powders used, cannot be used for manufacturing nanoporous materials. Porous materials are most often characterised by their porosity. Micropores, when the material of a skeleton sintered by SLS/SLM method is metal or its alloy, e.g. Ti, can be filled with other metal with lower fusibility, e.g. Al or Mg, e.g. by gaseous pressure infiltration, to produce a composite material or can be, e.g. inhabited by living human cells after meeting medical conditions. It is also possible to fill pores with liquid, e.g. oil. The concept of porous materials produced not only with the mentioned technologies, but also with natural ones, is used not only in materials science, but also in many other areas of applied science and engineering, in particular: filtration, mechanics (acoustics, geomechanics, soil mechanics, rock mechanics), engineering (petroleum engineering, bioengineering, construction engineering), geosciences (hydrogeology, petroleum geology, geophysics), biology and biophysics. A large number of additive manufacturing processes are now applied, and the main differences existing between them consist in the usage of different materials and the deposition method of layers of powder. Some of the methods consist of fabrication of layers by melting or softening the material, as is the case in selective laser melting (SLM) or direct metal laser sintering (DMLS), selective laser sintering (SLS), electron beam melting (EBM), spark plasma sintering (SPS), fused deposition modelling (FDM) or fused filament fabrication (FFF) [23]. In other cases, such as stereolithography (SLA), cure liquid materials are used. With laminated object manufacturing (LOM), thin layers are cut to shape and joined together (e.g., paper, polymer, metal). The main considerations in choosing a technology and a machine are generally speed, costs of the printer and choice and cost of the materials, and colour capabilities. Works were started at the beginning of this century to apply techniques similar to 3D printing in medicine, for producing prostheses and epilepsias, implants, and even tissue, although the challenge still is the printing of entire organs, despite the already known effects in this scope. Futurologists such as J. Rifkin [24], envision that 3D printing marks the beginning of the new stage of industrial revolution [25]. Using the power of the Internet, it may eventually be possible to send a blue-print of any product to any place in the world to be replicated by a 3D printer with "elemental inks” capable
of being combined into any material substance of any desired form [24, 25]. Special focus is laid in this paper on the possible use of additive manufacturing technologies, mainly selective laser sintering and metallic, polymeric and composite materials, which can be used for scaffolds production in tissue engineering.

6.1.4. Conditions for the performance of the research described in the paper

The conditions for the performance of the research according to the scope mentioned were ensured by implementation of investment projects for constructing and equipping research and didactic laboratories in scope of nanotechnology, technologies of material processes and computational materials science, including LANAMATE under the Operational Programme Infrastructure and Environment (2010-2014) [26], and MERMFLEG under the Regional Operational Programme of Silesian Voivodeship (2010-2013) [27], and also a head of the task L102 of the BIO-FARMA Project (2010-2012) [28] under the Innovative Economy Operational Programme concerning the improvement of the standard of laboratory resources in scope of nanotechnology and materials research. They are launched 3 new priority directions of study under the Operational Programme Human Capital. In 2008, after developing custom and fully original concepts with full documentation and plans of courses were started 2 macrobranches of studies, new in Poland, including “Nanotechnology and technologies of material processes” in the academic year of 2009/2010 and the fields of studies “Materials engineering”, including, especially, with a profile of “Dental Engineer” initiated in the academic year of 2010/2011. All the three newly created directions of studies were considered as having priority by the Ministry of Science and Higher Education, and were incorporated into a project lasting 4 years awarded by the Ministry of Science and Higher Education called INFONANO (2009-2014) [29], and into NANATRIM (2011-2015) [30], IMOTECH (2012-2015) [31], and QUAPINFO (2011-2015) [32] projects funded by the European Fund of Regional Development under the Operational Programme Human Capital. As part of such projects, completed at the end of 2015, several hundred students finished their courses in the field of “Nanotechnology and technologies of material processes”, “Materials engineering” and “Dental Engineering” and 10 PhDs were promoted in the field of “Materials engineering”. A modern building of the Scientific and Didactic Laboratory of Nanotechnology and Materials Technologies covering approx. 1500 m² was built at the cost of approx. 28.5 mPLN, which was
equipped with state-of-the-art equipment allowing to form the structure and properties of engineering materials, including also nanostructural materials. The Laboratory of Nanotechnology and Materials Technologies has 14 scientific and didactic laboratories, including 9 technological laboratories, 2 laboratories of computer aided design of material technologies and two for application of virtual reality in material technologies and quality control. The technologies handled at the laboratory include notably: fabrication of carbon nanostructural materials including graphene, carbon nanotubes and polymer nanofibers, laser surface treatment of metal, ceramic and photovoltaic materials, a laser processing centre, laser constitution of metal, ceramic and graded materials, hot and plastic working technologies, including intensive plastic deformation, plastic deformation simulation, vacuum surface engineering, casting of amorphous materials, including massive ones, comprehensive processing of polymer materials and production of polymer composites, and powders metallurgy. The Scientific and Didactic Laboratory of Nanotechnology and Materials Technologies is equipped with over 80 unique and modern technological devices allowing to manufacture and treat nearly all known engineering materials, including nanostructural materials. The Research Laboratory of Engineering and Biomedical Materials was fully converted under the MERMFLEG and BIO-FARMA Projects [27, 28] with the total value of ca. 22 mPLN. The scientific and research infrastructure of this laboratory arranged in a very modern way on the surface covering approx. 1500 m2 provides virtually all tools necessary for analysing a structure and properties of all groups of materials, both traditional ones and nanomaterials, biomedical and layers and coatings. Materialographic examinations of all groups of materials and layers and coatings are performed using advanced light microscopy techniques, including confocal microscopy, highresolution scanning electron microscopy (Supra 35 by Zeiss) and highresolution transmission electron microscopy (TITAN 80-300 by FEI) and conventional transmission microscopy (200CX by JEOL), and also atomic forces microscopy (XE 100 by Park Systems). The research is related to an analysis of chemical composition of materials using such methods as Glow Discharge Emission Spectrometry (GDS 500 and 850 by Leco), Raman spectroscopy (inVia by Renishaw) and FTIR spectroscopy (Niclolet by Thermo Scientific) and chemical composition evaluation in micro-areas, using energy spectroscopy methods and wavelength of backscatter X-ray radiation EDS and WDS and diffraction EBSD examinations. Ray phase analysis (XRD) examinations are undertaken using an X-ray diffractometer X’Pert Pro by Panalytical and a Pixel 3D detector. Phase
transformation examinations are also pursued using a hardening dilatometer with optional specimen deformation DIL 805AD by Bahr. The laboratory is supplied with a set of devices for corrosion tests. The tests are also followed of mechanical properties of materials, tribological, technological polymer materials, optoelectrical properties of materials and solar cells. A group of prosthodontics workshops endowed with very modern equipment is an important part of the Laboratory. The Computer Materials Science Laboratories are equipped with several hundred computer stations with comprehensive specialist software. The information provided indicates that one of the best conditions were created in Poland for research in the area of nanotechnologies, technologies of material processes, examinations of the structure and properties of engineering materials, especially nanostructural materials and coatings, and now they are excellent conditions for the development of interesting and fruitful scientific research, for excellent development of young scientific staff, including many PhDs, the results of which are included, in particular, in the description in this article and for studies for a few hundred BSc and MSc students in each one semester. The conditions mentioned also allowed to implement scientific research described in the paper.

6.1.5. The content of the paper

The key scientific theses of the paper were included to an inaugurating lecture antitled “Electron microscopy as a synergic tool of the nanotechnology development”, given in Zakopane on 7th December 2015 at a Plenary Opening Session of the International Scientific Conference “Achievements in Mechanical and Materials Engineering AMME’2015”.

The paper comprises several main sections. The first section gives an explanation of structural mechanisms and phase transformations taking place in newly created engineering nanostructural and microporous materials under the influence of the applied, advanced technological processes newly developed, and especially nanotechnological processes, using the most modern scientific and research equipment being at disposal of modern materials engineering, in particular with the common use of high-resolution transmission electron microscopy (HRTEM).

The results of investigations into the formation of the structure presented especially with using a high resolution transmission electron microscope (HRTEM) and surface properties results according to a different thickness scale of coatings or surface zone, from several hundred nanometres to several millimetres, are presented in the second part of the paper.
Important in this scope are the results of the FORSURF project [33], in which altogether nearly 500 experts from home and abroad participated, as a result of which, using technology foresight methods and using the so-called E-foresight developed under the project, being the authors’ undisputed accomplishment, 144 most promising surface engineering technologies were selected, including the report, technology cards and roadmaps [34-40].

Another aspect pertaining to the third part of the paper relate to nanostructural effects in solid materials, and especially the counteraction of cracking of new developed high-manganese austenite steels Fe-Mn-Si-Al by twinning or/martensitic transformation induced by the cold plastic deformation and their effect on the formation structural nanoelements influenced on mechanical properties and the strain energy per unit volume. High-manganese steels provide an extensive potential for automotive industries through exhibiting the two possible twinning induced plasticity (TWIP) and transformation induced plasticity (TRIP) mechanisms for the fracture counteraction.

The results of research of the development of special micro and nanocomposite materials designed mainly for use in regenerative medicine and regenerative dentistry are of great importance in view of the presented paper and they are included to the fourth part. This group of results includes hybrid additive technologies of structure and properties formation of newly created metal porous materials using selective laser sintering/laser melting (SLS/SLM). As part of the presented results important is research on polymer nanofibers achieved by electro-spinning, especially concerning the creation of long-resorbable composite nanofibers with a bioactive core and a bactericidal shell. The polymer nanofibers produced by electrospinning applied in regenerative medicine additives introduced have also substantial influence on the antibacterialness and antifungalness of nanofibers. Such materials can be used as a carrier of medicine, with the possibility of applying a therapeutic agent. The combination of results in the field of the development of special micro and nanocomposite materials and additive technologies of metal microporous materials together with investigations of polymer nanofibers achieved by electrospinning, set a basis for creating, apart from rigid porous implant-scaffolds, an innovative generation of rigid and elastic biological and engineering composite materials for regenerative medicine.
6.2. Discussing the results of own research concerning nanostructural composite materials

The most avant-garde research covered by this paper relate to the application of nanostructural carbon materials, according to the newly developed technology, including nanotubes, nanowires, nanoparticles, graphene, as well as natural halloysite nanotubes and montmorillonite and copper nanoparticles, as well as polymer nanowires electrospinned according to the custom method for strengthening and fabricating newly developed nanostructural composite materials and elements of dye-synthesised solar cells together with explaining the role of such objects in the manufacturing process and in structural mechanisms responsible for reinforcement, in particular using a high-resolution electron transmission microscope (HRTEM) and their influence on the functional properties important for potential applications.

6.2.1. The application of carbon and halloysite nanotubes in metallic nanostructural materials

Nanocomposite materials with a matrix made of aluminium alloys, including AlMg1SiCu, reinforced with carbon or halloysite nanofibers (whose deposits are located in Poland, as in one of 3 places globally apart from the USA and New Zealand), manufactured according to the developed custom original technology, consisting of 3 operations of preparing powders by high-energy mechanical synthesis or low-energy mixing, cold consolidation and hot pressing, exhibit – in relation to a pure alloy acting as a matrix, much better mechanical properties, e.g. in case of contents of 5% of multiwalled carbon nanotubes during high-energy grinding, even three times higher micro-hardness and compressive strength, and especially improved abrasive wear resistance, e.g. in case of a 15% addition of halloysite nanotubes, manifested by a nearly threefold reduction in volume loss during abrasion tests.

A greatly refined matrix structure and the occurrence of nanograins with the size of 5-10 nm should be indicated in particular as significant structural reasons explained using a high resolution transmission electron microscope (HRTEM). In the case where carbon nanotubes are employed, the matrix is reinforced with such nanotubes, as well (Figs. 1, 2). Needle like precipitates of Al₄C₃ carbide also occur as a result of interactions between the external layer of carbon nanotubes with Al from the matrix during mechanical alloying, then
Figure 1. Structure a) of the multiwalled carbon nanotubes forest on the silicon substrate (SEM), b) the Raman spectra of the multiwalled carbon nanotubes, c) structure of the multiwalled carbon nanotubes (HRTEM)

Figure 2. The structure of the a) AlMg1SiCu alloy (TEM), b) extruded AlMg1SiCu matrix composite reinforced with MWCNTs, c) nanostructural grains in the matrix (TEM), d) extruded AlMg1SiCu matrix composite reinforced with MWCNTs (HRTEM), e) well dispersed MWCNTs in the matrix of the extruded AlMg1SiCu matrix composite (HRTEM), f) the Al4C3 carbides formed as result of the interaction between the outer shells of CNTs and the Al matrix during mechanical alloying (HRTEM)
crystallising in hot pressing, the influence of which on the properties, and especially ductility, is most certainly not positive (Fig. 3). On the other hand, additional reinforcement with primary intermetallic phases AlFe$_3$ and Al$_4$(Fe,Cr,Mn)Si$_{0.74}$ and Al$_2$O$_3$Si phase created, most certainly, during mechanical grinding, takes place in nanocomposite materials reinforced with halloysite nanotubes (Fig. 4). In the case where halloysite nanotubes are used, an innovative technology of gaseous pressure infiltration was also developed (Figs. 5-8). The technology

![Image 1](image1.png)  
**Figure 3.** The structure of the a) the halloysite nanotubes (SEM), b) the aluminium alloy AlMg1SiCu composite material with reinforcement of the 15% halloysite nanotubes after mechanical alloying (STEM mode using of the energy-filtered TEM microscopy technique), c) the solid solution of aluminium matrix with ultra-fine grains in bulk composite material (TEM)

![Image 2](image2.png)  
**Figure 4.** The structure of the aluminium alloy AlMg1SiCu composite material with reinforcement of the 15% halloysite nanotubes with the primary intermetallic phases: a) AlFe$_3$, b) Al$_4$(Fe,Cr,Mn)Si$_{0.74}$, c) the Al$_2$O$_3$Si phase produced most probably during the mechanical milling process (TEM)
consists in the preparation of powders, consolidation and sintering of moulded parts of a mixture of halloysite nanotubes with the then removed carbon nano-fibers, in order to obtain relatively large open porosity alloying gaseous pressure infiltration with AlSi12 alloy. Crystalline structures of mullite, as well as cristobalite, and also quartz, were identified in the structure of sintered preforms. Aluminium was identified after infiltration in the structure of the nanocomposite material, as well as structural components identified earlier in the preform, as well as silicon grains surrounding a thin layer of the mullite area, as well as aluminium oxide (Al₂O₃). The hardness of the achieved nanocomposite materials is increased even 4,5-fold in relation to the hardness of AlSi12 alloy in the as-delivered condition, together with a growing fraction of the ceramic phase, but most of all sintering temperature of ceramic skeleton to
Figure 7. The structure of the sintered porous preforms before infiltration: a)-d) mullite, e) cristobalite, f) quartz (HRTEM)

Figure 8. The structure of the infiltrated AlSi12 matrix composite reinforced with sintered halloysite nanotubes fabricated by gas-pressure infiltration: a), b) nanostructural AlSi12 matrix, c) the Si grain surrounded by a thin layer of mullite (TEM)

1300-1500°C, due to diffusion from cristobalite during infiltration to the crystallising secondary Si at the matrix-reinforcement boundary, most probably with a fraction of a zone of a transition phase Al₂O₃ and nanometric precipitates of MgAl₂O₄ phase. The infiltrated
nanocomposite materials reinforced with porous ceramic skeletons are characterised by smaller wear than their matrix of AlSi12 alloy. The established technology of nanostructural composite materials creates an outlook for their implementation as structural parts in the aviation and automotive industry. The results of investigations concerning nanocomposite materials with a matrix made of aluminium alloys reinforced with carbon or halloysite nanotubes were published in articles [41-53] and in speeches delivered at scientific conferences in Poland and abroad, in PhD theses [54-56] and were received 9 awards for this aspect at numerous fairs of innovation and invention [57-70].

6.2.2. The polymeric nanostructural materials

Nanostructural composite materials with a polymer matrix are presented, including, notably, epoxy resin and poly(methyl methacrylate) reinforced, in particular, with halloysite nanotubes, montmorillonite nanoplates, nanowires and copper nanopowder. This aspect also encompasses layered polymer composites fabricated sequentially by injection moulding with reciprocating flows. The optimum mass fraction of halloysite nanotubes, as well as montmorillonite nanoplates in poly(methyl methacrylate), is 3% (Fig. 9). The appropriately selected surface treatment of such reinforcement using imidazolidinyl salt and organosilane compounds enables their homogenous distribution inside the polymer matrix, preventing their aggregation, which in turn could affect negatively the mechanical properties of the obtained nanocomposite materials. The best mechanical properties, including notably 1.5-time higher

![Figure 9](image-url)

**Figure 9.** The characteristics of the polyethylene PE matrix composite with montmorillonite MMT additions: a) the structure of PE-5% MMT (SEM), b) EDS spectrum from area of MMT particles, c) stress-strain curves of PE-MMT composites [73]
compressive strength as compared to pure poly(methyl methacrylate) and more than ten per cents as compared to a nanocomposite material reinforced with unmodified halloysite, is achieved by organophilisation using 1-Butyl-3-methylimidazolium hexafluorophosphate (BMIM). On the other hand, nanocomposite polymer materials with an epoxy resin Epidian 5 matrix crosslinked with triethylenetetramine, most advantageously at the temperature increased to 50°C, which considerably reduces the viscosity of epoxy resin, thus facilitating its connection with a reinforcement material with nanowires and copper nanopowder, exhibit better properties as compared to composite polymer materials reinforced with micrometric copper powder (Figs. 10, 11). Beyond doubt, copper nanowires are an attractive alternative for such materials as, e.g. carbon nanotubes. Reduced hardness occurs indeed in case of materials

Figure 10. The structure of platinum (a) and copper (b) nanowires manufactured on a) polished silicon substrate (HRTEM), b) glass substrate (HRTEM), c) structure of the epoxy resin matrix composite with Cu nanowires reinforcement (SEM)

Figure 11. The X-ray spectrum (a) and absorbance spectrum UV/Vis (b,c) of the epoxy resin matrix composite with Cu nanowires
reinforced with copper powder and nanopowder, but in case of reinforcement with copper nanowires, this hardness is increased. Detailed investigations of the structure of nanocomposite polymer materials reinforced with nanowires and copper nanopowder, in particular in a transmission electron microscope, as well as of fractures in a scanning electron microscope, indicate that micrometric copper powder is characterised by a dendritic shape, and copper nanopowder – by a ball-like shape. Nanometric copper powder is characterised by a much higher agglomeration tendency than copper nanowires. The shape and sizes of copper nanopowders and nanowires ensure the creation of percolation paths allowing to transfer an electric change despite a nonconductive matrix. UV/Vis examinations reveal an increased absorption peak for nanocomposite polymer materials reinforced with copper as compared to pure resin. The highest peak value and the largest wavelength range occurs for a 9% fraction of copper nanowires. It was found on the basis of UV/Vis examinations setting a basis for calculation of an energy gap and its relative location of Fermi energy that the best conditions in this regard are exhibited by copper nanowires reinforced nanocomposite materials. Volume resistivity represents the material’s ability to limit the intensity of electric current flow. The lowest volume resistivity value is seen for materials with a 3% fraction of copper nanowires. As the discussed nanocomposite polymer materials indicate better properties as compared to tradetional polymer composite materials, a broad range of such materials’ utilitarian importance is becoming apparent (Table 1). The results of investigations concerning nanostructural composite materials with a matrix made of polymers reinforced with halloysite nanotubes, montmorillonite nanoplates, nanowires and copper nanopowder, were published [71-84]

<table>
<thead>
<tr>
<th>Type strengthening</th>
<th>The mass value, %</th>
<th>The absorbance value max</th>
<th>Wavelength range, nm</th>
<th>Average volume resistivity, $\Omega$</th>
<th>The value of an electrical fault</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy resin with Cu nanowires</td>
<td>0.5</td>
<td>2.00</td>
<td>234-398</td>
<td>$2.38\cdot10^{12}$</td>
<td>63.1</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1.76</td>
<td>234-552</td>
<td>$1.12\cdot10^{11}$</td>
<td>63.0</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.84</td>
<td>258-546</td>
<td>$2.24\cdot10^{9}$</td>
<td>57.4</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1.82</td>
<td>262-544</td>
<td>$1.62\cdot10^{12}$</td>
<td>13.3</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>2.26</td>
<td>254-564</td>
<td>$6.91\cdot10^{11}$</td>
<td>10.8</td>
</tr>
</tbody>
</table>

Table 1. The influence of the Cu nanowires on the properties of the epoxy resin matrix composite with Cu nanowires reinforcement
presented at scientific conferences in Poland and abroad, in PhD theses [85-88] awarded by 6 awards for this aspect at numerous fairs of innovation and invention [82-94].

6.2.3. The application of the graphene and carbon nanotubes in dye sensitized solar cells and in nanocomposite materials of the MWCNTs-NPs type

The nanostructural carbon materials, including graphene and carbon nanotubes (CNTs), are very attractive for replacing platinum in a counter electrode of dye sensitized solar cells (DSSCs) due to their corrosive resistance, good electrical conductivity, and – most of all – due to the fact that platinum is one of the most expensive components of DSSCs. Regardless of the fact that platinum is a good catalyst of a redox reaction, the development of stable and profitable, but competitive, in terms of price, materials for counter electrodes (CEs) is necessary. This influences a further reduction in costs and ease of large scale production of DSSCs made of cheap materials, and, nevertheless, having high solar energy conversion capacity. A counter electrode plays important roles by catalysing the reduction of redox species after electron injection. Carbon nanotubes and graphene based counter electrodes were prepared on glass coated by transparent conductive oxide TCO. Carbon nanotubes CNTs solution was prepared by direct mixing with highly conductive mixture of two iono-mers: poly(3,4-ethylene-dioxythiophene) polystyrene sulfonate PEDOT: PSS used in order to prevent regregatation and then applied on the glass surface with fluorine doped tin oxide (FTO) (Fig. 12). A well

![Figure 12. The structure of the a) layers of conductive polymer PEDOT:PSS with multiwall carbon nanotubes used as a counter electrode for dye-sensitized solar cells (SEM), b) layers of graphene in distance 0.3309 nm (HRTEM), c) of a few layers of graphene (HRTEM)](image_url)
dispersed thin film of carbon nanotubes was obtained by introducing PEDOT:PSS as a wrapping agent for dye sensitized solar cells and applying on TCO glass by spin coating method. Nanocrystalline titania based photoanode was screen printed onto TCO glass and subsequently sintered. After then the nanostructural titania films was immersed into an ethanolic solution of ruthenium based dye. For the fabrication of DSSCs, nanocrystalline TiO$_2$ photoanode was prepared by spreading the TiO$_2$ paste onto FTO glass using screen printing method and subsequently sintered at 500°C for 30 min to convert anatase phase and make interparticle networks. After then TiO$_2$ films were immersed into ethanolic solution of ruthenium based dye for 12 h and rinsed with absolute ethanol to remove physically adsorbed dye molecules. Graphene oxide was mixed with PEDOT:PSS (in order to prevent reaggregation) and deposited on FTO glass by spin coating method followed by thermal annealing for 30 min at temperatures 250 or 500°C in hydrogen/argon atmosphere flow. One sample was dried at 105°C in an oven overnight. The nature of the carbon nanotubes and graphene-based counter electrode has been confirmed by the Raman scattering spectroscopy (Fig. 13). Graphene based counter electrodes are very transparent in the all range of solar spectrum and do not significantly alter the transparency of FTO electrode. Transmittance in case of carbon nanotubes electrode decreased. The investigated effect of carbon materials electrodes on efficiency of DSSC showed that the best efficiency has reduced graphene oxide

![Figure 13.](image)

*Figure 13. a) Raman spectra of graphene thin film substrates which was obtained using an excitation laser of 512 nm, b) transmittance spectrums of particular dye layers of dye-sensitised solar cells with MWCNTs measured with UV/Vis spectroscopy c) absorbance spectrums of particular dye layers of dye-sensitised solar cells with graphene measured with UV/Vis spectroscopy*
what can be caused by higher catalytic activity and increasing in the surface area of counter electrode in comparison to carbon nanotubes. The outcomes of such investigations are of special importance for application due to the development of building integrated photovoltaics. Such works in the field of carbon nanotubes and nanocomposite materials are complemented by participation in a research team under the supervision of another Professor engaged in investigations into the fabrication of nanocomposite materials of the MWCNTs-NPs type where NPs represent Pt, Pd, Rh, Re [95-106] (Figs. 14, 15). Such nanocomposite materials are fabricated by means of a direct method through the functionalisation of carbon nanotubes with chemical methods, e.g. etching in acids, e.g. nitric acid, sulphuric acid and then the synthesis of

**Figure 14.** The structure of the nanocomposite materials of the MWCNTs-NPs type a) multiwall carbon nanotubes decorated by Pt nanoparticles (TEM), b) system of atoms in nanoparticles of platinum decorating carbon nanotubes (HAADF HRTEM), c) platinum nanoparticles on the nanotube surface (HRTEM) [106]

**Figure 15.** The structure of the nanoparticles of the metals on the carbon nanotube surface a) Pt, b) Rh, c) Re (HRTEM) [106]
nanoparticles of NPs metals by the method of chemical reduction using, e.g. ethylene glycol or sodium citrate and/or high-temperature method in an insert atmosphere of argon or with participation of hydrogen. The purpose of the investigations is the possibility to use such materials, in particular, in sensors of very small concentrations of gases, for identification of markers in medical diagnostics and for the purpose of catalysis. The scientific articles were published [107-111] and the results of investigations were presented at scientific conferences [112, 113], and in PhD theses [114-116].
6.3. Discussing the results of own research concerning surface engineering

6.3.1. Nanostructural PVD and CVD coatings on the steels and ceramic tool materials

Structural effects exist at an atomic scale of several dozen or several hundred nanometres, discovered as a result of long-term, extensive and multifaceted research, occurring in the joint zones of surface coatings with a substrate made of all groups of tool materials, utilised for tools in various technological processes, notably machining and plastic working, including highspeed conventional and sintered steels, alloy cold work and hot work tool steels, carbide steels, sintered carbides, cermets, corundum, nitride and sialon ceramic materials, and also between layers in multilayer coatings, including 3rd-generation coatings, in particular Ti(C,N)+Al$_2$O$_3$+TiN i DLC+AlTiCrN and graded coatings, i.e. TiN + (Ti, Al, Si)N + TiN (Figs. 16-20). Probably the most important and fully proven discovery is demonstration that not adhesion, as is commonly reported even today by numerous references, is a physical phenomenon accompanying the joining of surface coatings with the substrate core. As demonstrated in the presented accomplishment, indeed the diffuse mixing of compounds occur in the joint zone with the substrate, as well as in the joint zones between particular layers in

![Figure 16. The changes of the elements concentrations of the TiCN and the sintered carbides substrate (GDOES) (a), the structure of the multi-component and multilayer coatings: b) TiN+(Ti,Al,Si)N+TiN on the sintered carbides substrate (SEM), c) Al$_2$O$_3$ + Ti(C,N)+Al$_2$O$_3$+TiN + Ti(C,N) on the sialon substrate (SEM)
Figure 17. a),b) The structure of the Ti(Zr,N) multi-layer coating on a substrate of sintered carbides (SEM), and c) interface zone between coatings and sintered carbides WC substrate (HRTEM)

Figure 18. The structure of the multilayer (Ti,Al,Si)N coating on the sintered carbides substrate; High Angle Annular Dark Field (HAADF, TEM) tomography in scanning/transmission electron microscope also called Z-contrast (b) enables the accurate identification of individual layers, better than contrast in bright field (BF, TEM) (a); c) connection between the coating (upper layer) and the substrate of sintered carbides (lower layer) at the atomic scale (HRTEM)

multilayer coatings, being decisive for their cohesion and, as a consequence, as demonstrated, for functional properties, e.g. in case of some inserts leading even to a 50 fold enhancement in the durability of cutting tools (Fig. 21). Such results of investigations have become a basis for developing various own graded coatings, also with the fraction of a diamond like surface layer, where, in one of seven indirect zones with the amorphous structure Si₃N₄, the areas of
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**Figure 19.** The structure of the multi-component coatings: a) TiN+$\text{Al}_2\text{O}_3$+TiN+$\text{Al}_2\text{O}_3$+TiN on the $\text{Al}_2\text{O}_3$+TiC substrate, b) nitrides AITiCrN on the substrate of hot-working alloy tool steel X40CrMoV5-1, c) AITiCrN and additionally with surface diamond like carbon on the substrate of hot-working alloy tool steel X40CrMoV5-1 (SEM)

**Figure 20.** The structure of the a) DLC surface layer and connected zone between b, c) DLC and CrAlSiN coatings, d) CrN coating and X40CrMoV5-1 steel, e) local clusters of $\text{Si}_3\text{N}_4$ in amorphous CrAlSiN matrix area, f) the clusters of pure Cr in amorphous CrAlSiN matrix area (HRTEM)
Figure 21. The comparison of the characteristics of the different coatings on the different substrates a) critical load b) microhardness c) tool life in cutting tests on C45E steel with parameters as follows \( f=0.10 \text{ mm/rot}, \ ap=1 \text{ mm}, \ vc=400 \text{ m/min} \)

(Cr,Al,Sn)N and Cr clusters were discovered from the substrate side. The usefulness of the prepared coatings was confirmed by numerous application examples at a laboratory and semitechnical scale in machining and plastic working, particularly in the intensive plastic working process KOBO. The results of such research were published in books [117-127], in articles and at scientific conferences abroad and at home [128-227] in PhD theses [228-236], and by the awarded s on numero us fairs of innovation and invention [237-244].

6.3.2. PVD and CVD coatings on the nonferrous alloys

Research was performed for the deposition of PVD coatings on a substrate of alloys of different nonferrous metals, including brass, aluminium alloys, and especially magnesium
alloys. Coatings were produced in a cathodic arc evaporation process and in a plasma assisted chemical vapour deposition process on a substrate made of cast magnesium alloys of MCMgAl3Zn1, MCMgA16Zn1, MCMgAl9Zn1, MCMgA112Zn1 covered with the analysed coatings with the following configuration: Ti/TiCN/CrN, Ti/TiCN/TiAlN, Cr/CrN/CrN, Cr/CrN/TiN, Ti/TiSiN/TiSiN and Ti/DLC/DLC. Due to the specificity of the material such as magnesium alloys, and in particular due to their low melting temperature, the deposition process of coatings was performed in the range to 180°C using two methods: plasma assisted CVD (PACVD) and cathodic arc evaporation (PVD CAE). The PACVD process, in which a relatively low surface treatment temperature can be achieved, was used for producing DLC carbon coatings in the atmosphere of C2H2 acetylene and at the set pressure. Targets with the diameter of 65 mm cooled with water were used in the other method for coating deposition by PVD, containing pure metals of (Cr, Ti) and alloys of TiAl i TiSi. The highest surface inhomogeneity as compared to the surface of other coatings, is exhibited by Ti/TiCN/TiAlN and Ti/TiCN/CrN coatings, in which numerous precipitates of solidified droplets were found and depressions formed as the solidified droplets drop out after finishing a PVD process (Fig. 22). A morphology of the surface of the obtained DLC coating differs largely from the morphology of the surfaces obtained in classical high-temperature CVD processes whose characteristic feature is the existence of, e.g. a network of microcracks, waves surfaces or surfaces with a circular shape. A sharp transition zone between a substrate and a layer was identified as a result of fractographic tests in a scanning electron microscope (SEM). Ti/TiCN/TiAlN and Ti/TiCN/CrN coatings have a layered structure, with a clearly marked transition zone between a graded coating and an antiwear coating, achieved as a result of using separate sources of metal vapours. In the case of Cr/CrN/CrN, Ti/TiSiN/TiSiN coatings, no visible differences were identified on the cross section. A layer of titanium nitride in case of a Cr/CrN/TiN coating shows a structure similar to a column like structure. Multilayer Ti/DLC/DLC carbon coatings fabricated with the CVD method do not exhibit a clear transition zone between the particular coatings. In the area where a thin coating exists, the purpose of which is to improve layer adhesion to the substrate, it was possible to identify a characteristic, light, continuous titanium layer, as confirmed with an EDS analysis. The results of diffraction tests obtained using a high-resolution transmission electron microscope confirm that, according to the assumptions, it was possible to identify the following phases, i.e. TiN, CrN and graphite,
Figure 22. a) The breakthrough of multilayer coating 15 x Ti/CrN on the brass CuZn40Pb2 substrate (SEM), b) the topography of the Ti/Ti(C,N)/(Ti,Al)N coating surface on the MgAl6Zn1 cast alloy (TEM), c) the structure of the thin foil of the Ti/Ti(C,N)/(Ti,Al)N coating on the MgAl6Zn1 cast alloy (TEM), d) the interface zone between the Ti/(Ti,Si)N/(Ti,Si)N coating and the MgAl6Zn1 cast alloy substrate (TEM), e) the metal drop of the Ti/(Ti,Si)N/(Ti,Si)N on the MgAl6Zn1 cast alloy substrate (TEM), f) the microhardness of the coatings on the MgAl6Zn1 cast alloy substrate

which are present, respectively, in the surface layers of Ti/TiCN/TiAlN, Ti/TiCN/CrN, Cr/CrN/CrN, Ti/TiSiN/ TiSiN, Cr/CrN/TiN and Ti/DLC/DLC (Fig. 22), and their chemical composition was confirmed with a glow discharge optical spectrometer GDOES. The character of changes in the joint zone, i.e. a higher concentration of elements forming part of the substrate, with an accompanying abrupt reduction in the concentration of elements forming the coatings, may signify that a transition layer exists between the substrate material and the coating, improving the adhesion of the deposited coatings to the substrate, despite the fact that the results cannot be interpreted unequivocally in connection with the inhomogeneous evaporation of the material from the specimens’ surface. Moreover, the existence of a zone with linearly changing contents of elements forming part of the investigated coatings was
confirmed with an optical spectrometer, which indicates their gradient character. It was proven in all the cases of the analysed coatings fabricated on light alloys of magnesium, that they have a nanocrystalline character in the investigated areas. Droplets of solidified metal could also be observed inside the Ti/TiSiN/TiSiN coating. The general range of surface roughness of the coated materials is within 0.12 to 0.32 μm. Two groups can be differentiated based on the hardness tests conducted, i.e. coatings with microhardness of up to 2000 HV, of CrCrN/CrN, Cr/CrN/TiN and Ti/TiSiN/TiSiN type and a group of Ti/TiCN/CrN, Ti/TiCN/TiAlN and Ti/DLC/DLC coatings characterised by the values of the measured hardness of 2000-2700 HV, which also to a large extent correlates with the abrasive resistance of such coatings. The best abrasive resistance is exhibited by materials coated with DLC carbon coatings, and the average friction coefficient of DLC coatings is adequately lower by the order of magnitude in comparison to the friction coefficient of the other studied coatings, due to the presence of graphite. The measurement results of a friction path for DLC coatings were at a level higher even 70 times than friction path measurements for, e.g. a Cr/CrN/CrN coating. The highest values of the critical load $L_{C1}$ and $L_{C2}$ determined in a scratch test, and, therefore, the best coating adhesion to the substrate was achieved for a Ti/DLC/DLC coating produced on an MCMgAl9Zn1 substrate. The other critical load values measured, signifying coating adhesion to the substrate, do not exceed 14 N. Ti/DLC/DLC and Cr/CrN/ CrN coatings, for which the lowest corrosion current density value was measured, have the best electrochemical properties. Open pits were identified in the structure of the examined coatings and substrate made of cast magnesium alloys after a corrosion test on the basis of metallographic tests, with the lowest occurrence rate existing for Cr/CrN/CrN and Ti/DLC/DLC coatings. The results of such research were published in a book [118, 119, 121-123, 245], in articles [201, 246-257], and at scientific conferences abroad, and at home and in a PhD thesis [258].

6.3.3. The laser treatment of steels

Another part of the paper, also in the domain of surface engineering, concerns the results of long-term and very detailed investigations into the reinforcement of a surface layer of steel, especially tool and high-speed steel by laser surface treatment, in which a four element surface reinforcement mechanism was revealed. An eutectic structure, with the chemical and phase composition different than the substrate, occurs most often as a result of the cladding of carbide, nitride or oxide powders and remelting in the surface zone, as a consequence of which
a quasi composite graded material is created at the surface with precipitates of fine primary or dispersively arranged carbides melted into the remelted matrix, and intensive cooling conditions lead to the progress of a martensitic transformation of the matrix identified at an atomic scale using high resolution transmission electron microscope (HRTEM) (Fig. 23). Moreover, the selftempering of martensite takes place along with alloy carbides release.

**Figure 23.** The structure of the X38CrMoV5-3 (a-c, e, f) and X40CrMoV5-1 (d) hot working alloy tool steels adequately after the laser remelting, cladding and alloying using high power diode laser HPDL, a) the fine eutectic structure resulting from complete remelting and alloying with the WC carbides in result obtaining the quasi-composite structure on the surface layer (SEM), b) the primary alloyed carbides in the boundary between the remelted zone RZ and heat affected zone HAZ (SEM), c) the hardness profile after remelting and alloying with TaC carbides, e) M₆C type carbide in surface layer as the result of the remelting and primary crystallization during laser treatment (TEM), f) the martensite α’ in the surface remelted zone (HRTEM), f) the effect of the laser treatment of hot working alloy tool steel with different carbides types on the surface hardness HRC (heat treated: 52 HRC; remelted: 61,7 HRC; alloyed with TaC: 67,4 HRC)
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processes in the tempered martensite. Improved steel surface hardness was confirmed at a laboratory scale, e.g. tool alloy steels for hot working even by more than 15 HRC to approx. 67.5 HRC and such steels’ greatly improved resistance to abrasive wear and thermal fatigue, decisive for the practical usability of this technology. The laser treatment of sintered austenitic and dual phase surfaces of steel resistant to corrosion leads, in turn, to a greatly refined structure and is crucial for improved mechanical properties and corrosion resistance. The results of such investigations are published in a book [118], in foreign material encyclopaedias as chapters [34, 123, 259-262], as a chapter in a domestic monograph [125] and also in articles [263-319], and in the same speeches at scientific conferences abroad, and at home in PhD theses [320-323], and at home [324], and at the international fairs of innovation and invention [325-334].

6.3.4. The laser treatment of light metals alloys

An important part of the paper relates to laser surface treatment of Mg and Al cast alloys as enabling the production of a surface layer with a thickness of under a millimeter to several millimeters and with special functional properties: high hardness and wear resistance, while maintaining the properties of the substrate material. Laser power and the type of the powder cladded into the surface conditions the structure and properties of the light metal casting alloy’s surface layer (Fig. 24). The material, following laser treatment made with the High Power Diode Laser (HPDL), exhibits different properties from those made with other high-power lasers; especially, it features a more homogenous remelting area and smaller surface roughness. In this case, opposite to laser steel treatment, some of reinforcing mechanisms only occur, i.e. as a result of the cladding of carbide, nitride or oxide powders and remelting in the surface zone, a quasi composite graded material is created at the surface with dispersively arranged carbides, e.g. SiC, WC or TiC ceramic powder cladded into the remelted matrix, e.g. MgAl12Zn1 or AlSi7Cu or AlSi9Cu alloys and the structure of the solidified material after laser treatment with a zonal construction with diver-sified morphology related to the crystallization of magnesium or aluminium alloys. A strong circulation of the liquid metal took place during laser cladding. After the laser bundle remelting, rapid solidification of the initially liquid material took place. Multiple changes in crystal growth direction have been observed for these areas. In the area located on the boundary between the solid and liquid phase, minor dendrites occur on the main axes oriented along the heat disposal directions.
The thickness of the laser-formed surface layer is of vital importance in the determination of the material properties, period of use, and final application of the material obtained. It was also found out that the examined layers consisted of three subzones – the remelted zone RZ, the heat affected zone HAZ, and the substrate material. Both RZ and HAZ (depending on the concentration of aluminium in the magnesium matrix, laser power applied, and ceramic powder) are of different thickness and shape. It is possible, on the basis of the cross-section micrograph, to evaluate the thickness of the powder feed depth, which is ca. 120 μm in the case of SiC and ca. 1.2 mm in the case of WC powder. In the case of the WC powder, the particles are located mainly on the bottom of the remelted zone RZ. It was found out that, disregarding the ceramic powder used, in the laser power range from 1.2 to 2.0 kW, the porosity of the composite layers obtained increases, in comparison to that of the raw casting surfaces of magnesium alloys. It was proven that along with the growth of the power applied, the area of occurrence of both RZ and HAZ increased, as well as the face of weld changes. An intensive heating of the surface causes the creation of the uneven areas and hollows in the surface layer of the Mg-Al-Zn and Al-Si-Cu cladded using carbide particles. The formation of the melted material in the remelting lake depends on parameters such as the type of substrate, laser power, cladding rate, and the laser power. Some of the alloy and ceramic parts embedded in the remelting zone are evaporated at high temperature occurring during laser treatment, therefore the characteristic hollows appear on the remelting surface. It was also found out that in the laser-treated surface layer, there were no pores or cracks in the coating produced, nor did any defects or failures occur in this layer. Occasionally, discontinuity of the layer can be seen as
a product of the heat transfer process and may be neutralized by properly adjusted powder quality and powder feed rate. As a result of the metallographic observations, it was confirmed that the structure of the composite layers produced is free of defects, with distinct grain refinement containing evenly distributed dispersion particles of TiC, WC, SiC carbide, or Al₂O₃ oxide applied, which was also confirmed by EDS investigation in scanning electron microscope SEM. The alloys with laser cladded particles of vanadium carbide (their share in the remelting zone being slight) are the exception to the rule. It was found out on the basis of examinations at an atomic scale using a high resolution transmission electron microscope (HRTEM) that despite the lack of total solubility of the cladded silicon carbides in the remelted matrix of Al alloy, new phases are released, which did not exist in this alloy prior to laser treatment, i.e. β’ Mg₉Si₅ and Ω’ Al₅Mg₈Si₆Cu₂, in which the distribution of individual atoms in such phases precipitated in the impact zone was also determined caused by diffusion of elements creating them in this zone (Figs. 25, 26). The described technology has great

![Figure 25. The structure of the precipitated phases β’ (Mg₉Si₅) or Q’ (Al₅Mg₈Si₆Cu₂) in the heat affected zone HAZ (a-f) (HRTEM) as result of the diffusion caused by cladded silicon carbides distributed during the laser treatment of the AlSi₉Cu alloy, (e) the distribution of individual atoms in precipitates of the β’ or Q’ phase](image-url)
Figure 26. The structure of the phase $Al_6Mn$ in the heat affected zone HAZ precipitated during the laser alloying of the $AlSi9Cu$ alloy with the silicon carbides $SiC$ powder as the result of the diffusion caused by cladded $SiC$ in the aluminium alloy matrix; a) TEM, b), c) HRTEM

influence on the improvement of hardness on the surface of laser treated Al and Mg alloys, and especially by cladding the powder of hard phases, which is also significant for improved resistance to abrasive wear of the analysed alloys and is crucial for potential practical applications of the so treated light alloys. In this aspect PhD theses were prepared [335-337], the results were presented on international invention, innovation and technology fairs [338], in publications and speeches at domestic and foreign conferences [339-355], and also in books [118, 119], and also in chapters in high-profile encyclopaedia publications [34, 123, 259-262].

6.3.5. The laser surface microtreatment of multicrystalline photovoltaic silicon and nanostructural antireflective layers on solar cells

The presented paper is associated also with the use of laser technologies of great ecological importance embraces the examinations of laser surface microtreatment of multicrystalline photovoltaic silicon. The production of solar cells from silicon is preceded with a crystallization process that produces two forms: mono- and multicrystalline. In order to enhance the performance of solar cells, it is necessary to increase the active surface area of silicon used, called surface texturisation. The custom silicon surface texturisation technology allows to abandon the necessary costly usage of monocrystalline silicon for this purpose and allows to use multicrystalline photovoltaic silicon in lieu. The production process of multicrystalline silicon with a random crystallographic orientation of grains is faster and
cheaper and the solar cells produced from them offer lower efficiency than the cells produced of its monocrystalline form. The hybride technology of laser texturization of multicrystalline silicon with chemical etching in alkali solutions, for example, KOH or NaOH (with such etching being the only process used for monocrystalline silicon) ensures higher efficiency at relatively low cost (Figs. 27 and 28). The hollows formed due to the activity of a laser beam are secondarily filled with a molten and incompletely evaporated material. In order to increase the active surface area they are used a laser perpendicular grooves, which are then subjected to alkaline etching to remove the melted layer are made. A layer of damaged material is formed

**Figure 27.** The surface topography of multicrystalline silicon formed a) due to the laser texturisation (SEM), b) after the laser texturisation with chemical etching in alkali solutions (confocal laser microscope), c) the unique hollow after the hybrid laser and alkaline texturisation (SEM)

**Figure 28.** The structure of the silicon a) in atomic scale (HRTEM), b) the hollow formed due to the laser texturisation (TEM), c) the structure in the hollow formed due to the activity of a laser beam (TEM)
on the entire laser textured area immediately after creating a lattice of grooves. The areas between the flashes of the neighbouring grooves are covered with clotted material ejected from the grooves and with products deposited from the gaseous phase released when the material is evaporated outside the groove. The laser-treated material undergoing chemical etching allows the proper texture in the form of parallel grooves in two directions perpendicular to each other. The surface quality after the hybrid laser and alkaline texturisation can be examined using a confocal laser microscope. By employing a nonstandard texturization method with laser treatment, a homogenous texture can be achieved across the polycrystalline silicon surface. Transmission electron microscopy allows for the examination of the effect of laser treatment on the dislocation structure of silicon. In turn using the high resolution transmission electron microscope allows for the identification of the decomposition of atoms in silicon. The location of those atoms can be computationally predicted by Convergence Beam Electron Diffraction method and results can be compared with the image obtained in the microscope. The technology of laser texturization of polycrystalline silicon with chemical etching allows the user to improve the optical and electrical properties of photovoltaic cells prepared from them. The light reflection coefficient was examined for untextured wafers after removing the surface layer damage formed while cutting a silicon block. The optical properties of the laser textured wafers are highly dependable upon the laser processing conditions. If the surface of wafers is textured corresponding to the lattice of grooves, this causes a decrease in the light reflection coefficient as compared to the coefficient for untextured wafers. As the etching of laser textured wafers is progressing gradually, the Reff coefficient is clearly growing only after removing 80 μm. Laser polycrystalline silicon surface texturing deteriorates the electrical properties of photovoltaic cells made of wafers prepared this way. When the damaged layer of material is removed through etching, the efficiency of photovoltaic cells is boosted and is largest when a 80 μm thick layer has been etched. The application of laser technology in the manufacturing process of solar cells with high solar radiation conversion efficiency has become an inherent part of the modern photovoltaic technology. Laser texturization is one of the most promising methods of formatting a polycrystalline silicon surface.

Moreover, an innovative technology has been developed of selective laser micro-treatment in order to apply electric contacts using powder and silver paste, ensuring good electrode adhesion to the silicon substrate and minimisation in the resistivity value of the contact area of the silicon solar cell front electrode determining the filling factor (FF), and
consequently the efficiency of cell photovoltaic conversion (Eff), which also influences its economic performance (Fig. 29). The specific surface area of the front electrode is a compromise between electric and optical losses created as a result of its shading. Moreover, examinations were performed of nanostructural antireflective layers obtained by atomic layer deposition (ALD) and sol-gel method on silicon photovoltaic cells for further minimisation of the light reflection coefficient (Figs. 30, 31). Both, the ALD as well as sol-gel method allowed

**Figure 29.** The structure of the electric contacts on the silicon-solar cell front electrode obtained by the selective laser micro-treatment using paste of the silver nanopowder a) the structure of the electrode made with scanning speed 50 m/s i laser beam power 40,5 W (SEM), b) 3-D topography of the electrode surface sintered at 920°C (confocal laser microscope), c) structure of the electrode surface sintered at 945°C

**Figure 30.** The Al$_2$O$_3$ thin film deposited on a polished silicon substrate by spin coating technique with the 1000 rev/min spin speed, a) the structure of the surface (HRTEM), b) the thickness distribution map of the Al$_2$O$_3$ thin film using spectroscopy ellipsometer, c) the thickness distribution diagram of the Al$_2$O$_3$ thin film
to deposit homogenous thin layers of Al\textsubscript{2}O\textsubscript{3} with advantageous geometric features and desired optical and mechanical properties. Especially the layers deposited by the ALD method were characterised by high homogeneity within its whole volume, high transparency and advantageous anti-reflective properties. It is worth highlighting that a series of trial silicon solar cells was made and tested using specialist apparatuses, including a solar light simulator and corescan and sherescan (Fig. 32). The tests of mechanical properties of thin layers were

**Figure 31.** SAED image of the Al\textsubscript{2}O\textsubscript{3} thin film deposited by ALD method at 300°C after 830 cycles registered: a) at the time of the beam incident on the sample – the amorphous structure, b) after one minute beam interaction with the sample – the thermal nanocrystallised structure, c) the thickness distribution map of the Al\textsubscript{2}O\textsubscript{3} thin film deposited on a polished silicon substrate by ALD using spectroscopy ellipsometer

**Figure 32.** a) The surface topography of the Al\textsubscript{2}O\textsubscript{3} thin film deposited by ALD method (AFM), b) the effect of the thickness of the Al\textsubscript{2}O\textsubscript{3} thin film deposited by ALD method on the reflection, c) the light current-voltage characteristics of the efficiency of the produced solar cells. The highest efficiency was obtained for solar cell with antireflection coating deposited after 830 cycles at 300°C, Eff = 12.51%; reference cell efficiency (without antireflection coating) is equal 7.22%
also carried out. The results of investigations concerning the laser micromachining of multi-crystalline silicon and laser deposition of electric contacts and deposition of antireflective layers were presented in publications [356-390] and speeches at domestic and foreign conferences, and also in books [118, 119], in PhD theses [391-393], were presented at international fairs of innovation [394-401].
6.4. The nanostructural effects in solid materials

6.4.1. The nanostructural TWIP and TRIP mechanisms fracture counteracting

Another aspect pertaining to the paper relate to nanostructural effects in solid materials, and especially the prevention of cracking of new developed high-manganese austenite twinning induced plasticity TWIP and transformation induced plasticity TRIP steels Fe-Mn-Si-Al by twinning or/and martensitic transformation induced by the cold plastic deformation and their effect on the formation structural nanoelements influenced on mechanical properties and the strain energy per unit volume. Modern automotive industry sets very high requirements of both production technology as well as the steel used for car body, components and other reinforcing elements. All materials used for car bodies must fulfill the requirement of adequate tensile strength and stiffness with simultaneous good elastic properties, responsible for the easy shaping. Important is also strain energy per unit volume, or impact energy absorption and density of the material due to the reduction in fuel consumption. New developed high-manganese austenitic steels containing 0.1-0.6% C, 15-35% Mn and addition of 2-4% Si and Al type 25-1-3, 25-3-3 and 18-1-3 have a very high level of tensile strength (up to 1100 MPa) and high elongation (up to 60%) (Figs. 33-35). New generations of steel for car bodies require to use such heat-treatment, which will allow to provide a more complex structure. Due to proper heat treatment, austenitic structure in these steels is obtained, and during cold plastic deformation martensitic transformation or mechanical twinning are occurring. Thermomechanical treatment of high-manganese austenitic steel consists of heating to an austenitizing temperature of about 1100-1200°C, repeated rolling with defined speed and reduction rates due to structure fragmentation. After hot rolling several type of cooling could be used, i.e. cooling in water directly from the temperature of last deformation in order to freeze the steel structure, natural air cooling or cooling in water after isothermal holding for several seconds in the temperature of the last deformation in order to occur process of static recrystallization. The use of thermomechanical treatment and cooling under controlled conditions results in improved mechanical properties of the elements made of high-man-ganese austenitic steels. Proper selection of the chemical composition and manufacturing technology offers the possibility of produce steel which guarantee to provide a structure for the provision of favourable
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6. Applications of newly developed nanostructural and microporous materials …

Figure 33. The strain-stress curves continuous compression tests of the high-manganese austenitic X8MnSiAlNbTi25-1-3 TWIP type (a, b) and X11MnSiAl17-1-3 TRIP type (c) steels in the temperature of 850 (a, c) and 1050°C (b) with 0.1, 1 and 10 s⁻¹ strain rate obtained using Gleeble 3800 thermo-mechanical simulator.

Figure 34. The results of the strain energy per unit volume of the high-manganese austenitic X8MnSiAlNbTi25-1-3 of the TWIP type steel a) after static tensile tests at room temperature and after the successive cold deformation, b) after static tensile tests in reduce temperature of deformation to -25°C and -70°C, c) after dynamic tensile tests with strain rate (500 s⁻¹) and (250 s⁻¹).

Figure 35. The results of the strain energy per unit volume of the high-manganese austenitic X11MnSiAl17-1-3 of the TRIP type steel a) after static tensile tests at room, cryogenic and elevated temperature, b) after dynamic tensile tests with strain rates 0.01, 250, 500 and 1000 s⁻¹.
combination of mechanical and plastic properties of steels. High-manganese Fe-Mn-(Al, Si) steels provide an extensive potential for automotive industries through exhibiting the two possible mechanisms for the fracture counteraction. In high-manganese TRIP, TWIP & TRIPLEX steels, the cracking or fracture does not take place during deep drawing, because of twinning induced plasticity (TWIP) (Figs. 36, 37) and transformation induced plasticity (TRIP) (Figs. 38-41) mechanisms. An important contribution is a description of structural mechanisms of the progress of both transformations and structural changes on the basis of numerous detailed structural tests, especially at an atomic scale using a high resolution transmission

**Figure 36.** The structure of the high-manganese austenitic X8MnSiAlNbTi25-1-3 of the TWIP type steel after static tensile test; a) bright field; b) dark field of the twins in austenite matrix with solution of the diffraction pattern, c) the twins inside the martensite α’ lath (TEM)

**Figure 37.** The structure of the high-manganese austenitic X8MnSiAlNbTi25-1-3 of the TWIP type after mechanical twinning induced by the cold working and after the successive cold deformation (HRTEM): a) the system of the parallel twins in the austenitic matrix, b) unique twin in the austenitic matrix, c) the system of crossed twins in the austenitic matrix
electron microscope (HRTEM). Results obtained for high-manganese austenitic steels with the properly formed structure and properties in the thermomechanical processes indicate the possibility and purposefulness of their employment for constructional elements of vehicles, especially of the passenger cars to take advantage of the significant growth of their strain energy per unit volume which guarantee reserve of plasticity in the zones of controlled energy absorption during possible collision resulting from activation of twinning for TWIP steels, supported with martensitic transformation to fabricate martensite $\alpha'$, and $\varepsilon$, induced cold working as the fracture counteraction factor. This is largely critical to the significant growth of

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure38.png}
\caption{The structure of the high-manganese austenitic X11MnSiAl17-1-3 of the TRIP type steel after static tensile test; a) bright field, b) dark field from (202) plain of the martensite $\alpha'$, c) diffraction pattern; solution of the diffraction pattern}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure39.png}
\caption{The structure of the high-manganese austenitic X11MnSiAl17-1-3 of the TRIP type steel after dynamic tensile test with the strain rate 1000 s$^{-1}$; a) bright field, b) dark field from (200) plain of the martensite $\alpha'$, c) diffraction pattern with the solution of the diffraction pattern}
\end{figure}
the passive safety of these vehicles' passengers. The TRIP, TWIP and TRIPLEX type steels with designated strain energy per unit volume after the cold deformation equal respectively 263.33, 227.50 and 258.85 MJ/m$^3$. Even higher growth of energy per unit volume yield substantially increases a deformation rate, even to 529.49 MJ/m$^3$ for TWIP type steel and to 481 MJ/m$^3$ for TRIP type steel. The results of investigations concerning high-manganese austenitic steels were presented in publications [402-421], and speeches at domestic and foreign conferences, and in chapter in high-profile encyclopaedia publication [422], in PhD theses [423, 424], and were presented at the international fairs of innovation and innovativeness [425-433].

**Figure 40.** The high-resolution structure of the high-manganese austenitic X11MnSiAl17-1-3 of the TRIP type steel after dynamic tensile test with the strain rate 1000 s$^{-1}$ with the magnification obtained using Fourier Transform of martensite $\alpha'$ (HRTEM)

**Figure 41.** The austenitic structures of the high-manganese austenitic X11MnSiAl17-1-3 of the TRIP type steel with intersected $\varepsilon$ martensite plates obtained after hot-rolling with a true strain 0.29 (a,b) and after static tensile test (c) (TEM): a) bright field, b) dark field, c) the twins inside the $\varepsilon$ martensite plate
6.5. The special micro and nanocomposite materials for use in regenerative medicine and regenerative dentistry

6.5.1. The microporous materials and composites, porous implant-scaffolds and innovative generation of biological-engineering composite materials for regenerative medicine

The results of research of the development of special micro and nanocomposite materials designed mainly for use in regenerative medicine and regenerative dentistry are of great importance in view of the paper. This group of developments, forming part of the evaluated accomplishment, includes hybrid additive technologies of structure and properties formation of newly created metal porous materials with the average size of micropores of 100-600 nm using selective laser sintering/laser melting (SLS/SLM) of titanium and TiAl6V4 and Co-Cr alloys and steel resistant to corrosion of the 18-8 grade combined with chemical treatment, by surface etching, in mixtures of HF + H2O (preferably by 8 min) or HCl + H2SO4 (preferably by 6 min at 100°C) of porous skeletons and the elaboration of innovative manufacturing technologies of composite materials by depositing an internal surface of micropores, e.g. with TiO2+TiN+Ti2N+αTi(N), natural protein, polysaccharide and synthetic polymers, hydroxyapatite (HA), composite materials: collagen + hydroxyapatite CaP-polymer tricalcium phosphate (TCP)-polycaprolactone (PCL), hydroxyapatite HA/poly(ester-urethane)(PU), by the atomic layer deposition (ALD) method or by methods of immersion, pressing, sol-gel method and by infiltration in case of creating microskeleton nonporous composite material (Fig. 42). Detailed technologies were established, and mechanical properties were examined in detail of the so manufactured microporous materials, microporous composite materials and microskeleton composite materials. Important in this scope are the results of the international BIOLASIN project [434]. The investigations carried out formed the basis for elaborating constructional assumptions, methodology of constructional, material and technology design of several types of medical devices which are to be applied in regenerative medicine and implantology. Completely innovative and patent protected implant scaffolds were developed, as devices used for implantation to replace the bone pieces removed surgically due to a disease, usually cancerous disorders or inflammatory conditions. An implant scaffold is comprised of a solid zone, typical for the implants used to date, and a porous hybrid zone fulfilling the functions...
**Figure 42.** The porous titanium implants-scaffolds in dental application: a) the palate model after conversion with a porous structure with multiplied unit cells, b) the surface topography of the scaffolds produced by SLS method (SEM), c), d) after etching in a hydrochloric acid and sulphuric acid solution for 6 minutes (SEM), e) the roughness of the implant-scaffold surface $R_a$ (LCM), f) the thin layer of PMMA polymer deposited onto the lower part of the porous scaffold-implant (SEM)

of scaffolds, with the size of micropores most often within the range of 100-600 µm and a varied shape (Fig. 43). Implant scaffold integration with joint implants is possible, and also deposition of bioactive material onto the surface of micropores forming the porous zone, with a thin layer of up to 500 µm thick. The porous zone in an implant scaffold ensures appropriate osteosynthesis of bone implants with bone stumps (Fig. 44) or, respectively, in the case of a structure integrated with joint implants with bone elements left after the removal of joints, enables the living tissue to outgrow across the porous zone after implantation, creating a durable and firm joint of an implant with a living tissue. Biological works as well as the implementation of such technologies, have been launched with the participation of potential manufacturers. A manufacturing method of a bone implant scaffold is established on the basis
of the data acquired using medical imaging methods, e.g. computer tomography, according to the size and shape of a patient’s bone loss, e.g. the size and shape of a bone loss in the forearm bone. A virtual model prepared in the format, e.g. STL, by means of appropriate software, e.g. AutoFab, forms a basis for establishing a virtual technological model of an implant scaffold, i.e. an implant which, in the place of connection with bone stumps, features a porous zone designed with a method of repeatable unit cells. The so developed virtual implant scaffold model is a basis for controlling a technological machine where a ready real bone implant
scaffold is produced with the selective laser sintering SLS method. In case of personalised implant scaffolds, their shape is adjusted to the shape and size of a patient’s bone loss located in different locations in a human body. Analogous is the manufacturing method of other implant scaffolds and prostheses, in particular such finding an application in regenerative dentistry and regenerative craniofacial surgery, including personalised dental implant scaffolds employed for treating tooth and bone losses in the area of a dental or craniofacial system. The fabrication and deposition of tissue cultures of osteoblasts by tissue engineering methods is associated with tissue transplantation, matrix implantation, implantation of cells with a matrix, the culturing of xenogenic and autologous cells at the stage of clinical activities and is entering the phase of trials. The participation of implantology doctors in a research team will allow to implement the created original implant and prosthetic systems enabling, respectively, to produce individually an implant scaffold of a tooth with its geometry reflecting the shape of a post-extraction alveolar bone with integrated abutments, using a single-procedure innovative surgical procedure of tooth extraction and implantation without having to bore in the periodontal tissue bone of the upper or lower jaw or to use typical implant scaffolds ensuring substantial improvement of osseointegration of such a medical device as compared to classical implants, while maintaining the classical implantation method, and also implant scaffolds of the craniofacial bone designed according to a patient’s individual anatomical features and to the extent of the planned surgery. The combination of results in the field of the development of special micro and nanocomposite materials and additive technologies of metal microporous materials together with investigations of polymer nanofibers achieved by electrospinning, set a basis for creating, apart from rigid porous implant scaffolds, an innovative generation of rigid and elastic biological and engineering composite materials for regenerative medicine. A rigid biological and engineering composite, TiAl6V4 titanium alloy or pristine titanium air, is used for losses created on the surface of a bone in the form of a new biologically active generation of plate implant prostheses. The said biological engineering composite has bactericidal properties and features. A composite of titanium alloy TiAl6V4 or pristine titanium air is fabricated by selective laser sintering of TiAl6V4 titanium alloy powder or pristine titanium, ensuring continuous porosity with the dimensions, preferably, of 300-800 nm, and air acts as a matrix. A reinforcing skeleton made of selectively sintered TiAl6V4 titanium allot powder or pristine titanium is a carrier of natural biologically active cells, cultured on its surface with tissue engineering methods, and may also notably act as a carrier of medicines, e.g.
anti-inflammatory medicines or bactericidal agents, e.g. silver. Composite biological engineering devices may be used for regeneration of, among others, soft tissues such as cartilage tissue, skin, for treatment of burns, cancerous lesions or for regeneration of bone losses. The results of such research were published in articles [435-442] and were presented at several international scientific conferences, and were also submitted to patent claims [443-446], were included to PhD thesis [447], and at international fairs of rationalisation and innovation [448, 449].

6.5.2. The polymer nanofibers and nanocomposites achieved by electrospinning

As part of the paper, important research into polymer nanofibers achieved by electrospinning can be distinguished, especially concerning the creation of long-resorbable composite nanofibers with a bioactive core and a bactericidal shell (Fig. 45). The selection of the external shell components can be controlled through selection of shell thickness, application of a polymer with smaller molecular mass, by mixing with a polymer material with shorter resorption time. The applicability of polymer fibers in medicine depends on biocompatibility and nontoxicity of the material applied, which is influenced by the chemical purity of the materials applied and the toxicity of the input solvents. The potential toxicity of nanofibers should therefore be eliminated, starting with selection of materials used for obtaining solutions (Fig. 46). Many other factors fundamental for the quality and properties of polymer nanofibers need to be taken into account to create single- and double component nanofibers. Two

![Figure 45. a) Nanofibers electrospinning schematic, b) simplified co-axial electrospinning](image-url)
solutions need to be used in co-axial electrospinning. Solvents with moderate volatility, such as, e.g. a mixture of formic acid and hydrochloric acid, support the transformation of a solution under the influence of an electrostatic field in the form of a nanofiber, as their evaporation time equals the time necessary for its production. In case of solvents with considerable volatility, e.g. a mixture of chloroform and methanol or tetrahydrofuran and dimethyl sulfoxide, they support the fabrication of microfibers, as the time, in which solvents are evaporated, is shorter.

The type of the collector used may also influence the solvent evaporation rate. In the case where a collector is flat, the fibers tend to stick together, which is not the case if a rotating collector is used, in connection with the movement of the gas over the surface of such a collector, in particular as a result of synergic interaction of rotation motion of the cylinder and a gas flow system in the chamber. During electrospinning, the solvent is evaporated in the space between the electrodes, and solvent vapours coming from the solution constantly enter the gas situated between electrodes. In case of a flat collector, gas flow over its surface is insufficient to evacuate vapours of the solvents created between the flat collector and nozzle, even despite an installed system of evacuation of volatile products from a working chamber. For this reason the fibers stick together if a flat collector is used. The type of the collector used is also decisive for the spatial arrangement of fibers. The higher isotropy of fibers is obtained by using flat collectors, whereas fibers anisotropy when using rotating collectors is increasing with the rotation speed of the collector. The properties of the solutions in which nanofibers are

**Figure 46.** The comparison of influence of solvents’ properties on the structure of the obtained polycaprolactone PCL fibers from the different solutions: a) mixture of formic acid and hydrochloric acid at a rate of 70:30, b) mixture of tetrahydrofuran and dimethyl sulfoxide at a rate of 70:30, c) mixture of chloroform and methanol at a rate of 70:30 (SEM)
manufactured, including viscosity and conductivity, are closely linked to the type and properties of solvents. The nanofibers obtained from a polymer material with higher molecular mass (70,000-90,000 g/mol) are thinner as compared to those of the fibers obtained using polymer with considerably smaller molecular mass (45,000 g/mol). If electrostatic voltage is indeed applied in the both mentioned solutions, a Taylor cone is created, however, it is more stable in case of a solution with higher molecular mass as the interactions between macroparticles are increased. This, on the other hand, translates into the intensification of friction forces created between macroparticles and is supportive to the fabrication of fibers with their diameter similar to each other and to a decreased number of defects such as beads on the surface of fibers. The opposite situation takes place when the molecular mass of polymers is decreased. The destabilisation of a Taylor cone with the shorter length of a macroparticles chain is conducive to the formation of fibers with different diameter.

The diameter of the fibers obtained may change after introducing additives, e.g. silver nitrate and chitosan, which are enhancing electric conductivity (Fig. 47). In the first case it is related to the presence of an atom of silver in a silver nitrate particle, while in the second case

**Figure 47.** Geometrical characteristics of core-shell composite obtained from: a) a coating solution of 10% polycaprolactone without additives and inner core solution of 4% of polycaprolactone without additives (TEM), b) the polycaprolactone solution with a 3% contribution of silver nitrate in the coating and 10% polycaprolactone solution containing no additives in the core (TEM), c) double-component fibers obtained by dissolving PCL granulate with the molecular mass of $M_w = 70,000-90,000$ g/mol using 10% mixture of hydrochloric acid and formic acid with mass ratio of 70:30 with addition of 25% of AgNO$_3$, photographs taken after precipitation of silver in 2% ascorbic acid solution (SEM)
with the presence of polar chemical groups chitosan is made of, and which includes – acetamido-2-deoxy-β-D-glucopyranose particles and 2-amino-2-deoxy-β-glucopyranose groups containing, notably, an atom of nitrogen. Such groups support the formation of hydrogen bonds, thus impacting the change of electric conductivity of the solutions obtained. When AlphaSan is introduced into a solution, despite containing 10% of silver, it reduces the electric conductivity of solutions. By introducing any of the additives, the viscosity of solutions is increased due to a higher density of the solution achieved. The higher viscosity of the solutions obtained related to the activity between macroparticles, does not translate into smaller diameter of the fibers obtained. Such additives are impacting, however, the BET, Langmuir specific surface area and the area of pores. If chitosan is introduced, the specific surface area is decreased related to a larger diameter of the fibers produced. The opposite tendency occurs when the fraction of AlphaSan and silver nitrate is increased, leading to an increase in the specific surface area of fibers, as agglomerates of AlphaSan and silver crystals on the surface of fibers exist. The Polymer nanofibers produced by electrospinning applied in regenerative medicine additives introduced have also substantial influence on the antibacterialness and antifungalness of nanofibers (Fig. 48). Silver nitrate and AlphaSan show high efficacy in fighting Gram+, Gram- bacteria and fungi, and macromolecular chitosan does not show antibacterial and antifungal properties. The additives mentioned are influencing the bioactive properties differently, by interacting with the cells of Normal Human Dermal Fibroblasts (NHDF). The highest bioactivity is characteristic for nanofibers containing an additive of low molecular hyaluronic acid, whilst macromolecular hyaluronic acid is of much lesser importance. The analysis made clearly shows a clear development trend of all the world markets of biomaterials and various medical products, and projections are very promising. Polymer nanofibers create significant applicational possibilities in this field. The outcomes of own investigations are serving this purpose. The composite materials components applied, including solvents, bacteriocidity and bioactivity, may find their applications in tissue engineering as membranes in controlled regeneration of bone tissue, as carriers of medicinal agents in bone surgery, as implantable surgical meshes and as scaffolds for a tissue culture. In turn, the composite coreshell nanofibers, by combining the antibacterial properties of the coating with bioactive properties of the core, are attractive materials for three dimensional tissue scaffold. Such materials can be used as a carrier of medicine, a treatment of hard healing
wounds, invasive surgery, neurosurgery, as a substrate for the culturing of a retina, material to reconstruct nerves and in dentistry or oncology, to replace the natural tissue removed because of a cancer with the possibility of applying a therapeutic agent, e.g., an antibiotic or a medicine used in cancer therapies, released after the dissolution of the coating of nanofibers. The results of such research were published in a book [450], in an articles [451-457] and were presented at international scientific conferences [458-462], and in patents applications [463, 464], were included to PhD thesis [465], and were presented at international fairs of rationalisation and innovation [466-468].
6.6. Final remarks

Several thoughts of, notably, Noble Prize Winners can be quoted at the end of this articles. It was the author’s endeavour to present here original achievements and own input into material science, nanotechnology, surface engineering and biomedical engineering. The inspiration were the words of Prof. A. Einstein (1879-1955), a Nobel Prize Winner in Physics in 1921, “I believe in intuition and inspiration. Imagination is more important than knowledge. For knowledge is limited, whereas imagination embraces the entire world, stimulating progress, giving birth to evolution. It is, strictly speaking, a real factor in scientific research”. But on the other hand, another message can be brought by the words of a French encyclopaedist, D. Diderot (1713-1784), that “Observation collects facts; reflection combines them; experimentation verifies the result of that combination. Our observation of nature must be diligent, our reflection profound, and our experiments exact.” For this reason, imagination setting the objectives of our investigations relies, each time, on a cycle of diligent laboratory tests. One should keep in mind that “The key to success is to risk thinking unconventional thoughts”, as T.G. Baylis Dr hc (born in 1937), an English inventor of a windup radio, said. An accident is often decisive for choosing the topic of own quests, often also scientific quests, or the necessity to choose the scope of research which is possible due to external circumstances, e.g. granting or not a research project. “Because we do not find what we look for, we should not resign from looking for what we can find” said G.W. Leibniz (1646-1716), a German philosopher, mathematician, physicist and diplomat. However “There is not greater fun than studying the nature”, as is captured beautifully by the words of J.W. von Goethe (1749-1832), a German poet, playwright, prose writer, scientist, politician. Prof. R.P. Feynman (1918-1988), a Nobel Prize Winner in Physics in 1965, noticed in the already quoted renown lecture in Pasadena, CA, USA of 1959 “(…) The principles of physics, as far as I can see, do not speak against the possibility of manoeuvring things atom by atom (…)”. “The price of abandoning is much higher than the cost of committing an error.” This sentence spoken by J. Eckhart von Hochheim (about 1260-1327/1328), better known as the Master Eckhart, a German mystic, philosopher and theologian, Dominican, indicates that all important initiatives should be taken, even if there is a presumption that the task can be performed even better. It is no surprise that the challenge posed by Prof. R.P. Feynman was addressed immediately, and nanotechnology has developed so dynamically. Prof. R.E. Smalley (1943-2005), a Nobel Prize Winner in
Chemistry in 1996 said “(...) We are about to be able to build things that work on the smallest possible length scales, atom by atom, with the ultimate level of finesse. (...)”. This substantiates the selection of the underlying, merit based topic of the article connected with nanotechnology and microporous materials. On the other hand, to clarify all structural mechanisms being the cause of the described advantageous changes in the properties of the examined materials, it is necessary to use modern advanced research methods of material engineering, and especially transmission electron microscopy, including HRTEM. In his Noble ceremony lecture, Prof. E. Ruska (1906-1988), a Nobel Prize Winner in Physics in 1986, shared his reflection “(...) We should not, therefore, blame those scientists today who did not believe in electron microscopy at its beginning. It is a miracle that by now the difficulties (in the area of electron microscopy) have been solved to an extent that so many scientific disciplines today can reap its benefits (...)". The aim of the paper is to stimulate the imagination, so that everyone of the readers can realise the direction in which goes the development of materials science and engineering, and that is where we should look for individual paths of the scientific development. Prof. A. Einstein claimed that we should constantly set new challenges. “Learn from yesterday, live for today, hope for tomorrow. The important thing is to not stop questioning.” A question was therefore asked, whether there is synergy between the achievements of Prof. R.P. Feynman, who described the essence of nanotechnology as the first one in the World’s history in 1959 and Prof. E. Ruska, who invented the electron microscope in 1931. The article presents numerous examples of own research, broadly supported by transmission microscopy and scanning electron microscopy methods. A thought was shared by W. Szymborska Dr hc (actually M.W.A. Szymborska 1923-2012), a Nobel Prize Winner in Literature in 1996: “Any knowledge that does not lead to new questions, becomes in a short time dead.” Hence each new result achieved led to new considerations. Prof. A. Einstein for mulated in a very imaginative way the attitude towards challenges that the modern times bring. “Life is like riding a bicycle. To keep your balance you must keep moving.” Whereas J. Galsworthy Dr hc multi (1867-1933), a Nobel Prize Winner in Literature in 1932 remarks that the fate of our future depends on our own activity. “If you don't think about the future, you cannot have one.” Technological progress in the future requires therefore intense research and development works now. Prof. H.W. Kroto (1939-2016), a Noble Prize Winner in Chemistry in 1996, encourages: “When choosing something worth doing, never give up and try not to let anybody down”. The Pope, Saint John Paul the 2nd
L.A. Dobrzański (actually Prof. K.J. Wojtyła 1920-2005) claimed that “The future starts today, not tomorrow”. This is a reason why the problems we perceive today cannot be postponed to the future. What is more “You cannot fight the future” as W.E. Gladstone (1809-1898), the then Prime Minister of the Great Britain, said. The possibilities of setting up things atom by atom, which were predicted by Prof. R.P. Feynman about 55 years ago, now become a normal technological practice including Materials Science and Engineering, and an attempt was made in this article to demonstrate it. Electron microscopy, especially high resolution transmission electron microscopy, made available as a research tool by Prof. E. Ruska more than 30 years earlier and now extremely modernised, allows to explain the basics of these technologies. It is thus demonstrated that there is a clear synergy between the points of view of Professors R. Feynman – a historically first in nanotechnology and Prof. E. Ruska – an inventor of the electron microscope. The general thesis of the paper was thus proved. For this reason, a topic of the opening lecture of the International Scientific Conference Winter-AMME’2015 was “Electron microscopy as a synergic tool of the nanotechnology development”, and the content of this article was presented there.

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References


6. Applications of newly developed nanostructural and microporous materials …


6. Applications of newly developed nanostructural and microporous materials …


M. Bilewicz (Advisor L.A. Dobrzański), Composite polymer layers manufactured sequentially by injection moulding with reciprocating flows, PhD theses, Silesian University of Technology, Gliwice, 2011 (in Polish).

M. Górniak (Advisor L.A. Dobrzański), The influence of organophilization of surface of halloysite nanotubes and montmorillonite nanoplates on properties of polymer, PhD theses, Silesian University of Technology, Gliwice, 2014 (in Polish).


B. Nieradka-Buczek (Advisor L.A. Dobrzański), Influence of copper nanowires on thermal conductivity and absorption of radiation of polymer nanocomposites, PhD theses in progress, Silesian University of Technology, Gliwice (in Polish).


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6. Applications of newly developed nanostructural and microporous materials …


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6. Applications of newly developed nanostructural and microporous materials …


[229] W. Kwaśny (Advisor L.A. Dobrzański), The structure and properties of coatings obtained in PVD process on sintered high speed steel, PhD theses, Silesian University of Technology, Gliwice, 2001 (in Polish).


[231] D. Pakula (Advisor L.A. Dobrzański), Structure and properties of PVD and CVD multilayer coatings resistant to abrasion on nitride ceramic tool Si₃N₄, PhD theses, Silesian University of Technology, Gliwice, 2003 (in Polish).


6. Applications of newly developed nanostructural and microporous materials …


6. Applications of newly developed nanostructural and microporous materials …


M. Bonek (Advisor L.A. Dobrzański), The structure and properties of surface layers obtained as a result of laser treatment of hot-work alloy tool steel, PhD theses, Silesian University of Technology, Gliwice, 2003 (in Polish).


M. Piec (Advisor L.A. Dobrzański), Structure and properties of laser remelted and alloyed surface layers of X38CrMoV5-3 tool steel, PhD theses, Silesian University of Technology, Gliwice, 2005 (in Polish).

E. Jonda (Advisor L.A. Dobrzański), The effect of laser remelting and alloying on the structure and properties of surface layers of X40CrMoV5-1 steel, PhD theses, Silesian University of Technology, Gliwice, 2007 (in Polish).

M. Bonek, L.A. Dobrzański, Gradient surface layers on tool steels performed by laser surface alloying process, Bronze Medal on 7th International Warsaw Invention Show IWIS 2013, Warsaw, Poland, 8-10.10.2013.


M. Bonek, L.A. Dobrzański, Gradient surface layers on tool steels performed by laser surface alloying process, Gold Medal on 16th Moscow International Salon of Inventions and Innovation Technologies «Archimedes» Moscow, Russia, 2-5.04.2013.

M. Bonek, L.A. Dobrzański, Gradient surface layers on tool steels performed by laser surface alloying process, Gold Medal on 5th Fair International Inventions and Innovations Exhibition FINEX 2013, Teheran, Iran, 4-7.02.2013.


J. Domagała-Dubiel (Advisor L.A. Dobrzański), The structure and properties of laser remelted and melted layers on Mg-Al-Zn cast alloys, PhD theses, Silesian University of Technology, Gliwice, 2010 (in Polish).

S. Malara (Advisor L.A. Dobrzański), Structure and surface properties of Mg-Al-Zn cast alloys with laser remelted ceramic particles, PhD theses, Silesian University of Technology, Gliwice, 2010 (in Polish).

W. Pakiela (Advisor L.A. Dobrzański), Influence of laser remelting of silicon and tungsten carbides on the structure and properties of surface layer of Al-Mg alloys, PhD theses, Silesian University of Technology, Gliwice, 2015 (in Polish).


6. Applications of newly developed nanostructural and microporous materials …


[426] L.A. Dobrzański, W. Borek, High-manganese steels with high strain energy per unit volume for automotive industry, Silver Medal on 16th Moscow International Salon of Inventions and Innovation Technologies «Archimedes» Moscow, Russia, 2-5.04.2013.


[432] L.A. Dobrzański, W. Borek, TWIP steels with high strain energy per unit volume for automotive industry, Bronze Medal on 9th International Warsaw Invention Show IWIS 2015, Warsaw, Poland, 12-14.10.2015.


6. Applications of newly developed nanostructural and microporous materials …


[465] A. Hudecki (Advisor L.A. Dobrzański), Composite nanofibers with a bioactive core and an antibacterial coating on the tissue scaffold, PhD theses, Silesian University of Technology; Gliwice, 2015 (in Polish).

