



The examples of the research of the nanostructured engineering materials and the concept of the new generation of highly innovative advanced pioneering nanostructured composite materials

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ABSTRACT

Purpose: The first part of the paper presents the outcomes of a dozen of own researches in the field of nanotechnology, carried out over the last several years. The second part of the paper presents the new Author's ideas on the predicted development of the new generation of highly innovative advanced pioneering nanostructured composite materials through the interaction of the extended nanoengineering components.

Design/methodology/approach: Each of the selected topics was briefly described, with special emphasis laid on the issue of structural and phase transitions, which are generally taking place in the newly created original engineering materials and their related original technologies. Each of the descriptions was arbitrarily illustrated with a metallographic photographs made with electron microscopes, most often a transmission microscope, mainly a high-resolution or scanning microscope. The scientific objective of the planned research is to recognise and explain the relevant structural mechanisms, in each case, of synthesis and/or production and formulation of the structure and properties of a new generation of pioneering nanostructured composite materials through the interaction of the extended nanoengineering components and to characterise and model their structure and properties depending on the compositional, phase and chemical composition and the applied synthesis and/or production and/or processing processes.

Findings: The research covered by the paper is pursued in the field of nanotechnology as the designing and manufacture of structures with new properties resulting from a nanosize. The planned research is of priority cognitive importance as theoretical considerations, indicate a great need to intensify scientific research to develop new groups of materials with completely unexpected foreseeable effects, resulting from the use of the extended nanoengineering components for manufacturing super advanced nanocomposite materials. Phenomena and processes at a nanoscale can be better recognised by producing a new generation of functional nanostructural materials.

Practical implications: The measurable scientific effects concern the cognitive nature of the planned research and are associated with the determination of: the effect of compositional, phase and chemical composition, of the newly developed technologies of fabrication and surface micro-treatment inside pores, of internal precipitated phases or nanoinclusions or surface treatment of micropores in order to apply nanomaterials enabling the improvement of specific properties on the structure and properties of the newly created nanocomposite materials with the extended nanoengineering components ensuring the improvement of specific properties and the modelling of the structure and properties of the researched newly created nanocomposite materials using artificial intelligence methods. The research will comprise the fabrication of materials with new unforeseeable properties fulfilling multiple functions.

Originality/value: Phenomena and processes at a nanoscale can be better recognised by producing a new generation of functional nanostructural materials (physicochemical basis of nanomaterials and nanostructures synthesis, with controlled architecture and properties, engineering of atomic and molecular bonds, models and theories explaining the properties of nanomaterials, surface phenomena, self-assembly phenomena in nanomaterials and nanostructures synthesis, magnetic phenomena in semiconducting and metallic nanostructures).

Keywords: Nanotechnology; Nanostructural materials; Nanostructured composite materials; Structural mechanisms; Phenomena and processes at a nanoscale

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MATERIALS MANUFACTURING AND PROCESSING

1. The contemporary significance of nanotechnology and prospects development research of the nanostructured materials and technologies for their fabrication

In accordance with the recommendations of the European Commission, *“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%”* [1]. 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 $60 \text{ m}^2/\text{cm}^3$ [2]. 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 $60 \text{ m}^2/\text{cm}^3$. *“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”* [3]. At present, nanotechnology determines a whole array of techniques and methods of manufacturing various objects or their elements with nanometric sizes, i.e. at the level of single atoms or particles at the level of linear sizes, at least in one direction 1-100 nm. The term *“nanotechnology”* was used for the first time in 1974 by a professor of the Tokyo University of Science, Norio Taniguchi (1912-1999) [4]. Richard Feynman (1918-1988), a Noble Prize winner in Physics in 1965, is, however, commonly regarded to be a father of nanotechnology. He gave a lecture on the 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 [5]. The term *“nanotechnology”* was applied by K. Eric Drexler in 1986 in the book [6], hence this term was popularised

and promoted the technological significance of nano-scale phenomena and devices, also in another book [7], which received the Association of American Publishers award for Best Computer Science Book of 1992. A 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 [8]. The documents provided that ***“Nanotechnology is science, engineering, and technology conducted at the nanoscale, which is about 1-100 nm”***[9]. It is therefore commonly thought that nanostructural materials are such where the particles, grains or other structural components existing in such materials have the size of less than 100 nm, at least in one direction, while nanomanufacturing is regarded as the manufacturing and treatment processes of such materials. The research in this area concerns the basic understanding and control of a matter at a nanoscale and translating this knowledge to application solutions based on nanotechnology and accelerated transition from elementary and development research to innovations and ensuring the development of future innovations.

The research covered by the paper is pursued in the field of nanotechnology as the designing and manufacture of structures with new properties resulting from a nanosize [10]. Nanotechnology is regarded as one of the key fields of science in the 21st century and the main driving force of economic and technological advancements in the nearest years [11-16]. The development of nanotechnology will relate to all the aspects of our reality and will surely contribute to industrial revolution. For this reason, nanotechnology holds great promise of developing products with unmet and unexpectedly advantageous physiochemical properties. The value of the global market of nanotechnological products is estimated by the BCC to be 15.7 billion USD in 2010, and the compound annual growth rate until 2015 was estimated to be approx. 11.1%, including nanomaterials for commercial applications strongly established at the market [17]. Such products include products for solar protection based on nanoparticles and thin-layer films for catalytic converter, such as nano-thin-film solar cells, nanolytographic tools and electronic memory at a nanoscale. The sales of nanodevices will be rising at a moderate rate. The compound annual growth rate in this industry in 2015 was 45.9%. Nanomaterials represented the highest share of the nanotechnological market in 2009. The compound annual growth rate for all nanomaterials in 2015 was 14.7% [18].

The scientific and research area belong to the priority development directions of Poland, as defined in the Long-term National Development Strategy, the 2020 National

Development Strategy and the National Smart Specialisation. The topic fully inscribes into the assumptions of the valid development strategy of the European Union “Europe 2020” and the Smart Specialisation Strategy. The subject of the topic is inherent to two Key Enabling Technologies (KETs) of the HORIZON 2020 programme pertaining to advanced materials, which can introduce new functionalities and improved properties, while adding value to existing products and processes, in a sustainable approach, mainly to sustainable development for new engineering leading to flexible manufacturing and improved production processes, to increase the competitiveness of European industry, partly including also nanotechnology.

Nanostructural materials basically can be grouped into zero-size nanostructures (e.g. nanoparticles, nanocrystals, quantum points), one-dimensional (e.g. nanofibers, nanotubes, nanowires), two-dimensional (nanolayers) and special nanomaterials – considered to be a separate group or a special kind of zero-, one- or two-dimensional nanostructures (fullerenes, carbon nanotubes, nanoporous materials). One-dimensional nanostructures are defined as objects whose dimensions exceed the value of 100 nm in one direction only. There are many expressions used in the literature to describe one-dimensional nanostructures, notably: nanowhiskers, nanofibers, nanorods, nanowires, nanotubes. Some of them are used alternately, whilst the usage of others is limited to structures having specific characteristics (e.g. nanotubes are hollow inside). It is generally accepted in this group that “nanowhiskers” and “nanorods” are characterised by much smaller length than the other structures [19]. In some market sectors where alternative materials have limited efficiency or a higher unit price, one-dimensional nano-objects attract significant attention (a good example is the use of carbon nanofibres as alternative ones in relation to carbon nanotubes as electron emitters in flat screens) [20]. As forecast, the sales of products made of one-dimensional nano-objects will be growing sharply over the next 5 years, as various newer high-tech applications are to be employed in the above industries, to be launched into production in other segments, such as the consumer, medical, biological or pharmaceutical segment. The compound global annual growth rate for the market of products made of one-dimensional nano-objects is expected to account for 37.2% in 2015-2020, versus 34.3% until 2015, generating an aggregate annual revenue of nearly 2.2 billion USD until 2020 [18]. It has been estimated that mechanical and chemical industry accounted for 73.2% of overall revenues in 2010. The compound annual growth rate in this industry is to be 35.3% in 2015-2020, against 33.4% in 2015. The electronic industry is experiencing the fastest growth with

the compound annual growth rate of 50.7% in 2015 to 2020 vis-à-vis 45.3% in 2010-2015 [21]. It was projected that the CAGR for the global nanocomposites market has exceeded 27.1% until 2014, while the CAGR for the entire global nanocomposites market including ceramics was 12.5% [22].

It should be noted that in order to explain nanostructural effects, the complementary use of subtle and most avant-garde research methods of modern materials engineering have to be employed. Materialographic examinations are performed using advanced light microscopy techniques, including confocal microscopy, high-resolution scanning electron microscopy (Supra 35 by Zeiss) and high-resolution 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 (Nicolet 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 tests are also followed of mechanical properties of materials, tribological, technological polymer materials, optoelectrical properties of materials and solar cells and corrosion tests.

The first part of the paper presents the outcomes of a dozen of own researches, selected symbolically, in the field of nanotechnology, carried out over the last several years [2,23-27]. It was decided that each of the selected topics was briefly described, with special emphasis laid on the issue of structural and phase transitions, which are generally taking place in the newly created Author's and original engineering materials and their related original technologies. Each of the descriptions was arbitrarily illustrated with a set of 3 metallographic photographs made with electron microscopes, most often a transmission microscope, mainly a high-resolution or scanning microscope.

The second part of the paper presents the new Author's ideas on the predicted development of the new generation of highly innovative advanced pioneering nanostructured composite materials through the interaction of the extended nanoengineering components. The scientific objective of the research is to recognise and explain the relevant structural mechanisms, in each case, of synthesis and/or production and formulation of the structure and properties

of a new generation of pioneering nanostructured composite materials through the interaction of the extended nanoengineering components and to characterise and model their structure and properties depending on the compositional, phase and chemical composition and the applied synthesis and/or production and/or processing processes [19]. The consequence of such actions will be the development of a new generation of highly innovative advanced pioneering nanostructured composite materials. The planned research is of priority cognitive importance as theoretical considerations, indicate a great need to intensify scientific research to develop new groups of materials with completely unexpected foreseeable effects, resulting from the use of the extended nanoengineering components for manufacturing super advanced nanocomposite materials. Phenomena and processes at a nanoscale can be better recognised by producing a new generation of functional nanostructural materials (physicochemical basis of nanomaterials and nanostructures synthesis, with controlled architecture and properties, engineering of atomic and molecular bonds, models and theories explaining the properties of nanomaterials, surface phenomena, self-assembly phenomena in nanomaterials and nanostructures synthesis, magnetic phenomena in semiconducting and metallic nanostructures). It is hard to overestimate the effects, and this requires investigations into the basis of developing the synthesis and/or production and/or processing of such completely new groups of new-generation nanostructural engineering materials. The research is of an interdisciplinary nature, with its scope covering achievements in the field of materials engineering, physics, chemistry and biology. The project's results may have direct influence on the development of electronics and photonics, medicine and pharmacy, environmental protection, automotive industry, space industry, machine industry, textile and clothing industry, cosmetic industry, agriculture and food sector. The measurable scientific effects concern the cognitive nature of the planned research and are associated with the determination of: the effect of compositional, phase and chemical composition, of the newly developed technologies of fabrication and surface micro-treatment inside pores, of internal precipitated phases or nanoinclusions or surface treatment of micropores in order to apply nanomaterials enabling the improvement of specific properties on the structure and properties of the newly created nanocomposite materials with the extended nanoengineering components ensuring the improvement of specific properties and the modelling of the structure and properties of the researched newly created nanocomposite materials using artificial intelligence methods. The research will comprise the fabrication of materials with new unforeseeable properties fulfilling

multiple functions. The functions result from, especially, or are greatly intensified by using nanomaterials (catalytic, electric, optical, magnetic, textile nanomaterials) employing the technologies of nanomaterials surface engineering, connected with producing nanolayers and nano-coatings (nanocomposite, with heat barrier, anti-wear, hydrophobic and biocompatible ones).

It is feasible to achieve the new generation of highly innovative advanced pioneering nanostructured composite materials through the interaction of the extended nano-engineering components, by recognising and explicating the materials science grounds and by developing the basis of the technology together with explaining the relevant structural mechanisms, in each tested case, of synthesis and/or production and formulation of the structure and properties of such materials and the characterisation and modelling of their structure and properties depending on the compositional, phase and chemical composition and the applied technological processes of synthesis and/or production and/or processing, with confirming the highly probable future application areas, using the unexpected effects of formulating such materials' functional properties.

2. Laser surface treatment of Mg alloys

The laser surface treatment of the casting alloy MCMgAl12Zn1 enables the production of a surface layer with a thickness of under a millimetre to several millimetres and with special functional properties. Following the treatment of the alloy surface with the HPDL laser, as a result of the cladding of SiC and WC carbide powders

and remelting, a quasi composite graded material is formed in the surface zone, with dispersively arranged carbides cladded into the remelted matrix. 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.

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 WC and SiC carbides, which was also confirmed by EDS investigation in scanning electron microscope SEM. It was found 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 with a nanometric scale, which did not exist in this alloy prior to laser treatment, i.e. β' Mg_9Si_5 and Ω' $\text{Al}_5\text{Mg}_8\text{Si}_6\text{Cu}_2$ (Fig. 1), in which the distribution of

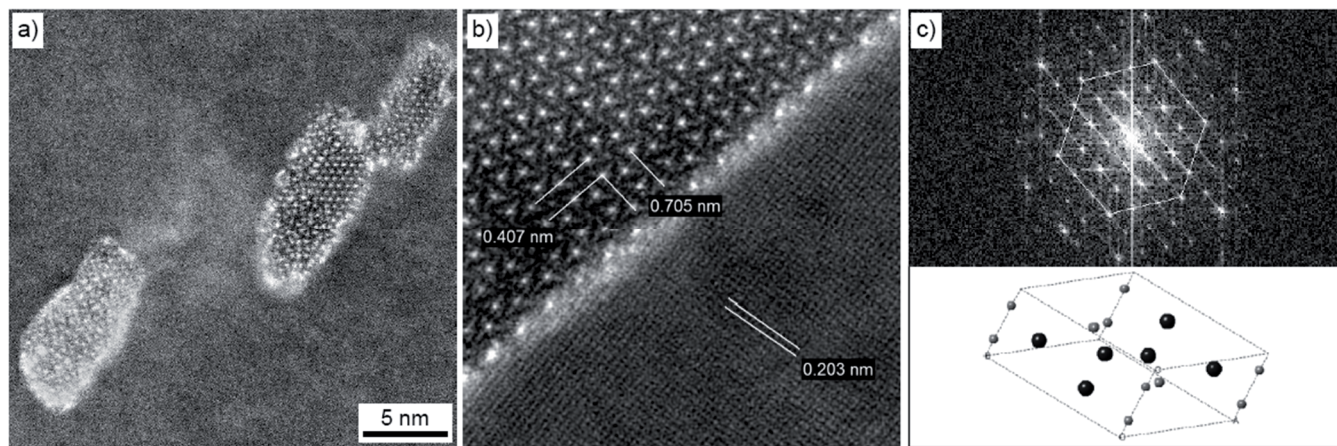


Fig. 1. The structure of the precipitated phases β' (Mg_9Si_5) or Ω' ($\text{Al}_5\text{Mg}_8\text{Si}_6\text{Cu}_2$) in the heat affected zone HAZ of the laser treated the AlSi9Cu, a) the distribution of the precipitates of the β' or Ω' phase in the matrix (HRTEM), b) the distribution of individual atoms in precipitates of the β' or Ω' phase (HRTEM), c) diffraction pattern and the distribution of individual atoms in precipitates of the β' or Ω' phase

individual atoms in such phases precipitated in the impact zone was also determined caused by the diffusion of elements creating them in this zone. The described technology has great influence on the improvement of hardness on the surface of laser treated 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 [2].

3. Forming the nanostructure in austenitic high-manganese steels by TWIP mechanism

Structural mechanisms, mainly twinning during the cold plastic deformation of the newly developed custom high manganese X8MnSiAlNbTi25-1-3 and X73MnSiAlNbTi25-1-3 steels of the twinning induced plasticity TWIP type, are decisive for increasing the store of cold plastic deformation energy. By way of controlling the conditions of hot plastic working of the investigated steels, a structure of dynamically recovered, dynamically recrystallised or partially statically and/or metadynamically recrystallised austenite can be created, and by employing thermo-mechanical treatment consisting of hot plastic deformation and adjustable cooling, the structure of the newly developed steels can be considerably refined, especially for a higher concentration of carbon participating in the processes of the release of dispersion carbides created with microadditives and to ensure the expected strength properties.

The maximum tensile strength R_m in a static tensile test at room temperature is 587 MPa for X8MnSiAlNbTi25-1-3 steel and 698 MPa for X73MnSiAlNbTi25-1-3 steel. Tensile strength is subject to significant changes along with changes in the test temperature. The maximum values were obtained at the temperature of -70°C , of 693 MPa for X8MnSiAlNbTi25-1-3 steel and 726 MPa for X73MnSiAlNbTi25-1-3 steel, and the lowest at the temperature of 200°C , respectively, 496 and 561 MPa. X8MnSiAlNbTi25-1-3 steel shows the highest relative elongation of 42.5-44.5% after thermomechanical working, whereas differences in the relative elongation of X73MnSiAlNbTi25-1-3 steel are smaller and account for 39.3-42.5%. In case of the both examined steels, the highest elongation occurs at the temperature of -25°C and at room temperature.

If a rate of plastic deformation at constant room test temperature is increased by, respectively, 250, 500 and 1000 s^{-1} , which corresponds to rupture rates of,

respectively, 4, 7 and 14 m/s , the total elongation is increased to the maximum value of 56% for X8MnSiAlNbTi25-1-3 steel and 50% for X73MnSiAlNbTi25-1-3 steel at the deformation rate of 250 s^{-1} and decreased from 15% (X8MnSiAlNbTi25-1-3 steel) and to 25% (X73MnSiAlNbTi25-1-3 steel) with a further increase in a deformation rate. An increase in the rate of plastic strain to 1000 s^{-1} is increasing tensile strength from approx. 660 to approx. 910 MPa for X8MnSiAlNbTi25-1-3 steel and from approx. 690 to 1100 MPa for X73MnSiAlNbTi25-1-3 steel.

The strain energy per unit volume, E_{zp} , i.e. energy which can be accumulated during dynamic loading, e.g. in a road collision of vehicles, calculated as a field area under the actual stress-actual strain curve, depending on the test temperature and thermal working conditions for X8MnSiAlNbTi25-1-3 steel, range between 81 and 293 MJ/m^3 , and between 110 and 339 MJ/m^3 for X73MnSiAlNbTi25-1-3 steel. X8MnSiAlNbTi25-1-3 steel exhibits the highest average value of strain energy per unit volume of 239 MJ/m^3 at room temperature, and X73MnSiAlNbTi25-1-3 steel the value of 301 MJ/m^3 . The both investigated steels demonstrate much lower E_{zp} values at 200°C . In case of plastic strain at room temperature at high rates, the strain energy per unit volume value is increased for X8MnSiAlNbTi25-1-3 steel by 80% to 431 MJ/m^3 at a strain rate of 1000 s^{-1} and by 110% to 574 MJ/m^3 for X73MnSiAlNbTi25-1-3 steel. The maximum value of strain energy per unit volume is exhibited by X73MnSiAlNbTi25-1-3 steel for the highest strain rate applied in the tests of 1000 s^{-1} . X8MnSiAlNbTi25-1-3 steel shows the strain energy per unit volume lower by approx. 10% for each of the applied cold strain rates.

Austenite is the structure of the both steels subjected to a static tensile test. In case of the both steels, even a small deformation of 5 or 10% leads to the elongation of grains in the direction of the acting tensile forces. The presence of intersecting slip bands is found in austenite grains and in annealing twins. By increasing specimen elongation to 20-30%, the intersecting slip bands and deformation twins are densified in a static tensile test. The structures of the specimens deformed until rupture are characterised by austenite grains strongly elongated in the direction of stretching and by deformed austenite grains with a large density of slip bands and deformation twins.

It was found by examining thin foils in a transmission electron microscope, especially in a high-resolution microscope, that the structure of the newly developed high manganese austenitic X8MnSiAlNbTi25-1-3 and X73MnSiAlNbTi25-1-3 steels in the state after thermo-mechanical working, and then after a static tensile test, consists mainly of strongly deformed austenite grains with

a high density of dislocation with numerous twins with various intersecting slip systems. The basic mechanism of TWIP (TWinning Induced Plasticity), closely linked to

cold plastic deformation by the activation of twinning in the intersecting systems, was confirmed with the use of a high-resolution electron transmission microscope (Fig. 2).

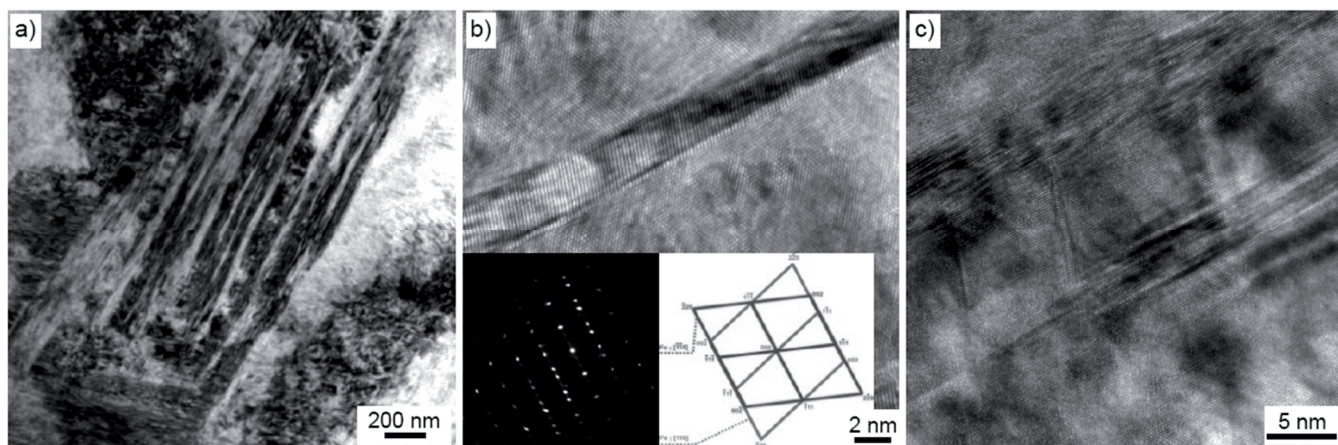


Fig. 2. The structure of the high-manganese austenitic X8MnSiAlNbTi25-1-3 of the TWIP type steel after mechanical twinning induced by the cold working and after the successive cold deformation during static tensile test: a) the twins in two twinning systems in the austenite matrix (TEM), b) unique twin in the austenitic matrix (HRTEM), with the solution of the diffraction pattern, c) the system of crossed twins in the austenitic matrix (HRTEM)

An increase in the strain energy per unit volume of cold plastic deformation energy of the investigated steels sets a basis for applying them in the automotive industry for sheets and structural components of cars as reinforcements and controlled zones of plastic deformation, behaving in a controlled and pre-defined manner, during dynamic cold plastic deformation occurring, in particular, in a road accident. It is therefore possible to use the plastic deformation energy of the investigated steels in such conditions to prevent rupture until their plastic deformation lasts. Fractures are prevented in structural parts and bodywork of a car during an accident or road collision by absorbing a large store of the then produced energy. This verifies positively the concept of preventing the fractures of structural parts and bodywork of a car during an accident or road collision by absorbing a large store of the then produced energy, to induce structural changes occurring in the conditions of dynamic plastic deformation of critical parts of the car made of such steels. A relatively high strain energy per unit volume ensures energy absorption and prevents premature fracture of the damaged car components.

It was demonstrated that a raised strain energy per unit volume of cold plastic deformation energy is essential for preventing the cracking of the analysed groups of steels. The TWIP type steels with designated strain energy per unit volume after the cold deformation equal, respectively,

227.50 MJ/m³. Even higher growth of energy per unit volume yield substantially increases a deformation rate, even to 529.49 MJ/m³ [2].

4. Forming the nanostructure in austenitic high-manganese steels by TRIP mechanism

The newly developed high manganese X11MnSiAl17-1-3 steel of the transformation induced plasticity TRIP type exhibits – after casting – a homogenous austenite structure with numerous twins. The average diameter of austenite grains is 150-200 μm. Following the thermoplastic working, consisting of hot pressing in several stages, both in the Gleeble 3800 laboratory simulator as well as in semi-industrial conditions, the steel possesses a homogenous structure of the phase γ. The structure of steel after cold deformation in static conditions is represented by austenite grains which, already at small deformation of 5 or 10%, undergo elongation in the direction of the stretching force with the occurring deformation twins intersected with numerous slip bands. The structure of the steel deformed statistically until rupture is represented by austenite grains strongly deformed and elongated with a large density of deformation twins and slip bands. It was found through

tests in a transmission electron microscope that static cold plastic deformation causes the partial transformation of austenite into martensite α' and martensite ϵ (Fig. 3).

The presence of a martensitic phase in the structure was also confirmed with an X-ray qualitative phase analysis. No substantial effect of the type of cooling on the fraction of phases in steel was however found, which points out that the phase is a result of plastic deformation. Static elongation in the temperature range of 150-200°C causes slight variations in strength and in plastic properties of this steel. Steel is deformed by mechanical twinning in the temperature of 150 and 200°C. Strength and plastic properties are clearly raised as the test temperature is lowered from 100°C to 80°C. The plastic deformation of steel takes place in such conditions by twinning in two systems. At room temperature, total and uniform elongation reach the value of, respectively, 40 and 32%. Tensile strength is also rising explicitly to $R_m=620$ MPa. The steel deformed plastically in a static tensile test at the temperature heightened to 23°C has numerous and densely intersecting slip bands and mechanical twins. If temperature is further reduced from 23 to -25 and then to -70°C, elongation is slightly decreased by 30% and then it suddenly grows to 53%. Tensile strength is also on the constant rise to 850 MPa. The investigated high manganese steel subjected to plastic deformation at the temperature of -25°C possesses an austenitic structure with scarce slip bands. The slip bands were clearly densified after lowering the temperature to -70°C. Plastic deformation temperature is also significantly influencing the strain energy per unit volume of cold plastic deformation energy E_{zp} determined by a field area

under the strain curve. At the temperature increased from 200 to 100°C, the E_{zp} value has a low value of 8 to 150 MJ/m³. As the deformation temperature falls to 80°C, a value of the average strain energy per unit volume is rising. E_{zp} equals approx. 256 MJ/m³ at room temperature. When deformation temperature is decreased to -25°C, the E_{zp} value drops to 232 MJ/m³, and E_{zp} suddenly rises to 353 MJ/m³ at the temperature of -70°C. An austenite and martensite structure was revealed for X11MnSiAl17-1-3 steel through tests results for steel thin foils after completion of mechanical tests at a lower and higher temperature. The structure of martensite α' and ϵ was revealed in diffraction tests of the steel subjected to a static tensile test at a temperature reduced to -25°C. All the structural effects mentioned are of nanometric sizes, and steel properties at a macroscopic scale are changing as a result.

Tensile strength tests for X11MnSiAl17-1-3 steel were made at room temperature also in dynamic conditions with, respectively, the plastic deformation rate of 0.01, 250, 500 and 1000 s⁻¹. The yield point $R_{p0.2}$ of X11MnSiAl17-1-3 steel reaches the highest value of 942 MPa during fast deformation of 1000 s⁻¹. The same steel deformed plastically at a lower strain rate has the $R_{p0.2}$ value of 827-909 MPa. This steel, when deformed in static conditions, has a nearly half lower yield point $R_{p0.2}$ of approx. 486 MPa. The elongation of the investigated high manganese austenitic steel X11MnSiAl17-1-3 in the conditions of static cold plastic deformation is about 42%, and may reach even 64% if the strain rate is increased to 1000 s⁻¹. An increased strain rate leads also to an increased

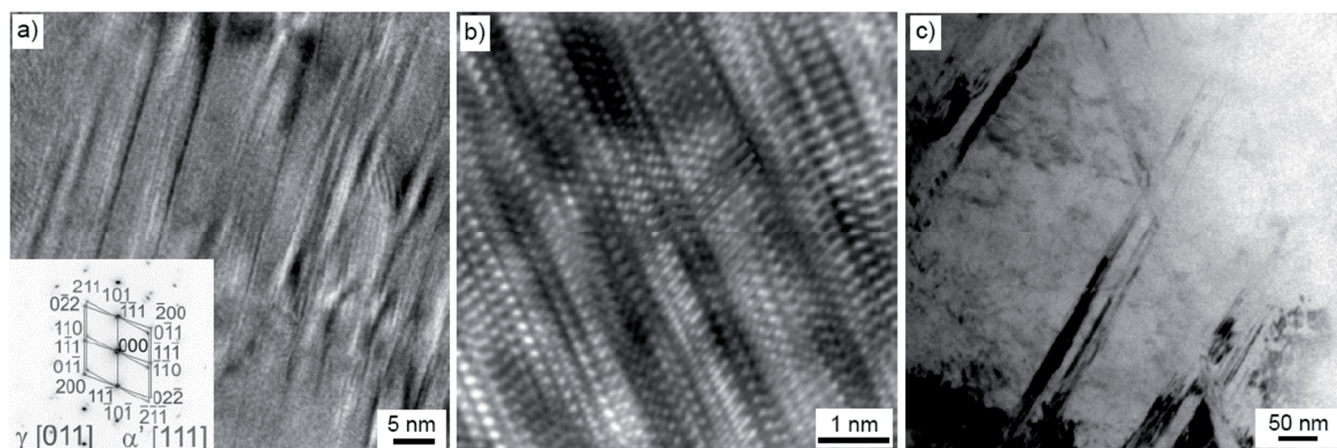


Fig. 3. The structure of the high-manganese austenitic X11MnSiAl17-1-3 of the TRIP type steel after a), b) dynamic tensile test with the strain rate 1000 s⁻¹, c) hot-rolling with a true strain 0.29 and after static tensile test, a) Kurdjumov-Sachs orientation between the austenitic matrix and martensite α' (HRTEM), b) the magnification obtained using Fourier Transform of martensite α' (HRTEM), c) intersected ϵ martensite plates (bright field TEM)

strain energy per unit volume of cold plastic deformation E_{zp} . The highest value of strain energy per unit volume of cold plastic deformation energy for a strain rate of 1000 s^{-1} equals to 481 MJ/m^3 and is nearly two times higher than the value E_{zp} obtained in static conditions. This corresponds to the best strength ($R_m=942 \text{ MPa}$, $R_{p0.2}=826 \text{ MPa}$) properties obtained in such test conditions.

X11MnSi17-1-3 steel, after a static and dynamic tensile test, is characterised by an austenitic structure with numerous mechanical twins and intersecting slip bands. Intersecting slip bands dominate in the steel deformed from the velocity of 0.1 s^{-1} . Mechanical twins in the steel deformed with the rate of 250 s^{-1} are $40\text{--}60 \text{ }\mu\text{m}$ wide and the distance between particular slip bands is approx. 7 to $10 \text{ }\mu\text{m}$. If a strain rate is increased to 500 s^{-1} , slip bands are densified and twinning intensity grows. When steel is deformed with the rate of 1000 s^{-1} , this influences the occurrence of numerous slip bands and mechanical twins in the material structure. Twinned austenite is mainly found in the steel deformed in a dynamic tensile test (Fig. 3), after deformation at a rate of 250 s^{-1} and also martensite ϵ and α' (Fig. 3), and austenite and martensite α' occurs after deformation at a rate of 500 and 1000 s^{-1} . The Kurdjumov-Sachs crystallographic relationship was identified between austenite and martensite $(011)\gamma \parallel (111)\alpha'$, with the directions of $[110]\gamma$ and $[010]\alpha'$, and $[\bar{1}01]\gamma$ and $[\bar{1}\bar{1}1]\alpha'$ (Fig. 3). Martensite α' was identified on the diffractions attained from the marked areas with a high-resolution electron transmission microscope HRTEM. The presence of austenite and martensite α' was confirmed by the X-ray phase analysis method.

5. PVD and CVD multilayers coatings

One of the essential directions of own research associated with nanotechnology is to constitute – on the substrates of sintered tool material, including sintered sialons, nitride ceramics and cemented carbides – the newly developed nanocrystalline multiphase coatings deposited by physical vapour deposition (PVD) with cathodic arc evaporation techniques (CAE), as well as by the high-temperature chemical vapour deposition (CVD) method, with the intention to enhance the cutting properties of such materials by improving significantly the life of the tool cutting edge. Such coatings have not been applied to date onto any tools made of the materials mentioned, investigations are known, however, concerning the deposition of similar coatings onto tools made of classical sintered carbides and cermetals and in a CVD process on nitride ceramics.

Indexable inserts made of sintered carbides and sialon and nitride tool ceramics were deposited in the process of cathodic arc evaporation (CAE-PVD) with the following multiphase coatings: $(\text{Al,Ti})\text{N}$, $(\text{Ti,Al})\text{N}$, $(\text{Al,Cr})\text{N}$, $(\text{Ti,Al})\text{N}+(\text{Al,Cr})\text{N}$, $(\text{Al,Cr})\text{N}+(\text{Ti,Al})\text{N}$, $\text{TiN}+\text{multi}(\text{Ti,Al,Si})\text{N}+\text{TiN}$, $\text{TiN}+(\text{Ti,Al,Si})\text{N}+\text{TiN}$, as well as in a high-temperature CVD process with multilayer coatings based on $\text{Ti}(\text{C,N})$, Al_2O_3 , TiN and TiC phases. The thickness of the investigated PVD coatings obtained on sintered carbides and tool ceramics spans between 0.7 to $5.0 \text{ }\mu\text{m}$, while the thickness of CVD coatings between 1.7 to $10 \text{ }\mu\text{m}$. Regardless the location, all the layers forming part of the coatings tightly adhere to each other and do not show any fractures and discontinuities. It was also found based on fractographic tests made with a scanning electron microscope that the PVD and CVD coatings obtained are deposited evenly and adhere tightly to the tested substrates. The particular layers in multilayer coating systems have a compact structure without delaminations and defects and tightly adhere to each other. The fractographic tests of sintered carbides and tool ceramics with coatings deposited by the PVD and CVD method do not reveal a fracture delamination along the separation area between the coating and the substrate, which also indicates good adhesion of the coatings produced to the substrate. A qualitative phase composition analysis carried out with the X-ray diffraction method confirms that coatings exist containing TiN , $\text{Ti}(\text{C,N})$, AlN and CrN phases and an Al_2O_3 phase in case of CVD coatings on substrates made of sintered carbides and tool ceramics. It was found as a result of a GDOES analysis that a concentration of elements forming part of the substrate is increased in the bonding zone from the surface of coatings with a reduction, at the same time, in the concentration of elements forming part of the coating. This fact may be linked to the presence of a transition zone of a diffusive character between the substrate material, and the coating, as suggested by the authors in the earlier works. The existence of a transition layer should be associated with the higher desorption of the substrate surface and with the formation of defects in a substrate as well as with the mixing of elements in a bonding zone due to the activity of high-energy ions. The existence of diffusive transition layers is supportive to the good adhesion of coatings to the substrate. The critical load value L_c (AE) for PVD coatings is between 13 and 131 N , and for CVD coatings – between 15 to 110 N . As regards coatings deposited by the PVD method onto sintered carbides, the best substrate adhesion is exhibited by a $(\text{Ti,Al})\text{N}$ coating, for which a critical load value $L_c = 109 \text{ N}$, whereas the weakest substrate adhesion is seen for a $\text{Ti}(\text{B,N})$ coating, where $L_c = 34 \text{ N}$. The coatings deposited

by the CVD method onto a substrate made of sintered carbides show a high critical load of $L_c = 93$ N for a $\text{Ti(C,N)}+\text{Al}_2\text{O}_3+\text{TiN}$ coating and $L_c = 110$ N for a $\text{Ti(C,N)}+\text{TiN}$ coating. The highest critical load of $L_c = 112$ N for coatings obtained by PVD on nitride and sialon ceramics is shown by an $(\text{Al,Ti})\text{N}$ coating, whilst the lowest of $L_c = 13$ N for a Ti(B,N) coating. A critical load for coatings obtained by CVD on nitride and sialon ceramics is between 27 to 83 N. The surface morphology of coatings produced with the PVD technique is characterised by a high inhomogeneity because numerous droplet-shaped particles are present. The occurrence of such morphological defects is connected with the essence of the cathodic arc evaporation process. The sizes of such particles range between the tenths of a micrometer to a dozen or so micrometers. The presence of depressions was also discovered, which are formed, most probably, by solidified droplets being ejected after the end of the PVD process. For the coatings applied with the CVD method onto a substrate made of sintered carbides and tool ceramics, heterogeneity is seen in surface morphology related to the presence of multiple pores and networks of microcracks characteristic for such a process. When an Al_2O_3 layer is on the substrate surface, however, or if this layer is in the under-the-surface zone (upper TiN layer is very thin), then the particles are needle-like or angularly shaped. It was found as a result of thin foils tests with an electron transmission microscope that coatings deposited in cathodic arc evaporation show a nanocrystalline structure. It was confirmed in a diffraction analysis that isomorphic phases exist with titanium nitride TiN in case of $\text{TiN}+\text{multiTiAlSiN}+\text{TiN}$ and Ti(B,N) coatings, and an AlN

phase with a hexagonal lattice in case of an $(\text{Al,Ti})\text{N}$ coating. The presence of TiN and Al_2O_3 phases in $\text{TiN}+\text{Al}_2\text{O}_3$, $\text{TiN}+\text{Al}_2\text{O}_3+\text{TiN}+\text{Al}_2\text{O}_3+\text{TiN}$ -type coatings was also confirmed, as assumed, in the investigations of coatings obtained by the CVD method. The Al_2O_3 layer structure with a rhombohedral lattice is characterised in its cross section by fine grains and grain size below 500 nm. A fine-crystalline structure of the TiN phase with a regular lattice is visible in the same cross section of thin foils between Al_2O_3 phase grains. The HRTEM examinations of layers with a high concentration of Al prove the existence of nanograins with a differentiated orientation of planes showing the presence of long-range order typical in crystalline materials between which areas with a smaller degree of order were identified. Structural observations and diffraction images using imaging in the HRTEM mode and the corresponding Fourier FFT transforms confirm that the fabricated nitride coatings based on Al, Ti, Cr, Si exhibit a nanocrystalline and nanocomposite structure (Fig. 4). The profile and surface analyses of chemical composition variations performed with a high-resolution electron transmission microscope, confirming the existence of transition layers between the substrate and coating and between individual layers with a varied concentration of Al and Ti, may signify the existence of diffusive transition areas and thus contribute to the high adhesion of substrates produced with the cathodic arc evaporation method.

The surface microhardness of the examined tool materials is greatly raised by depositing PVD and CVD coatings. The highest hardness is seen for multicomponent $(\text{Al,Ti})\text{N}$ coatings, multi-layer $\text{TiN}+\text{multi(Ti,Al,Si)N}+\text{TiN}$ coatings obtained by PVD, which accounts for nearly

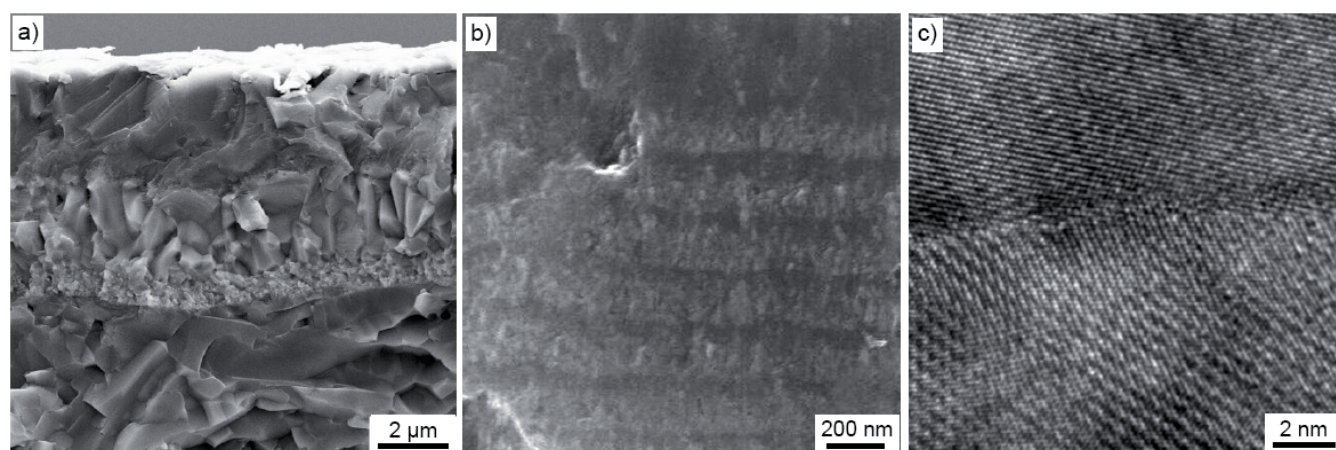


Fig. 4. The structure of the a) multi-component and multilayer coatings $\text{Al}_2\text{O}_3+\text{Ti(C,N)}+\text{Al}_2\text{O}_3+\text{TiN}+\text{Ti(C,N)}$ on the sialon substrate (SEM), b) Ti(Zr,N) multi-layer coating on a substrate of sintered carbides (SEM), c) interface zone between the coating (upper layer) and the substrate of sintered carbides (lower layer) at the atomic scale (HRTEM)

100% growth in surface layer hardness in relation to the hardness of the uncoated material. The hardness of the examined coating systems is conditioning their abrasive wear, as seen most clearly for the TiN+Al₂O₃ coating – the hardest of the CVD coatings, thus contributing to the lower wear intensity of a tool cutting edge in cutting. To summarise, high abrasion resistance as well as good cutting properties of the tested tool ceramics with PVD and CVD coatings deposited are stemming from increased micro-hardness. The service life of the examined sintered tool materials was identified based on technological cutting tests. It was found as a result of cutting ability tests that the highest service life of $T = 72$ min was achieved for a cutting edge coated with an (Al,Ti)N coating, when the life of an uncoated cutting edge made of sialon ceramics was estimated at $T = 11$ min. A (Ti,Al)N coating has the greatest effect on the cutting edge life of $T = 60$ min for sintered carbide plates when the durability of an uncoated tool is $T = 2$ min. A broad cutting edge durability range depending on the type of the applied coating was attained both, for coated sintered carbides and coated tool nitride and sialon ceramics.

6. PVD gradient coatings

The own results of investigations in the area of the nanotechnology have become a basis for developing various own graded coatings, also with the fraction of a diamond-like surface layer. Indexable inserts made of sintered carbides and sialon and nitride tool ceramics were deposited in the process of cathodic arc evaporation (CAE-PVD) with graded coatings of the following type: Ti(B,N), (Ti,Zr)N, Ti(C,N), Ti(C,N)+(Ti,Al)N, TiN+(Ti,Al,Si)N+(Al,Si,Ti)N. Ten-layer nanocrystalline surface coatings of the (Cr,Al,Si)N and (Al,Ti,Si)N type were applied alternatively by the modified Lateral Arc Rotating Cathodes (LARC) technique onto a substrate made of the investigated ceramic-metallic tool materials. CrN or TiN, respectively, were used as near-the-core layers, by placing onto them graded layers (Cr,Al)N/(Al,Cr)N and (Ti,Al)N/(Al,Ti)N, respectively. Eight multilayers were successively deposited onto such layers with a variable composition in the following order: (Cr,Al,Si)N+(Al,Cr,Si)N+(Cr,Al,Si)N+(Al,Cr,Si)N+(Cr,Al,Si)N+(Al,Cr,Si)N+(Cr,Al,Si)N and, respectively, (Ti,Al,Si)N+(Al,Ti,Si)N+(Ti,Al,Si)N+(Al,Ti,Si)N+(Ti,Al,Si)N+(Al,Ti,Si)N+(Ti,Al,Si)N+(Al,Ti,Si)N. The total thickness of CrAlSiN and AlTiSiN coatings is 2.5-3.0 μm . Nanocrystalline nitride TiAlSiN, CrAlSiN, AlTiCrN, CrN layers were deposited onto dies for extrusion made of hot-

work alloy tool steels after ion etching of the substrate and deposition of a Cr-based transition layer by physical vapour deposition PVD, arc method and then after reduction of temperature of deposition of low-friction layers DLC by PVD assisted with PACVD [28]. Regardless the technology and location, all the layers forming part of the coatings tightly adhere to each other and do not show any fractures and discontinuities. In addition, fractographic tests of tool materials with the deposited coatings do not reveal any delamination along the separation area between the coating and the substrate, and show that the coatings obtained adhere strongly to the substrate.

A linear analysis was performed with a scattered X-ray radiation energy (EDS) spectrometer and a surface analysis of elements distribution using Energy-filtering transmission electron microscopy (EFTEM) was carried out to confirm the existence of changes in chemical composition of individual sublayers of a CrAlSiN+DLC coating. The character of changes in the intensity of the elements points out that the sublayers mentioned exist. Variations in the atomic concentration of Ti(B,N), (Ti,Zr)N, Ti(C,N), (Al,Ti)N graded coatings in the direction perpendicular to their surface, and concentration variations in the transition zone between the coating and the substrate material, depending on the number of layers deposited, were examined in a GDOS glow discharge optical spectrometer. The examinations confirm the existence of the relevant elements in the graded layers. A curve of variations in a concentration of the elements forming the coatings shows their gradient structure. It was found as a result of a GDOES analysis that a concentration of elements forming part of the substrate is increased in the bonding zone from the surface of coatings with a reduction, at the same time, in the concentration of elements forming part of the coating. This fact may be linked to the presence of a narrow transition zone of a diffusive character between the substrate material, and the coating. A profile analysis GDOS of chemical composition in the function of distance from the surface with the deposited (Cr,Al,Si)N and (Al,Ti,Si)N coatings on a substrate made of the investigated ceramic-metallic tool materials, as well as the identified variations in a concentration of particular elements and the existence of transition zones of a diffusive character between particular layers and between a coating and a substrate material from the investigated ceramic-metallic tool materials were evaluated, as indicated earlier, with reference to the other investigated materials and multi-layer coatings.

On the basis of investigations performed with an electron transmission microscope, (Cr,Al,Si)N and (Al,Ti,Si)N coatings were characterised, deposited onto a tool ceramic-

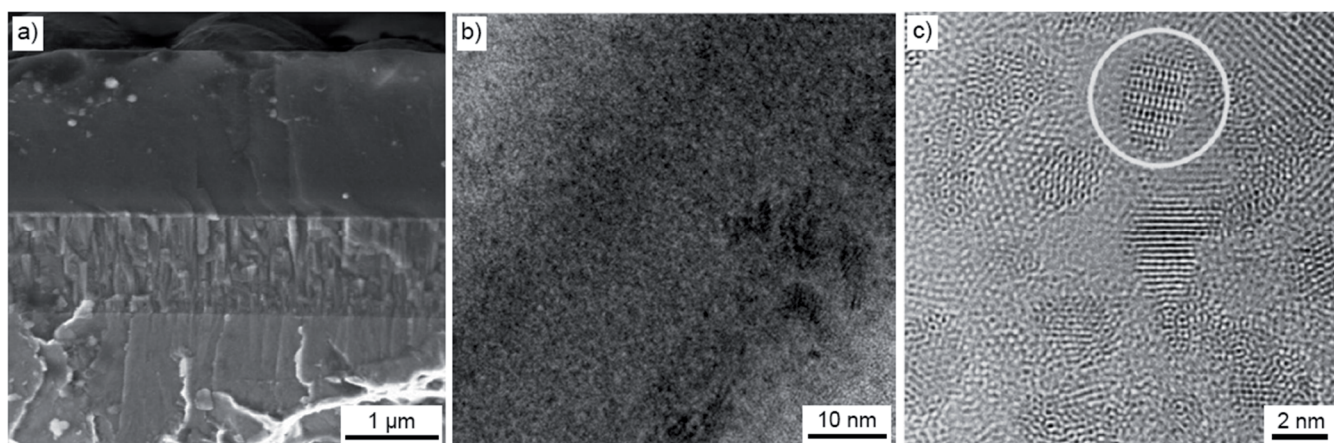


Fig. 5. The structure of the multi-component gradient coatings: a) AlTiCrN and additionally with surface diamond like carbon on the substrate of hot-working alloy tool steel X40CrMoV5-1 (SEM), b) DLC and CrAlSiN coatings (HRTEM), c) local clusters of Si_3N_4 in amorphous CrAlSiN matrix area (HRTEM)

metallic material, fabricated with the cathode arc evaporation (CAD) method with lateral arc rotating cathodes, composed of several layers, and transition zones were investigated between the substrate and the coating, as well as between the individual layers in the scanning-transmission mode, with BF and HAADF detectors. It was concluded based on the tests of thin foils from the cross section that they have a nanocrystalline and nanocomposite structure within the entire volume and they do not show discontinuities, cracks and porosity and have high homogeneity and a compact structure. The existence of several layers in nitride coatings was identified, both, based on Cr, Al and Si, as well as Al, Ti i Si, exhibiting a varying thickness and chemical composition depending on the distance from the substrate. A layer deposited directly onto the near-the-core TiN layer shows a gradient character with a linearly decreasing concentration of Ti, accompanied by a heightening concentration of Al and the successive eight layers are characterised by a variable concentration of, respectively, Cr or Ti and Al. The results of the tests for the CrAlSiN+DLC coating obtained using the transmission electron microscopy confirm the amorphous character of a low-friction DLC layer. The TEM images obtained for very high magnifications of DLC layers created on different indirect layers do not show the presence of long-range order typical for an amorphous structure. It was found – by examining thin lamellas with a high-resolution transmission electron microscope from the cross section of nitride layers, CrAlSiN, AlTiCrN and CrN, produced with the PVD technique – that the layers feature a compact structure with high homogeneity and a grain size between 5 to 10 nm depending on the layer type. In one of seven indirect zones

of such a complex gradient coating, crystalline CrN (CrAlSiN) grains sized several nanometres deposited in an amorphous Si_3N_4 matrix exist in the nitride layer CrAlSiN from the substrate side, deposited in an amorphous Si_3N_4 matrix, which may signify the layer's nanocomposite structure (Fig. 5). The essence of high adhesion of the layers formed to the substrate material and between individual layers in coatings is the existence of transition zones between particular layers and with a substrate made of steel, as in case of a CrAlSiN+DLC coating, including between an external low-friction DLC layer and a hard nanocrystalline nitride CrAlSiN layer as well as between the core of the coated tool and a CrAlSiN layer.

The usefulness of the prepared coatings was confirmed by numerous application examples at a laboratory and semi-technical scale in machining and plastic working, including for cutting tools, as well as for tools for the intensive plastic working process KOBOL. The durability of tools and their wear resistance in operational conditions is being enhanced for the mentioned coatings as compared to uncoated tools.

7. Preparation of the biological-engineering nanocomposites and the electrospun biodegradable nanofibers for medical applications

An Author's concept was developed of biologically active composite engineering materials and implant-scaffolds, where porous zones with appropriately sized

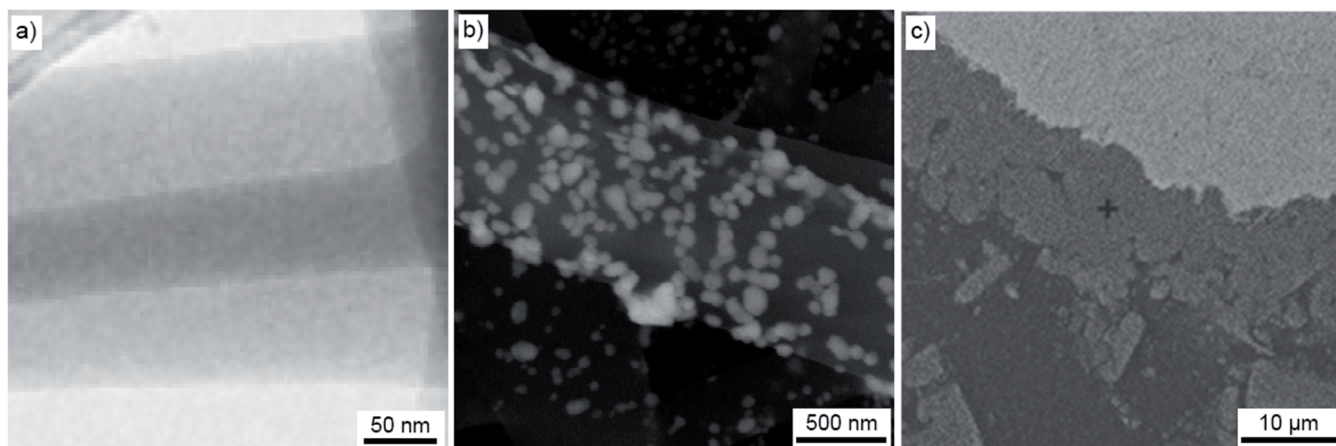


Fig. 6. a), b) Geometrical characteristics of core-shell composite obtained from: a) a coating solution of 10% polycaprolactone without additives and inner core solution of 4% of polycaprolactone without additives (TEM), b) double-component fibers obtained by dissolving PCL granulate with the molecular 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), c) structure of transition phase of AlSi7Mg0.3/Ti composite material (SEM)

pores and the internal surfaces of pores coated with materials, support the growth of living human cells in case where post-surgery or post-injury losses have to be filled, especially in the treatment of cancerous diseases. Polymer fibres and nanofibres can be used as engineering materials being a skeleton of such biological-engineering composite materials when it comes to flexible materials or titanium or TiAl6V4 alloy in case of a rigid solution (Fig. 6).

Investigations were carried out here for polymer nanofibers achieved by electrospinning, especially of long-resorbable composite nanofibers with a bioactive core and a bactericidal shell. 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 non-toxicity 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. 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 [2].

Two 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. 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.

The diameter of the fibers obtained may change after introducing additives, e.g. silver nitrate and chitosan, which are enhancing electric conductivity. 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 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. The polymer nanofibers produced by electrospinning applied in regenerative medicine additives introduced have also substantial influence on the antibacterialness and antifungalness of nanofibers. Silver nitrate and AlphaSan show high efficacy in fighting Gram+, Gram- bacteria and fungi, and macromolecular chitosan does not show antibacterial and antifungal properties [2]. Polymer nanofibers create significant applicational possibilities in this field. The composite core-shell 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. The investigations of polymer nanofibers achieved by electrospinning, set a basis for creating porous implant-scaffolds, an innovative generation of elastic biological-engineering composite materials for regenerative medicine.

Constructional assumptions and a technology of porous microskeletons made of titanium and TiAl6V4 alloy, produced by Selective Laser Sintering (SLS), were established mainly to use, as composite elements, biologically active engineering materials or implant-scaffolds, where porous zones with appropriately sized pores are coated on the internal surfaces of pores with materials supporting the growth of living cells. New materials were also developed, based on such experience, with predictable, broad potential applications in various fields, notably in the automotive, machine, aviation and electronic industry, with a matrix made of cast aluminium alloys and with titanium reinforcement or from TiAl6V4 alloy of skeleton microporous materials manufactured by Selective Laser Sintering (SLS).

AlSi12/Ti and AlSi7Mg0.3/Ti composite materials infiltrated using two types of titanium microskeletons with the pore size of ~ 350 and ~ 250 μm and the porosity of, respectively ~ 66 and $\sim 56\%$ and the bending strength of, respectively, 65 and 100 MPa, underwent tensile strength tests and were compared to the strength of AlSi12 and AlSi7Mg0.3 aluminium alloys and solid titanium produced by Selective Laser Sintering (SLS). The bending strength of solid titanium of 1682 MPa is nearly ten times higher than for AlSi12/Ti alloy, but only more than four times higher than for the composite material AlSi12/Ti. The reinforcement of aluminium alloys with porous titanium skeletons has a beneficial effect also on the mechanical properties of the composite materials developed. Hexagon cross base units cells were selected experimentally, and a spatial microskeleton lattice was achieved by multiplying them with the assumed pore size of 450 μm and the unit cells arranged at the angle of 45° relative to the axis y of the system of coordinates.

Microporous titanium skeletons produced by SLS were used for the development of composite materials. In order to produce the mentioned composites, the titanium microskeletons fabricated by SLS were subjected to pressure infiltration with AlSi12 and AlSi7Mg0.3 alloys in the liquid state with the temperature of 800°C for 2 min. under the pressure of 2-3 MPa of gas situated underneath the liquid matrix material level. The matrix material is crystallising following infiltration, thus forming a composite material with the skeleton.

The presence of $\alpha\text{-Al}$ and $\alpha\text{-Ti}$ phases was confirmed in the structure of AlSi12/Ti and AlSi7Mg0.3/Ti pressure-

infiltrated composite materials with a matrix made of cast aluminium alloys and reinforcement made of skeleton microporous titanium materials manufactured by Selective Laser Sintering (SLS) by the X-ray diffraction method. A nanostructural AlSiTi phase also exists, whose presence was confirmed on the scattered X-ray radiation energy (EDS) chart. The pores of the titanium microskeleton are filled thoroughly with the matrix material as a result of infiltration, without any voids in the matrix-and-reinforcement bonding zones, and a titanium microskeleton retains its shape and structure, which can be exactly separated in the composite material structure.

8. Preparation and application of metallic nanowires

Nanostructural composite 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 copper nanowires and copper nanopowder, exhibit better properties as compared to composite polymer materials reinforced with micrometric copper powder (Fig. 7). Beyond doubt, copper nanowires are an attractive alternative for such materials as, e.g. carbon nanotubes. Reduced hardness occurs indeed in case of materials 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 copper 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 copper nanowires ensure the creation of percolation paths allowing to transfer an electric charge despite a non-conductive 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 occur 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

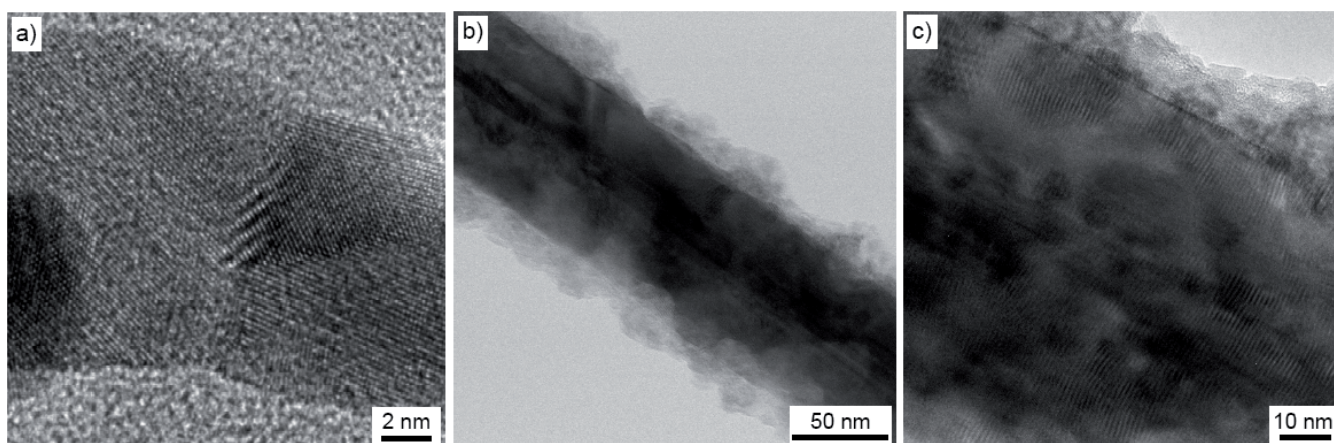


Fig. 7. The structure of a) platinum and b), c) copper nanowires manufactured on a) polished silicon substrate (HRTEM), b), c) glass substrate (HRTEM)

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 traditional polymer composite materials, a broad range of such materials' utilitarian importance is becoming apparent.

9. Nanocomposite materials reinforced with halloysite nanotubes fabricated by powder metallurgy

HNTs halloysite nanotubes supplied were used as the reinforcement of nanostructured composite materials with an EN AW-AlMg1SiCu alloy matrix. Halloysite nanotubes (Fig. 8a) are multiwalled, cylindrical, hollow objects with the diameter less than 100 nm and length of about 500 nm to over 1.2 μm . Constant research interest in metallic composite materials seen in the recent years is closely linked to the fast growth of the motor industry and with seeking constantly new, better constructional solutions, which would be lightweight, and also reliable and highly strong, as well as with search for new composite materials. Such works are becoming even more important in Poland, because this is the place where, apart from the USA and New Zealand, one of the three global deposits of halloysite, i.e. nitrided aluminium silicide $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot \text{H}_2\text{O}$, is located.

A reason supporting the use of halloysite nanotubes as a reinforcement of unique aluminium alloy matrix composite

materials is to ensure high thermal conductivity for such materials whilst maintaining low linear expansion, unlike composite materials reinforced with, e.g. ceramic particles. Nanostructured composites reinforced with halloysite nanotubes can be competitive to hypereutectic silumins and Al/SiC, Al/ Al_2O_3 composites used for this aim. Nanocomposite materials were produced by mechanical milling in a centrifugal ball mill, compression and sintering of a mixture of air-sputtered EN AW-AlMg1SiCu aluminium alloy powder with the nominal size of particles of not more than 100 μm and of halloysite nanotubes HNT with the mass fraction of, respectively 5 and 10% and then cold pressing in a mould with the socket diameter of 26 mm and under the pressure of 300 MPa, and then extruded at 460-480°C using a graphite suspension in oil as a slip sub-stance, without degassing, in a shield jacket. Direct extrusion of the cold pressed rod-shaped composite materials consisted of placing a moulding in a thick-wall sleeve closed from one side with a punch, and from the other side – with a die with a forming opening. At the temperature of 460-480°C, under the influence of pressure exerted by a punch, the material was moulded through a die opening, with the deformation factor of 10.57, and a rod was produced with the diameter of 6 mm and density near the theoretical density. The deformed particles were tightly joined, thus creating a homogenous morphologic structure free of pores and discontinuities. The amorphisation of the halloysite reinforcing phase takes place already after more than ten minutes of milling. The use of mechanical milling leads to a high degree of deformation, which – coupled with a decreased size of grain below 100 nm and the dis-persion of the reinforcing refined particles – is reinforcing the material. Halloysite

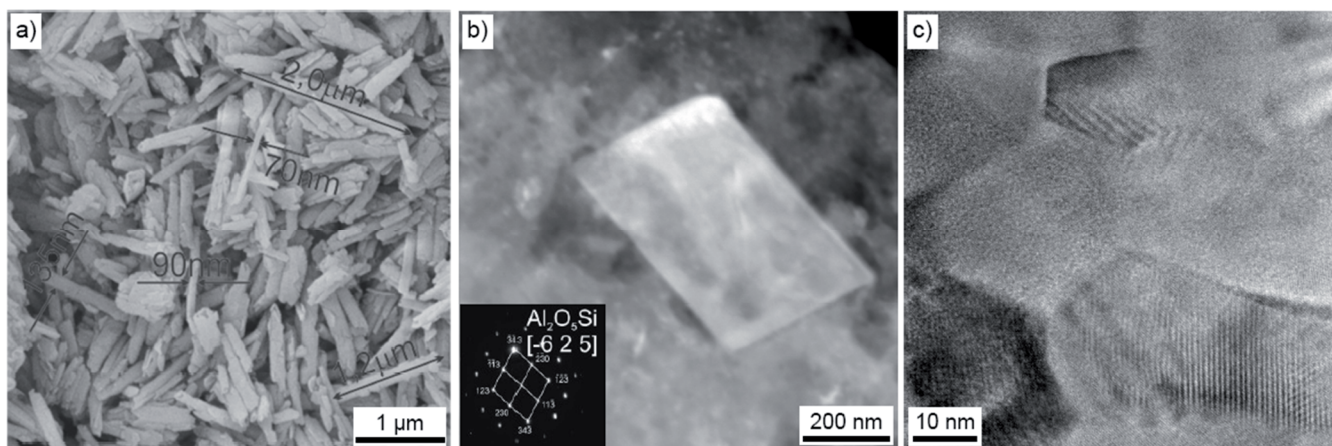


Fig. 8. The structure of the a) halloysite nanotubes (SEM), b), c) aluminium alloy AlMg1SiCu composite material with reinforcement of the 15% halloysite nanotubes, b) the primary $\text{Al}_2\text{O}_3\text{Si}$ phase produced most probably during the mechanical milling process (HRTEM), c) with the occurrence of nanometric grains even 5-10 nm in the matrix (HRTEM)

reinforcing phases in the created composite materials are distributed very uniformly as a result of plastic consolidation by hot pressing, and the proof that consolidation is carried out correctly, is also the material achieved, with a very fine structure, deprived of any agglomerates of reinforcing particles. Apart from a highly fine structure, the studied composite materials consist of two phases with a contrasting structure. The lack of pores, voids and the tightly adhering phases signify that the matrix and reinforcement particles are well bonded during mechanical synthesis as well as in plastic consolidation. Examinations in the transmission mode also allowed to identify the presence of a solid aluminium solution with nanometric grains, intermetallic primary phases AlFe_3 and $\text{Al}_4(\text{Fe,Cr,Mn})\text{Si}_{0.74}$ and the $\text{Al}_2\text{O}_3\text{Si}$ phase created most probably during the mechanical milling process. A highly fine structure, especially the existence of grains with the size of several nanometres, was shown by means of high-resolution electron microscopy. A high degree of plastic deformation, a fine structure with nanometric sizes as well as dispersive reinforcement with particles of halloysite and oxides, all caused by mechanical milling, have an obvious effect on a nearly 3-fold growth of microhardness. It was found, however, after plastic consolidation, that microhardness of the created materials fell by 30% compared to the milled powders, which may be connected with recovery and partial recrystallisation caused by the effect of higher temperature in extrusion. Nevertheless, the produced composite materials are characterised by microhardness ranging between 110-150 $\text{HV}_{0.1}$, which clearly exceeds the values attained for a conventional EN AW-AlMg1SiCu alloy even after correct heat treatment.

10. Composite materials reinforced with sintered halloysite nanotubes fabricated by gas-pressure infiltration

Aluminium alloy matrix composite materials with enhanced mechanical properties and wear resistance, much higher than the functional properties of the matrix material, can be manufactured through the pressure infiltration with a liquid aluminium alloy of porous ceramic skeletons fabricated by sintering halloysite nanotubes (Fig. 9). If halloysite is heated at temperature above 980°C , structural transformation is seen of halloysite into mullite, which is a ceramic reinforcing phase in such nanostructural composite materials.

Porous ceramic skeletons, being the final reinforcement of composite materials with an EN AC- AlSi12 alloy matrix, were fabricated by the mechanical milling in a centrifugal ball mill, by compression and by the sintering of halloysite nanotubes HNT with carbon fibres forming the structure and size of open pores and a slipping agent in the form of powdered micronised amide wax with the mass fraction of 1%. The so prepared powder mixtures were formed by cold uniaxial pressing in closed dies on a platen hydraulic press under the pressure of 100 MPa for 15 s, and then heated in an oven at $1100\text{--}1500^\circ\text{C}$ for 1 hour as a result of slow heating to the carbon fibre degradation temperature, heating at 800°C , to degrade them within the whole volume of the specimens, reheating to the appropriate sintering temperature, sintering and then cooling. The presence of a solid solution of aluminium $\alpha\text{-Al}$ and silicon eutectics $\alpha+\beta$, being a matrix of composite materials

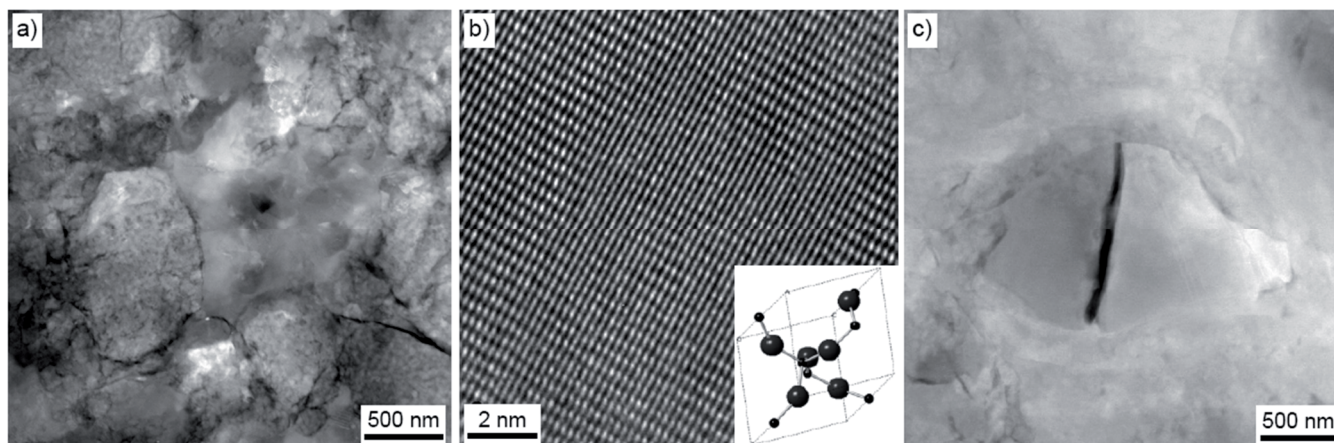


Fig. 9. The structure of the infiltrated AlSi12 matrix nanocomposite reinforced with sintered halloysite nanotubes fabricated by gas-pressure infiltration a) nanostructural AlSi12 matrix (TEM), b) cristobalite reinforcement (HRTEM), c) the Si grain surrounded by a thin layer of mullite (TEM)

and mullite $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, being the reinforcement in form of sintered skeletons, was found in the composite materials reinforced with skeletons made by the sintering of halloysite nanotube, whereas manufacturing conditions of porous reinforcing skeletons do not exert significant impact on the structure. Significant structural differences are caused by variations in the sintering temperature of such skeletons as numerous precipitates of coarse-grained silicon occur as a result of sintering at 1300 and 1500°C, having a tendency to crystallise on the surface of the ceramic phase, whose share increases as the fraction of reinforcement increases. About a 200 nm thick transition zone exists between an aluminium solution and mullite $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, with relatively large grains, larger than mullite grains in the external – from the side of mullite – part of the transition zone, with the presence of an aluminium solution and oxygen and a lower concentration of silicon in relation to mullite. SiO_2 phase is thermodynamically unstable in the presence of aluminium, it is reacting with it by creating aluminium oxide, moreover, coarse-grained precipitates of pure silicon are created during infiltration and diffusion on the matrix-reinforcement boundary, as a result of which the matrix corresponds to the structure of a hypereutectic alloy. Following the infiltration and decomposition of cristobalite SiO_2 , mullite $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ constitutes the only component of a ceramic skeleton, with no interaction between it and liquid aluminium. As the fraction of mullite is increasing, so is rising the hardness of the composite materials produced as a result of pressure infiltration, with the highest value of 114.6 HRF present after infiltration at 1500°C with a 70% fraction of ceramic phase, whilst the lowest, of 64.9 HRF, after infiltration at 1100°C. The bending

strength is increased considerably to 276 MPa in case of reinforcing with skeletons sintered at the temperature of 1300°C with a 60% fraction of HNT, and to 307 MPa after sintering porous skeletons at 1500°C with a 50% fraction of HNT, as compared to the strength of 224 MPa for an EN AC-AlSi12 alloy forming the matrix. When the fraction of reinforcement is increased, so is decreased the bending strength of the discussed composite materials.

11. Aluminium matrix composites reinforced with multiwalled carbon nanotubes

Original nanocomposite materials reinforced with MWCNTs (Fig. 10) were produced in high-energy mechanical milling and hot pressing. The material for the investigations was prepared using, as a matrix material, air-sputtered EN AW-AlMg1SiCu aluminium alloy powder whose particle size did not exceed 100 µm, with reinforcement by means of 2 and 5% with MWCNTs. The composite powders obtained in mechanical milling in a centrifugal ball mill with micronized ethylene-bis-stearamide-wax as a slip agent with the mass fraction of 1%, were cold pressed in a mould with the socket diameter of 26 mm and under the pressure of 300 MPa, and then extruded at 460–480°C using a graphite suspension in oil as a slip substance, without degassing, in a shield jacket. Direct extrusion of the cold pressed rod-shaped composite materials consisted of placing a moulding in a thick-wall sleeve closed from one side with a punch, and from the other side

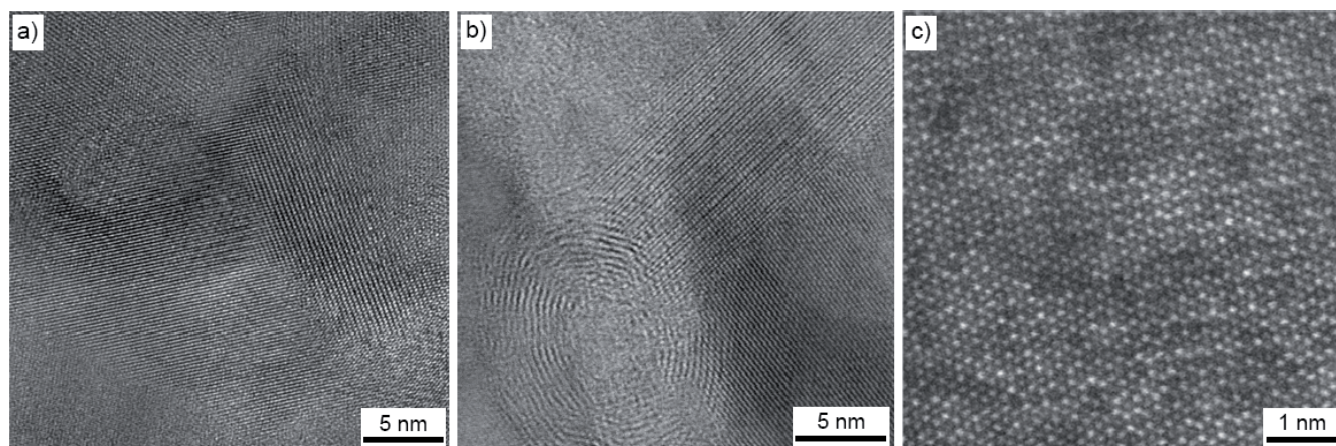


Fig. 10. The structure of the extruded AlMg1SiCu matrix nanocomposite reinforced with MWCNTs, a) nanostructural grains in the matrix (HRTEM), b) well dispersed MWCNTs in the matrix (HRTEM), c) the Al_4C_3 carbides (HRTEM)

– with a die with a forming opening. At elevated temperature, under the influence of pressure exerted by a punch, the material was moulded through a die opening, with the deformation factor of 10.57, and a rod with the desired shape and dimension was achieved and with density near the theoretical density.

Primary circular particles are deformed, flattened and have a plate-like form in the initial stage of mechanical synthesis. A tendency to join the earlier deformed particles prevails when milling the powders, further leading to increasingly larger composite material components being formed. Changes in the shape and size of the ground powders result from individual particles being welded due to collisions with grinding mediums or with the mill walls. The conglomerates of flattened particles formed as a result of welding are becoming much more reinforced, harder, and hence susceptible to cracking. As milling advances, the particles are fragmented and re-joined, and this finally contributes to the random orientation of the welded particles' boundaries. A relatively equiaxial shape of the milled powder's particles informs that the process has reached the predefined status. The deformed particles were tightly joined, thus creating a homogenous morphologic structure free of pores and discontinuities. Powders with the volume fraction of 5% of MWCNTs have the smallest particle size.

The bands (D and G, G'), distinctive for MWCNTs, confirm – in a Raman spectrum – the presence of carbon nanotubes in AlMg1SiCu alloy powder. The intensity of the band D is higher for all powders as compared to the band existing for MWCNTs themselves, which signifies a higher number of defects, carbon impurities with sp^3 bonds and defects on the side walls as a result of breaking sp^2 bonds created in high-energy mechanical milling. The

intensity of the G' bands has decreased significantly as a result of defects.

The nanocomposite materials reinforced with MWCNTs produced in high-energy mechanical milling and hot pressing are characterised by the lack of matrix structure discontinuities, which means that powder consolidation was performed correctly. Structure examinations in a high-resolution transmission electron microscope were carried out on a nanocomposite material with a fraction volume of 5% of MWCNTs fabricated from powder milled for 10 hours. The examined material has a homogenous, nanocrystalline structure, with symmetric grains sized 50–70 nm.

Apart from the phase α -Al, Al_4C_3 carbide with a distinct morphology of rods with the diameter of 5–10 nm and length of 20–30 nm was also identified in the material subjected to plastic consolidation, i.e. pressing and hot extrusion of powders after high-energy milling. Al_4C_3 carbides are released in those places where previously carbon nanotubes existed, which most probably derives from the diffusion of Al atoms between the side walls of MWCNTs, as a result of breaking the sp^2 bonds created in high-energy mechanical milling. The precipitation of Al_4C_3 carbide supports the enhancement of mechanical properties of the coating, most probably due to activating a mechanism the same as precipitation strengthening acc. to Orowan [29]. As the volume fraction of MWCNTs rises to 5%, and as milling time is increased, the microhardness of the achieved nanocomposite materials reinforced with MWCNTs rises by almost 200%, as compared to the microhardness of the material produced from the input, unmilled powder. The highest microhardness of 168 ± 7 HV is seen for a nanocomposite material reinforced with

5% vol. of MWCNTs, fabricated from powder milled for 10 hours and is higher by 55% than the hardness of the extruded AlMg1SiCu alloy produced from powder milled over the same time.

12. Application of the carbon nanotubes and graphene based counter electrodes for dye-sensitized solar cells

As part of intensive investigations into the alternative types of photovoltaic cells which may contribute to their decreased manufacturing costs, the most promising works concern Dye-sensitized Solar Cells (DSSCs) with the efficiency of 7.1%, connected with the use of nanostructural carbon materials. The numerous advantages of DSSCs include much higher flexibility as compared to silicon cells, low toxicity, high transmittance, selectable colour, easy production and small sensitivity to solar radiation incidence angle. The cells play an important role in the concept of developing modern, environmental and user friendly architecture owing to their high transmittance and the related applicability in building integrated photovoltaics (BIPV). As elastic substrates can be used, DSSCs can be used as parts of clothes, bags, tents, serve as a source of supply for portable electrical devices, e.g. notebooks or cell phones and can be used in solar energy driven cars. A conventional dye-sensitised cell consists of two glass substrates with a layer of conductive oxygen TCO deposited on the surface, between which electrolyte is located. One TCO glass plate with a catalytic material deposited on the substrate is a counter electrode, whilst the other, with titanium oxide deposited on the surface and the absorbed dye, is a photoanode. By changing the chemical composition and the structure of the main parts of dye-sensitised cells (photoanode and counter electrode), it is possible to improve efficiency and reduce their manufacturing costs, hence they become an alternative for conventional silicon photovoltaic cells. One of the solutions is to apply the nanostructural carbon materials (Fig. 11), which can be used as: an electrocatalyst on a counter electrode, alone or with other functional materials, thus ensuring an alternative for costly platinum nanoparticles, as an electrolyte filling increasing conductivity, as a component of a nanostructured photoanode allowing to reduce the degree of electron recombination with a reduced redox pair. 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 [2]. Graphene electrodes can be deposited onto a conductive substrate with the additives of a polymer binder, however, this encounters problems with required adhesion to conductive glass, though. For this reason, the most promising path, at a large scale, may be to produce graphene oxide by chemical oxidation, and then its chemical or thermal reduction. This is also supported by easy solubility in a water environment and in polar organic solvents, allowing to deposit it onto the substrate or to mix with other substances, which is not possible with primary graphene. It is also thought that the surface damages caused during the oxidation of graphene planes are responsible for electrocatalytic activity and thus the use of graphene oxide is more advantageous than of perfect graphene. The research planned this way was therefore successfully completed by using carbon nanotubes and reduced graphene oxide.

A counter electrode plays important roles by catalyzing the reduction of redox species after electron injection. Carbon nanotubes and graphene-based and reduced graphene oxide-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 ionomers: poly(3,4-ethylenedioxythiophene) polystyrene sulfonate PEDOT:PSS used in order to prevent reaggregation and then applied on the glass surface with fluorine doped tin oxide (FTO). A well 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 nanostructured titania films was immersed into an ethanolic solution of ruthenium based dye. For the fabrication of DSSCs, nanocrystalline TiO₂ photoanode was prepared by spreading the TiO₂ 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 TiO₂ films were immersed into ethanolic solution of ruthenium based dye for 12 h and rinsed with absolute ethanol to remove physically

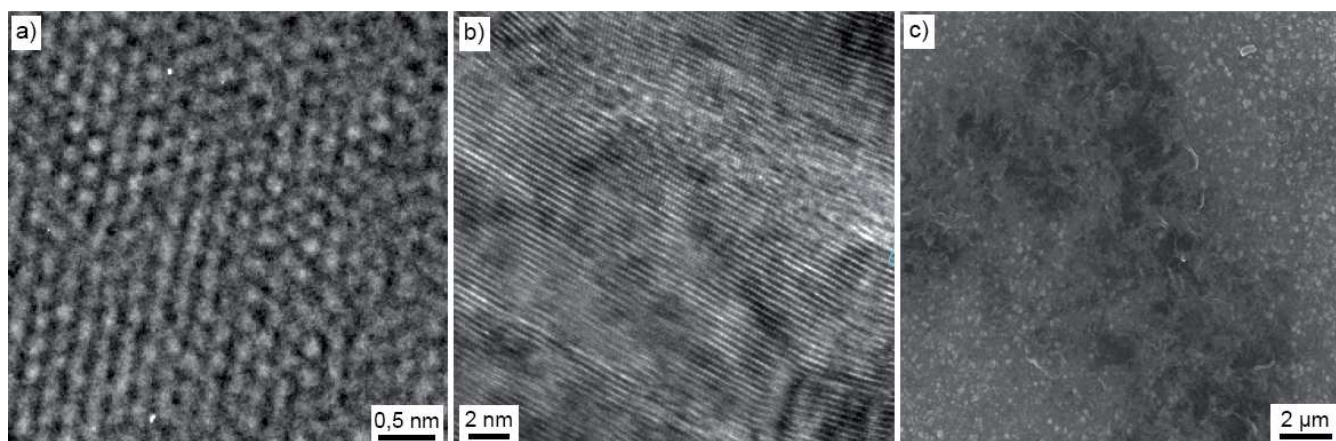


Fig. 11. The structure of a) the layers of graphene in distance 0.3309 nm (HRTEM), b) a few layers of graphene (HRTEM), c) layers of conductive polymer PEDOT:PSS with reduced graphene oxide used as a counter electrode for dye-sensitized solar cells (SEM)

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. 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 what can be caused by higher catalytic activity and increasing in the surface area of counter electrode in comparison to carbon nanotubes [2]. Graphene-based counter electrodes are very transparent in the all range of solar spectrum and do not significantly alter the transparency of FTO electrode. If reduced graphene oxide is introduced into a photoanode, this raises the efficiency of solar radiation energy absorption, as a result of which the conversion efficiency of solar radiation to electric energy rises by 1.03%. A costly platinum layer can be replaced by a layer of reduced graphene oxide from PVP (Polyvinylpyrrolidone) and with the layer of a high conductivity PEDOT:PSS polymer deposited onto the surface, which decreases efficiency relatively little as compared to a much more costly platinum counter electrode. If efficiency is decreased by 0.3% in relation to a reference cell with a platinum counter electrode and if the efficiency of 3.77% is reached for a dye-synthesised cell with a photoanode with reduced graphene oxide and a counter electrode from reduced graphene oxide and PVP with the deposited PEDOT:PSS layer on the surface, this may contribute to

reduction in the manufacturing costs of a dye-synthesised cell. If an original own technology is developed of thermal exfoliation of graphene oxide, and of manufacturing dye-synthesised photovoltaic cells with the reduced graphene oxide used for a photoanode and for a counter electrode – by appropriately applying the screen printing method and spin-coating technique – the production of repeatable layers with the set thickness is ensured, free of any structural defects and impurities.

The obtained research results and the own technologies developed allow to implement them realistically in production practice as being competitive towards the DSSCs produced now, mainly for economic reasons connected with relative reduction in production costs of such cells against the cells produced these days.

13. The preparation of nanocomposites: carbon nanotubes with precious metals

A special group of nanocomposite materials are multi-, two- and singlewalled decorated carbon nanotubes or such combined with nanoparticles of noble metals, forming MWCNTs-NPs type nanocomposites where NPs represent Pt, Pd, Rh, Re and nanotubes filled inside with nanowires of such elements [30-39] (Fig. 12). It can be thought that these are one of the smallest nanocomposite materials developed to date as engineering materials. The fabrication technology was developed of nanocomposite materials of the MWCNTs-NPs type.

Such nanocomposite materials are fabricated by means of a direct method through the functionalisation of carbon

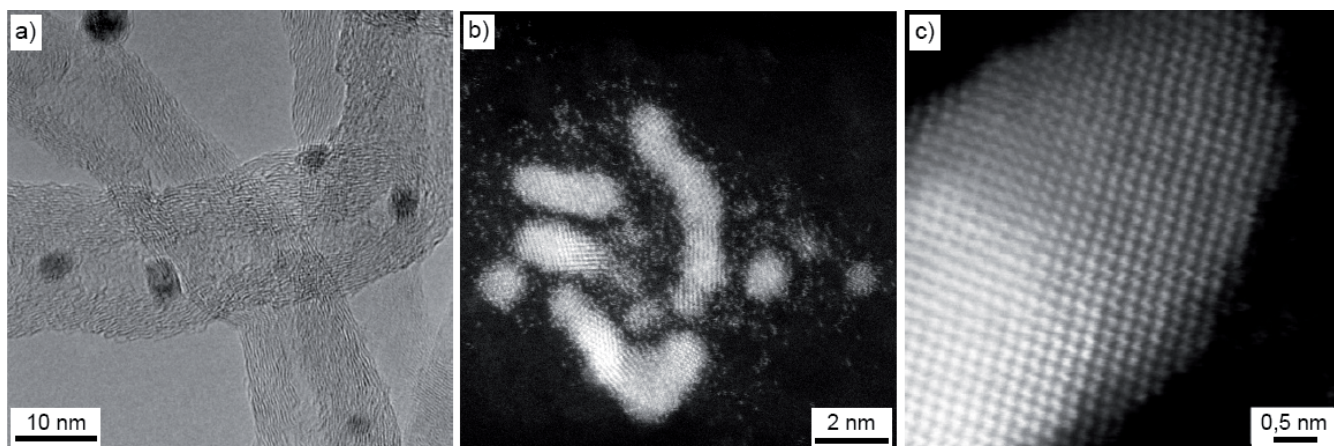


Fig. 12. The structure of the nanocomposite materials of the MWCNTs-NPs type a) multiwall carbon nanotubes decorated by rhodium nanoparticles (TEM), b) system of atoms in nanoparticles of platinum decorating carbon nanotubes (HAADF HRTEM), c) rhenium nanoparticle on the nanotube surface (HRTEM)

nanotubes with chemical methods, e.g. etching in acids, e.g. nitric acid, sulphuric acid and then the synthesis of 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 inert atmosphere of argon or with participation of hydrogen or by thermal functionalisation. The purpose of the investigations is the possibility to use such nanocomposite materials, in particular, in sensors of very small concentrations of gases, for identification of markers in medical diagnostics and for the purpose of catalysis [2].

14. The concept of the logical recurrence and inverted logics of a classical paradigm of materials science

The basis of the new undertaken research idea will be the systematisation of the nanometric objects and structural mechanisms allowing to improve the properties of new pioneering nanostructured composite materials with the extended nanoengineering components, as objects which are applied in such materials or which occur in them as a result of the sequence of technological operations applied [40]. From a substantial point of view, the research will consider several different phenomena with a different genesis, which are in a complementary way combined into a single topic, due to the expected effect, i.e. improvement of specific properties. A certain general formal notion is introduced in the research description: the extended nanoengineering components containing, among others, carbon

and halloysite nanotubes, metallic nanowires, including, e.g. Pt, Ag and Cu, polymer nanofibres, used as direct components of the analysed composite materials, but also surface layers deposited by ALD, PVD and CVD techniques, but also nanostructured objects created within the material structure as a result of technological processes, such as, e.g. Al_4C_3 carbide, mullite or Ω' phase, most often in the form of rods with nanometric sizes. The mentioned nanostructured objects identify the scope of this research. The goal is to generalise, in a scientific manner, the incidentally identified structural effects and to undertake systematic research using highly specialised research apparatuses with the highest possible resolution available for contemporary materials engineering, including real time investigations, e.g. to analyse structural changes during the plastic deformation of thin foils with a high-resolution transmission electron microscope (HRTEM).

The mentioned nanostructured objects identify the scope of the designated research. The own works of the Author performed until now described among others in the previous twelve chapters of this paper and the experience gathered, mostly technological experience, encourage to generalise, in a scientific manner, the incidentally identified structural effects and to undertake systematic research using highly specialised research apparatuses with the highest possible resolution available for contemporary materials engineering, including real time investigations, e.g. to analyse structural changes during the plastic deformation of thin foils with a high-resolution transmission electron microscope (HRTEM).

A classical paradigm of materials science provides that – in order to ensure the assumed usable functions – the

appropriate material should be selected, most often engineering material (i.e. such produced artificially) and, through appropriate technological processes, it should possess the designed shape and the intended structure should be formed ensuring the desired properties and expected functionality as shown on the diagram above.

A relationship between the material and the usable function is noticeable from a standpoint of an average designer designing any usable product, and other elements of this octahedron, illustrating the mentioned paradigm, are becoming a specific logical black box for such a person (Fig. 13).

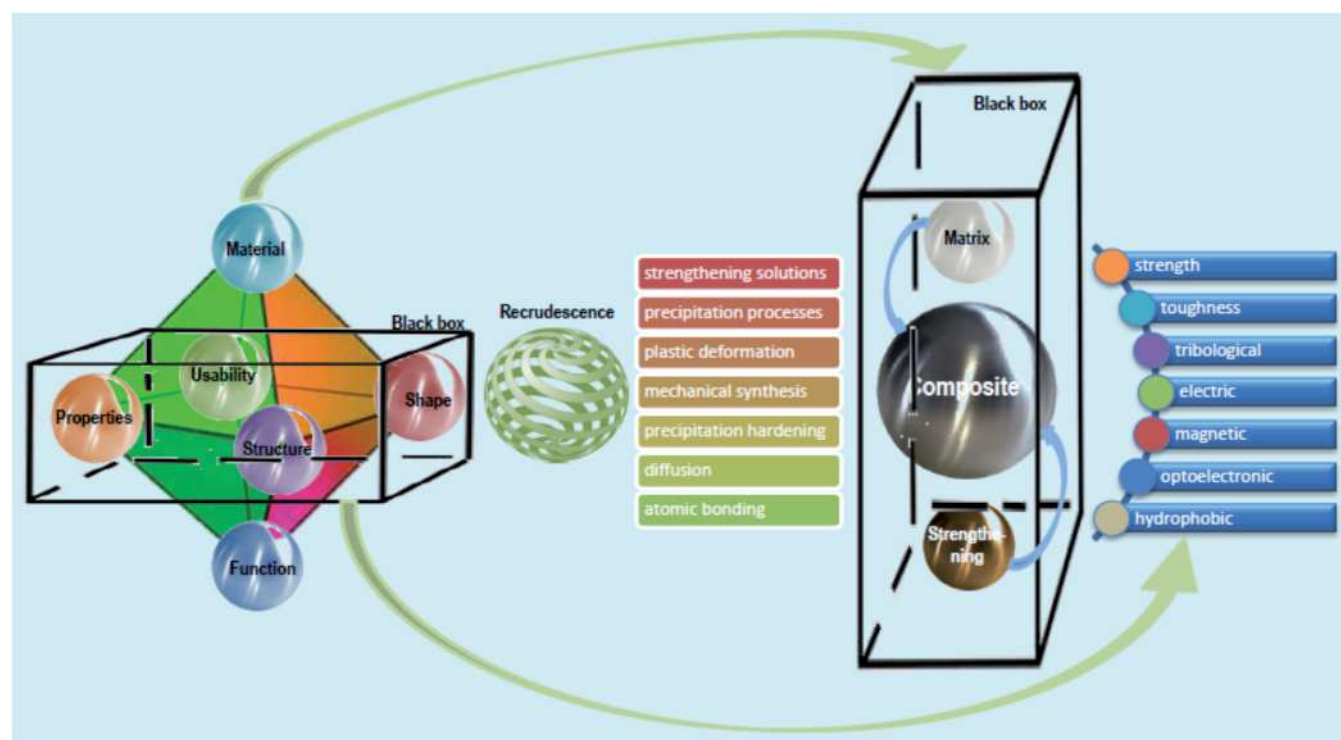


Fig. 13. The scientific essence of the research concept consists of logical recrudescence and inverted logics of a classical paradigm of materials science

The scientific essence of this research idea consists of logical recrudescence and inverted logics. A material being a nanocomposite made up of matrix and reinforcement is placed in a specific logical black box and somehow becomes a background of the further main considerations. A logical scheme of the undertaken actions calls for analysing and investigating different structural mechanisms listed here as examples (strengthening solutions, precipitation processes, plastic deformation, mechanical synthesis, precipitation hardening, diffusion, atomic bonding) and their impact on various properties of functional materials, also with their examples provided (strength, toughness, tribological, electric, magnetic, optoelectronic, hydrophobic). Very comprehensive research experience is required for this, along with the possibility and ability of utilising a very extensive array of complementary and ultramodern research equipment for the characterisation of material

structure and properties. The systematic investigations of such mechanisms and structural phenomena will allow to acquire and systematise new knowledge in the field of nanotechnology and to scientifically generalise the occurring structural effects. Investigations for many different nanocomposite materials presented further in this description, covered by the field of interest, have been planned in order to scrutinise and systematise the mentioned effects. The compositional and chemical composition of nanocomposite materials can be ultimately selected in a methodological manner by identifying the regularities between such structural effects and appropriate properties and by modelling them with artificial intelligence methods and by performing systematic research. It may seem (although it only seems so) that specific materials are of secondary importance. It will turn out that, finally, the so developed new generation of pioneering nanostructured composite

materials with the extended nanoengineering components will become the main result of the research recognising and systematising, in prior, the structural effects which may occur in such materials. This is a modern and original cognitive approach, examining philosophically the essence of the issues, not only their technological importance.

These are just few examples of research into nanostructural effects which may be decisive for unexpected changes in properties and the resulting areas of potential applications for a new generation of highly innovative advanced pioneering nanostructured composite materials with the extended nanoengineering components. The properties of the newly developed nanocomposites are determined by the properties of their matrix, the properties of the reinforcing phase, the geometry of the reinforcing phase (number, length, diameter, structure and orientation of extended nanoengineering components) and the quality of linkage between the matrix and the reinforcing phase. A chance for fabricating a new generation of innovative pioneering nanostructured composite materials with the extended nanoengineering components, featuring innovative properties, is offered by appropriate selection and correct application of diversified matrix materials (metallic, ceramic, polymer or air), the use of the extended nano-objects with a diverse chemical composition, structure and morphology, the use of the available or the establishment of new nanocomposite fabrication technologies and the use of the available or the establishment of new technologies for nanofiber structure and surface modification for extended nano-objects, and also the internal surfaces of pores and other processes leading to the improved combination/improved wettability/adhesion of nanostructural composite materials components, as well as the utilisation of the available or modification of the known manufacturing methods of extended nano-objects. The innovativeness of the achieved nanomaterials is dependent upon resolving the research problems mentioned above. The project's innovativeness should be considered in terms of investigating the impact of the applied input technologies, especially nanotechnologies, on the properties of the obtained nanocomposite materials with the extended nanoengineering components, as well as internal precipitated phases or nanoinclusions or surface treatment methods of micropores in order to apply nanomaterials enabling the improvement of specific properties.

Hypotheses will be tested practically concerning the feasibility of fabricating advanced porous and composite functional nanostructural materials. The available stands for producing nanocomposites will be designed, constructed and accommodated or improved. Hence, the possibilities of modifying a structure, surface, admixing and

deposition will be largely improved and the extent of such modifications' influence on the properties of the nanostructures produced will broaden.

The information presented indicates a very broad scope of scientific focus, covered by the presented research concept in the Table 1, which requires launching a very extensive, costly and long-term research programme to study all the aspects of creating so many new groups of nanocomposite materials with extended nanoengineering components.

15. The planned scientific objectives for the investigated nanostructured composite materials with the extended nanoengineering components

The planned research encompasses a search for a new generation of highly innovative advanced pioneering nanostructured composite materials through the interaction of extended nanoengineering components, and the outcomes of such research are very promising and may bring substantial cognitive results and, over time, may contribute towards launching numerous new products in which they will find their applications. The scientific objective of the planned research is to recognise and explain the materials science grounds and to develop the basis of the technology together with explaining the relevant structural mechanisms, in each case, of synthesis and/or production and formulation of the structure and properties of a new generation of pioneering nanostructured composite materials through the interaction of the so defined extended nanoengineering components and to characterise and model their structure and properties depending on the compositional, phase and chemical composition and the applied synthesis and/or production and/or processing processes, with confirming the highly probable future application areas, using the unexpected effects of formulating such materials' functional properties. The consequence of such actions will be the development of a new generation of highly innovative advanced pioneering nanostructured composite materials.

Special characteristics of one-dimensional nano-objects justify a search for new uses of such materials. The diameter of not more than 100 nm, decisive for their unique properties, is very often also a barrier for their application. Efforts have been made for this reason to produce hierarchical, three-dimensional structures and to combine them with other materials, i.e. to produce nanocomposite materials. The analyses mentioned indicate that all the

Table 1.

The scope of scientific focus covered by the presented research concept [19]

Potential, new properties of composite functional nanostructural materials with extended nanoengineering components and potential areas of application			
Nanofiber type	Matrix material	Potential, new properties resulting from combining nanocomposite components	Potential area of interest
Carbon structural nano-objects (nanotubes, graphene) or inorganic nano-objects (e.g. halloysite nanotubes)	metal	improvement of mechanical properties improvement of thermal and electric conductivity	automotive industry, aviation industry, space industry
	ceramics	improvement of thermal and electric conductivity	electronics and photonics, medicine, automotive industry, space industry, machine industry
	polymer	improvement of electric properties possible development of hierarchical structure	electronics and photonics, medicine and automotive industry, textile and clothing industry
	air	possible development of hierarchical structure, raised porosity	electronics and photonics, medicine and pharmacy, environmental industry
Polymer structural nano-objects (e.g. electrospun nanofibres)	metal	higher porosity (after removing nanofibers)	electronics, medicine, environmental industry, automotive industry, space industry
	ceramics	higher porosity (after removing nanofibers)	electronics, medicine, environmental industry, automotive industry, space industry
	polymer	improvement of mechanical properties bacteriocidity, resistance to chemical factors, possible development of hierarchical structure	electronics and photonics, medicine and pharmacy, automotive industry, textile and clothing industry
	air	improvement of mechanical properties bacteriocidity, resistance to chemical factors, possible development of hierarchical structure	electronics and photonics, medicine and pharmacy, environmental protection, automotive industry, textile and clothing industry
Metallic nanowires	polymer	improved electric conductivity and of other properties	electronics and photonics, car industry
Nanolayers	metal	improved mechanical properties, including hardness, abrasive and wear resistance	tool industry, implants, automotive industry
	ceramics	improved mechanical properties, including hardness, abrasive and wear resistance	tool industry, implants, automotive industry

structural effects occurring at a nanostructural scale, which are setting groundwork for the development of a new generation of pioneering nanostructured composite materials with the extended nanoengineering components, have also essential cognitive importance. They are also a material expected by industrial markets, which even more substantiates the fact that the research is up-to-date, attractive and needed. In such case it is reasonable to limit the scope of the research to selected areas only that can be solved in question with the adequately high success indicator. The

description of the state of the art for the subject of the research has been limited to the issues initially selected with an analysis by the method of weighted scores [41-43] serving to analyse preferences, using the procedural benchmarking technique and the initially performed foresight research as a basis for comparative assessment allowing to narrow down the scope of the project to 7 groups of the most prospective materials considering their potential applications and the expected physiochemical properties, as given in the Table 2.

Table 2.
The selected nanocomposite materials planned for the future investigation

Groups of the most prospective materials	Literature on already completed research in the area	Short description of the selected nanocomposite materials planned for the future investigation
Structural carbon or inorganic nano-objects + metal	[44-66]	obtaining a new generation of custom, original, light nanocomposites with improved electrical, thermal and mechanical properties (Mg, Al + carbon nanotubes) and original hybrid technologies of manufacturing such materials with a possibility of potential applications in the car, aviation, space and electronic industry and the examination of structural transformations occurring in such materials and their influence on specific properties
Structural carbon or inorganic nano-objects + polymer	[67-77]	obtaining a new generation of custom, original, light nanocomposites with improved photovoltaic properties (polymer + carbon nanofibres, graphene, graphene oxide) and original hybrid technologies of manufacturing such materials with a possibility of potential applications in the photovoltaic industry for electrodes of dye-synthesised photovoltaic cells and the examination of structural transformations occurring in such materials and their influence on specific properties
Metallic nanowires + polymer	[78-94]	obtaining a new generation of custom, original, light nanocomposites with high aesthetic values (transparent) with improved electrical and thermal properties (polymer + nanowires Cu, Ag, Au, Pd, Pt) and original hybrid technologies of manufacturing such materials with a possibility of potential applications in the car industry, for housings of electronic devices, for elements of solar cells and the examination of structural transformations occurring in such materials and their influence on specific properties
Nanostructural layers + metal/ inorganic substrate	[95-110]	obtaining a new generation of custom, original atomic ALD layers with a graded structure and adjustable thickness and biocompatible or optical properties and original hybrid technologies of such surface treatment of materials with a possibility of potential applications for photovoltaic cells or microporous skeletons and the examination of structural transformations occurring in such materials and their influence on specific properties
Laser treated layers + light metals or steel	[111-115]	obtaining a new generation of custom, original, light nanocomposites with improved mechanical surface properties (Mg, Al + clad carbides + inter-metallic precipitates) and original hybrid technologies of manufacturing such materials with a possibility of potential applications in the car and aviation industry and the examination of structural transformations occurring in such materials and their influence on specific properties
Air will be used as a matrix, which will allow to obtain ultimate materials	own information	obtaining a new generation of custom, original porous materials with high absorptivity, air and liquid permeability, barrierity and low density (nanofibrous polymer + air) as semi-products for filling pores with active substances in the liquid state, with the method indirect between infiltration and surface coating inside the pores, e.g. with lubricants, fire- or heat-insulating substances imparting special properties after solidification, and original hybrid technologies of manufacturing such materials with a possibility of potential applications in the textile and clothing industry, in the defence and civil industry (fire service), e.g. uniforms and protective clothes, especially non-flammable clothes

Table 3.

The scientific objectives planned for investigations for each one selected nanocomposite materials

Scientific goal	The scientific objectives planned for investigations for each one nanocomposite materials
Technology	the development of original custom hybrid manufacturing technologies and locally dedicated surface micro-treatment using advanced hybrid methods of technological processes of synthesis and/or fabrication and/or processing and, alternatively, surface micro-treatment inside the pores of a new generation of highly innovative advanced pioneering nanostructured composite materials with the extended nanoengineering components
Structure	the recognition of phenomena and structural mechanisms by using advanced methods the examination of the structure of a new generation of highly innovative advanced pioneering nanostructured composite materials through the interaction of the extended nanoengineering components using the most advanced methods of modern materials engineering, in order to recognise and explicate the phenomena and processes taking place during and as a consequence of their fabrication, micro-treatment and in application conditions
Properties	the recognition of the influence of structural phenomena and mechanisms on a set of properties by applying advanced examination methods of physiochemical, mechanical, tribological properties of a new generation of highly innovative advanced pioneering nanostructured composite materials with the extended nano-engineering components
Modelling	the generalisation of the influence of structural phenomena and mechanisms on a set of properties by applying advanced artificial intelligence methods, mainly neural networks, to model the structure and properties of the researched new generation of highly innovative advanced pioneering nanostructured composite materials with the extended nanoengineering components, newly created nanocomposite materials with the extended nanoengineering components depending on the compositional, phase and chemical composition and the applied technological processes of fabrication and surface micro-treatment inside pores

The planned research into a new generation of custom, highly innovative advanced pioneering nanostructured composite materials with the extended nanoengineering components is interdisciplinary, as it pertains not only to materials engineering, but also physics, chemistry, and also biology and medicine, wherever such are applicable. Research into the materials produced will make it possible to scrutinise more thoroughly the phenomena and processes of their fabrication, surface micro-treatment and in the conditions of clinical applications. The research is intensively employing ultramodern devices for the characterisation of the structure of the newly prepared materials and advanced research methods. Four scientific objectives presented in the Table 3 are needed for investigations for each one composite materials selected in the Table 2.

Hypotheses regarding the possibility of producing this highly innovative group of engineering nanocomposite materials will be practically tested. The research's innovativeness should be considered in terms of investigating the impact of the applied input technologies on the properties of the obtained nanocomposite materials, and, alternatively, methods of internal treatment of pores.

The so designed research permits to make scientific generalisations, very important taking into account the

theoretical grounds of nanotechnological processes, and the theory of nanostructured materials, especially nanocomposite materials, and will allow to achieve the overriding scientific objective of the research. In general, the project is of priority cognitive importance as theoretical considerations and the Author's initial analyses and occasional results of research provided in the literature, usually in the incipient phase of development, indicate a great need to intensify scientific research to develop new groups of materials with completely unexpected foreseeable effects, resulting from the use of the extended nanoengineering components defined above for manufacturing super advanced nanocomposite materials. It is hard to overestimate the effects, and this requires investigations into the basis of developing the synthesis and/or production and/or processing of such completely new groups of new-generation nanostructural engineering materials.

The cognitive nature of the research are associated with the determination of:

- the effect of compositional, phase and chemical composition on the structure and properties of the newly created nanocomposite materials with the extended nanoengineering components ensuring the improvement of specific properties,

- the effect of the newly developed technologies of fabrication and surface micro-treatment inside pores on the structure and properties of the newly created nanocomposite materials with the extended nanoengineering components ensuring the improvement of specific properties,
- the impact of internal precipitated phases or nano-inclusions or surface treatment of micropores in order to apply nanomaterials enabling the improvement of specific properties of the newly developed nanocomposite materials with the extended nanoengineering components,
- the modelling of the structure and properties of the researched newly created nanocomposite materials with the extended nanoengineering components depending on the compositional, phase and chemical composition and the applied technological processes of fabrication and surface micro-treatment inside pores using artificial intelligence methods, mainly neural networks.

The research will comprise the fabrication of materials with new unforeseeable properties fulfilling multiple functions. The functions result from, especially, or are greatly intensified by using nanomaterials (catalytic, electric, optical, magnetic, textile nanomaterials) employing the technologies of nanomaterials surface engineering, connected with producing nanolayers and nano-coatings (nanocomposite, with heat barrier, anti-wear, hydrophobic and biocompatible ones). The research is of an interdisciplinary nature, with its scope covering achievements in the field of materials engineering, physics, chemistry and biology. The research's results may have direct influence on the development of electronics and photonics, medicine and pharmacy, environmental protection, automotive industry, space industry, machine industry, textile and clothing industry, cosmetic industry, agriculture and food sector. Phenomena and processes at a nanoscale can be better recognised by producing a new generation of functional nanostructural materials (physicochemical basis of nanomaterials and nanostructures synthesis, with controlled architecture and properties, engineering of atomic and molecular bonds, models and theories explaining the properties of nanomaterials, surface phenomena, self-assembly phenomena in nanomaterials and nanostructures synthesis, magnetic phenomena in semiconducting and metallic nanostructures). Some answers are still to be clarified for the given fundamental research questions [19]. The research must necessarily utilise intensively ultramodern devices for the characterisation of nanostructures and nanomaterials and advanced research methods. The possibilities of modifying a structure, surface, admixing and

deposition will be largely improved and the extent of such modifications' influence on the properties of the nanostructures produced will broaden.

16. Final remarks

Nanotechnology is a new and dynamically developing research field. The purpose of this article was to demonstrate that those aspects have inherently stepped beyond the research domain of modern materials engineering, and they are not only exotic research problems followed by some laboratories only, as some researchers seem to think, by even evading this topic in their research work. It has been confirmed many times already, as also evidenced in this article, that *"(...) the principles of physics, as far as I can see, do not speak against the possibility of manoeuvring things atom by atom (...)"*¹. There are no doubts anymore that nanotechnology creates a common opportunity *"(...) to build things that work on the smallest possible length scales, atom by atom, with the ultimate level of finesse. (...)"*². The aim of the paper is also to stimulate the imagination, so that each reader 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, to solve the every expanding scope of the problems to be solved. This is confirmed by the words saying that we should constantly set new challenges: *"Learn from yesterday, live for today, hope for tomorrow. The important thing is to not stop questioning."*³ We should continue our research efforts because *"any knowledge that does not lead to new questions, becomes in a short time dead."*⁴ The fate of our future depends on our own activity. This is very graphically suggested by the words saying that *"life is like riding a bicycle – to keep your balance you must keep moving."*⁵ *"If you don't think about the future, you cannot have*

¹ as stated a little more than a half century ago by Prof. R.P. Feynman (1918-1988), a Nobel Prize Winner in Physics in 1965, in his famous lecture in Pasadena, CA, USA at the end of December 1959

² as noticed by Prof. R.E. Smalley (1943-2005), a Nobel Prize Winner in Chemistry in 1996

³ as stated by Prof. A. Einstein (1879- 1955), a Nobel Prize Winner in Physics in 1921

⁴ as stated by W. Szymborska Dr hc (actually M.W.A. Szymborska 1923-2012), a Nobel Prize Winner in Literature in 1996 in her Noble Speech

⁵ as stated by Prof. A. Einstein, a Nobel Prize Winner in Physics in 1921

*one*⁶. Technological progress in the future requires, therefore, intense research and development works now. ***“When choosing something worth doing, never give up and try not to let anybody down”***⁷.

Nanotechnology development is an immense challenge for the World of Science across the Globe. By paraphrasing the words of Prof. R.P. Feynman, recognised to be the Father of nanotechnology, we can say that there's plenty of room for many researchers (There's Plenty of Room... at the Bottom). But it is the time to take up the challenges. These are very interesting, fascinating cognitive problems, but also huge opportunities brought by the market following them. It is hard to overestimate the role of engineers in this evolving process. This environment cannot lose such an emerging opportunity. It is the reason that the Author of the paper presents his idea for creating the new generation of highly innovative advanced pioneering nanostructured composite materials through the interaction of extended nanoengineering components. The Author hopes that for a next few years he will have the chance for making this research and to obtain this advanced group of nanomaterials.

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⁶ as noticed by J. Galsworthy Dr hc multi (1867-1933), a Nobel Prize Winner in Literature in 1932

⁷ as encouraged by Prof. H.W. Kroto (1939-2016), a Noble Prize Winner in Chemistry in 1996

Prof. K. Labisz, Prof. K. Lukaszewicz, Dr D. Łukowiec, Dr M. Macek, Prof. J. Mazurkiewicz, Prof. D. Pakuła, Dr M. Pawlyta, Dr M. Prokopiuk vel Prokopowicz, Dr M. Staszuk, Dr M. Szindler, Prof. T. Tański, Dr B. Tomiczek, Dr A. Wierzbicka, Dr W. Wolany, who participated in preparing own collective publications from which the Author took the materiallographic photos for illustrate this paper.

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