323. The Advanced Structural Materials for Living Beings Implants

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(Received 5 September 2007; accepted 10 October 2007)

Abstract. The paper deals with development of bioinert and bioactive biomaterials, different application of structural materials, including metallic materials, nanomaterials, nanostructured materials, biomaterials, ceramics, polymers, hybrid materials, functional graded materials, composites. Also are discussed multi-functional engineering materials with gradient properties, engineering materials for challenging application conditions, including aggressive environment and light-weight, multi-material (hybrid) systems where advanced materials are combined with more conventional / structural materials and materials production or joining technologies. Interdisciplinary approach to biomedicine materials research and production is very promising and horizontal cooperation of different national technology platforms is discussed.

Keywords: biomaterials, biocomposites, polymer composites, implants, biomaterials wear and fatigue, technology platforms.

1. Introduction

Materials that are used in contact with biological systems are commonly called biomaterials. In medical applications, biomaterials are rarely used as isolated materials but are more commonly integrated into devices or implants. Although biomaterials are primarily used for medical application, they are also used in the equipment for processing biomolecules, for implants to regulate fertility in cattle, ect.

The first generation of materials was developed for use inside the human body in the 1960s and 1970s. A common feature of most of these materials was their biological inertness. Subsequently the field of biomaterials began to shift from a bioinert to bioactive materials. By the mid-1980s, bioactive materials had reached the clinic in a variety of orthopaedic and dental applications. They included various compositions of bioactive glasses, ceramics, glass-ceramics and composites, as well as a range of bioresorbable polymers.

Widespread clinical application of different structural materials is hindered mainly by high cost and limited scale in the mass-production of tissue-engineered products. Access to nanotechnology has offered a completely new perspective to the material scientist to mimic the different types of extra-cellular matrices present in tissues. Nanotechnology dramatically improve the functionality and longevity of implanted materials. Nanomaterials and/or nanocomposites with enhanced mechanical properties could replace the classic materials that fatigue-fail due to crack initiation and propagation. Bioactive glasses and macroporous foams can activate genes that stimulate regeneration of living tissues. The biological environment is harsh and can lead to rapid or gradual breakdown of many materials. Implant materials can solubilize, crumble, become rubbery, or rigid with time. Nanotechnology can assist in the development of intelligent biomaterials, which are designed to positively react to changes in their immediate environment.

The term *Advanced Engineering Materials & Technologies* refers to the following pillars: - multi-functional engineering materials with gradient properties; - engineering materials for challenging application conditions, including aggressive environment and light-weight; - multi-material (hybrid) systems where advanced materials are combined with more conventional / structural materials; - materials production or joining technologies.

Material surface compatibility mean the chemical, biological, and physical suitability of an implant surface to the host tissues. Structural compatibility is the optimal adaptation to the mechanical behavior of the host tissues. Therefore, structural compatibility refers to the mechanical properties of the implant material, such as elastic modulus and strength, implant design (stiffness, which is a product of elastic modulus) and optimal load transmission (minimum interfacial strain mismatch) at the implant/tissue interface. Optimal interaction between biomaterial and host

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is reached when both the surface and structural compatibilities are met.

Clinical experience clearly indicates that not all off-the-shelf materials (commonly used engineering materials) are suitable for biomedical applications. The various materials used in biomedical applications may be grouped: metallic materials, nanomaterials, nanostructured materials, biomaterials, ceramics, polymers, hybrid materials, functional graded materials, multimaterials and different coatings of base materials. These materials are used in engineering coupled with "conventional" structural materials like gold, tantalum, stainless steel, cobalt alloys (alloyed with Cr, Mo, W, Ni), aluminium and titanium alloys, composites, polymers (Teflon, polymethyl-methacrylate, polyurethane, cellulose), advanced ceramics, glasses, coatings, adhesives, polymer matrix composites, etc. for the engineering products, systems and processes in the different areas.

Classical materials science activities in the past largely focused on bulk properties of different materials by characterizing them experimentally and analyzing them theoretically in terms of continuum mechanics models. This situation has changed over the last few years. Both experimental and theoretical tools have improved considerably so that much stronger links between basic physical and chemical properties at the atomic/molecular structural level and the overall properties of the material have been established [1].

2. Metallic materials

Metallic materials are often used as biomaterials to replace structural components of the human body. This is because, when compared to polymeric and ceramic materials, they possess more superior tensile strength, fatigue strength, and fracture toughness. Metallic biomaterials – such as 1.4404 (X2CrNiMo17-12-2) stainless steel, cobalt-chromium alloys, pure titanium, and Ti–6Al–4V alloys are typical metallic biomaterials used for production of implants mainly because of their excellent mechanical and corrosion properties (Table 1). Although originally developed for industrial purposes, these materials have been tried for biomaterial uses due to their relatively high corrosion resistance and excellent mechanical properties. However, when used as biomaterials, these materials pose several problems. These problems include toxicity of corrosion products, fracture due to corrosion fatigue and fretting corrosion fatigue, lack of biocompatibility, and inadequate affinity for cells and tissues. Moreover, the elastic moduli of current metallic biomaterials are not well matched with that of natural bone tissue, resulting in stress shielding effects that can lead to reduced stimulation of new bone growth and remodeling which decreases implant stability.

The release of nickel trace elements – which cause toxicity – has prompted the development of nitrogen-containing nickel-free austenitic stainless steels. These steels are now available for production of implant of bone plates and screws. Ti–6Al–4V alloys do not contain nickel as an alloy element, though nickel is included as a trace impurity.

In terms of corrosion resistance in the human body, type 1.4404 stainless steels are inferior compared to cobalt–chromium alloys and titanium alloys. Large amounts of type 1.4404 (316L) stainless steel are used for implant devices because they are less expensive than cobalt–chromium alloys, pure titanium, and titanium alloys.

Table 1. Physical and mechanical properties of various implant materials in comparison to natural bone

Properties	Natural bone	Stainless steel	Co–Cr alloy	Ti alloy	Magnesium alloy	Hydroxyapatite
Density (g/cm^3)	1.8–2.1	7.9–8.1	8.3–9.2	4.4–4.5	1.74–2.0	3.1
Elastic modulus (GPa)	3–20	189–205	230	110–117	41–45	73–117
Compressive yield strength (MPa)	130–180	170–310	450–1000	758–1117	65–100	600
Fracture toughness (MPa·m$^{1/2}$)	3–6	50–200	N/A	55–115	15–40	0.7

Corrosion resistance of steel increases with increase of chromium content. Corrosion-resistant steels are made by adding more than 12% of chromium, which results in the formation of a thin, chemically stable, and passive oxide film.

Stainless steels are classified into three categories according to their microstructure: ferritic stainless steels, martensitic stainless steels, and austenitic stainless steels.

Martensitic stainless steels are essentially alloys of chromium and carbon, where the chromium content is generally less than 18%. They posses a distorted bcc crystal structure and are obtained by rapid cooling from the austenitic phase to the ferritic phase. Martensitic stainless steels are generally resistant to corrosion only to relatively mild environments.

Amongst the three categories, ferritic stainless steels are the only ones which do not contain nickel. However, ferritic stainless steels are inferior to other stainless steels in terms of strength, toughness, workability, weldability, and corrosion resistance. Moreover, a critical prerequisite for orthopedic implant materials is the complete absence of ferromagnetism. Therefore, in many aspects, ferritic stainless steels are inadequate and inappropriate candidates of implant materials because the microstructure of stainless steel implants must be fully austenitic.

More than 18% of chromium is necessary to obtain the stable and homogeneous ferritic structure. As ferritic stainless steels have not the phase transformation from austenitic to ferritic, heat treatment is not effective in increasing strength. In general, strength increases with increase of chromium content. However, when chromium

stainless steels containing higher than 18% chromium are heated at 400–500 °C for long hours, they become extremely brittle. This is because they decompose into Fe-rich α′ and Cr-rich α″ phases which cause the brittleness. Carbon is detrimental to corrosion resistance in stainless steels. On the other hand, to confer particular characteristics such as heat resistance, machinability, enhanced corrosion resistance, and increased strength, some grades may contain molybdenum, titanium, niobium, nickel, silicon, aluminum, phosphorus, and sulfur.

Austenitic stainless steels have numerous advantages, namely:

- austenitic stainless steels are characterized by very low yield strength-to-tensile strength ratio and high formability,
- to increase strength, cold working and successive strain aging treatment can be applied,
- austenitic stainless steels are superior to ferritic stainless steels in corrosion resistance because the crystallographic atomic density of the former is higher than that of the latter,
- austenitic stainless steels are essentially nonmagnetic.

In terms of disadvantages, austenitic stainless steels generally have higher sensitivity toward pitting corrosion and stress corrosion cracking and also have lower crevice and intergranular corrosion resistances than ferritic stainless steels.

Intergranular corrosion occurs preferentially at the grain boundaries of a stainless steel. Stress corrosion cracking is a corrosion mechanism in which the combination of susceptible alloy, tensile stress, and corrosive environment leads to cracking of the metal.

Corrosion resistance of steel type 1.4404 improved by adding 2.0–3.0 % of molybdenum, increasing nickel from 8.0–10.0 % to 12.0–15.0 %, and reducing carbon to less than 0.03 %. The presence of molybdenum as an alloying element in stainless steel reduces both the number and the size of nucleations and metastable pits. Corrosion resistance of nickel-containing austenitic stainless steels can be improved by adding nitrogen. However, the release of nickel ions into the human body can be inevitable when they are used as implants with fretting sites (such as the combination of plates and screws). Therefore, it is absolutely imperative to develop nickel-free austenitic stainless steels which are required for producing implants intended for long-term implantation.

From the chemical composition perspective, nitrogen is the most promising nickel-substituting element. Nitrogen increases austenite stability and corrosion resistance, and prevents the formation of σ-phase.

Appropriate nitrogen-containing nickel-free austenitic stainless steels are known to exhibit a variety of exceptional properties like high strength, high ductility, high work-hardening capacity, improved wear resistance and corrosion resistance. This enhanced hardening behavior is due to the effect of nitrogen on the structural development during cold work, which is characterized by planar dislocation arrangement and extensive twinning.

Plastically deformed austenitic stainless steels show magnetism. This is because a martensite phase is formed due to stress-induced transformation. However, the characteristic property of nitrogen-containing nickel-free austenitic stainless steel is extremely low magnetizability. High nitrogen-containing nickel-free austenitic stainless steel did not show any pitting corrosion in electrolytes. Due to its combination of outstanding mechanical properties and excellent corrosion resistance, nitrogen-containing nickel-free austenitic stainless steels is superior to 1.4404 stainless steel in terms of corrosion, erosion–corrosion, and sliding wear–corrosion resistance. Nitrogen-containing nickel-free austenitic stainless steels may be available for the production of implant devices such as screws, wires and bone plates. However, in austenitic stainless steels, the degree of precise machinability is low as the work hardening is high. Therefore, the production of a small precise device such as stent from austenitic stainless steels is expensive.

Commercial purity titanium has long been used for biomedical stents, lead wires and trauma fixation devices. The mechanical strength of commercial purity titanium remains below the normal thresholds considered for hard tissue replacement. The annealed Ti–6Al–4V alloy today remains the largest single titanium alloy used for biomedical device manufacture.

While commercial purity titanium and alpha–beta titanium alloys remain the primary titanium materials used for current biomedical application the past decade has shown a substantial increase of metastable beta titanium alloys. The Ti–29Nb–13Ta–4.6Zr alloy, after water quenching from the β-phase temperature displays a mixture of β phase and orthorhombic martensite and has an elastic modulus of 65 GPa. The average β grain size and the volume fraction of martensite has an important influence on this material's mechanical properties. The strength of this alloy can also be increased significantly by aging. This increase in strength comes at the expense of ductility and elastic modulus. Yield strengths as high as 1100 MPa have been attained after ageing at 450 °C for 48 h [2].

Magnesium is an exceptionally lightweight metal. With a density of 1.74 g/cm^3, magnesium is 1.6 and 4.5 times less dense than aluminum and steel, respectively. The fracture toughness of magnesium is greater than ceramic biomaterials such as hydroxyapatite, while the elastic modulus and compressive yield strength of magnesium are closer to those of natural bone than is the case for other commonly used metallic implants. The major drawback of magnesium in many engineering applications — its low corrosion resistance, especially in electrolytic, aqueous environment. Corrosion of the magnesium-based implant involves the formation of a soluble, non-toxic oxide that is harmlessly excreted in the urine. Thus, it is projected that magnesium and its alloys be applied as lightweight, degradable, load bearing orthopedic implants, which would remain present in the body and maintain mechanical integrity over a time scale of 12–18 weeks while the bone tissue heals, eventually being replaced by natural tissue. The unfortunate complication is that pure magnesium can corrode too quickly in the physiological pH (7.4–7.6) and high chloride

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environment of the physiological system, loosing mechanical integrity before the tissue has sufficiently healed and producing hydrogen gas in the corrosion process at a rate that is too fast to be dealt with by the host tissue. Several possibilities exist to reduce the corrosion rate of magnesium by using alloying elements (rare earth elements) and protective coatings. Alloying is an essential step to improve mechanical properties and corrosion resistance of magnesium.

The modern magnesium rare-earth alloy consisted of 4 wt% lithium, 4 wt% aluminum and 2 wt% of a rare earth element mixture of cerium, lanthanum, neodymium and praseodymium.

The rapid corrosion rate of magnesium in the electrolytic physiological environment is one of the greatest limitations for its use in orthopedic applications. Unprotected magnesium exposed to a typical atmosphere will develop a gray oxide film of magnesium hydroxide ($Mg(OH)_2$) which slows corrosion. Protective coatings and surface treatments can also be applied to improve the corrosion resistance and biological compatibility of magnesium-based implants. Protective coatings for magnesium must be non-toxic, and aim to improve the biocompatibility/bioactivity of the implant.

Porous magnesium metal implants suitable for biomaterial applications have been prepared using argon gas injection to molten magnesium. In contrast to monolithic materials, porous materials under a compressive load are characterized by a shortened region of linear elasticity ending at the yield strength which is followed by a long plateau exhibiting a constant flow stress to large strains. The number, size, shape and connectivity of pores have significant effects on the Young's modulus and yield stress. Samples with suitable compressive strengths between 12 and 17 MPa were obtained with 35–50% porosity and fixed pore size of 250 μm, or by fixing the porosity at 45% and varying the pore size between 100 and 400 μm [3].

3. Polymers

A large number of polymers are widely used in various applications such as polyethylene (PE), polyurethane (PU), polytetrafluoroethylene (PTFE), polyacetal (PA), polymethylmethacrylate (PMMA), polyethylene terepthalate (PET), silicone rubber (SR), polyetheretherketone (PEEK) are used in various biomedical applications [4, 5]. This is mainly because they are available in a wide variety of compositions, properties, and forms (solids, fibers, fabrics, films, and gels), and can be fabricated readily into complex shapes and structures. However, they tend to be too flexible and too weak to meet the mechanical demands of certain applications e.g. as implants in orthopedic surgery. Also they may absorb liquids and swell, leach undesirable products (e.g. monomers, fillers, plasticizers, antioxidants), depending on the application and usage. Moreover, the sterilization processes (autoclave, ethylene oxide, and cobalt-60 irradiation) may affect the polymer properties.

Since the fiber reinforced polymers i.e. polymer composite materials exhibit simultanously low elastic modulus and high strength, they are proposed for orthopedic applications. The development of polymer composite biomaterials include: absence of corrosion and fatigue failure of metal alloys and release of metal ions such as nickel or chromium which may cause loosening of the implant, patient discomfort, and allergic skin reactions.

Metals alloys and ceramics are radio opaque and in some cases they result in undesirable obstacles in X-ray radiography. In the case of polymer composite materials the radio transparancy can be adjusted by adding contrast medium to the polymer. Moreover the polymer composite materials are fully compatible with the modern diagnostic methods such as computed tomography and magnetic resonance imaging as they are non-magnetic.

4. Ceramic materials

As compared to metals, ceramics are regarded as favorable materials for joints or joint surface materials. Alumina, titania, zirconia, bioglass (or bioactive glasses), carbon, and hydroxyapatite (HAP) are widely considered as biocompatible ceramics. Ceramics are known for their good biocompatibility, corrosion resistance, and high compression resistance. Drawbacks of ceramics include: brittleness, low fracture strength, difficult to fabricate, low mechanical reliability, lack of resilience, and high density. Low fracture toughness of ceramic materials make them a difficult choice for load bearing applications.

Ceramic materials for implants fall under two main groups, namely, (a) bioactive (calcium phosphate, glass-ceramic, hydroxyapatite), and (b) bioinert (pyrolytic carbon, alumina, zirconia). The bioactive materials are extensively used as coatings on metallic implants as they promote rapid bone growth. The bioinert ceramics have a different fracture toughness. Because of the low fracture toughness, alumina hip balls are restricted in size to greater than 28 mm. Zirconia, on the other hand has a higher fracture toughness, but suffers from potential biodegradation and radiation [6].

The use of zirconia in biomedical applications was reported in 1969. Considerable research has focused on zirconia and yttria ceramics that are characterized by fine grained microstructures. These ceramics are known as tetragonal zirconia polycrystals (TZP).

Calcium phosphate ceramics are widely used for hard tissue replacement due to their biocompatibility and osteoconductive properties. Porous ceramics with 100–300 μm pores are preferred since they allow bone to grow into the implant, promoting mechanical fixation with the natural bone.

Alumina ceramics were evaluated due to their excellent properties of high strength, good biocompatibility and stability in physiological environments. Due to lack of chemical bonding between sintered alumina and tissue, its applications as a potential bone substitute are limited. Alumina, because of the ability to be polished to a high

surface finish and its excellent wear resistance, is often used for wear surfaces in joint replacement prostheses.

Alumina and titanium dioxide have been used as nanoceramics separately or in nanocomposites with polymers such as polymethlylmethacrylate.

Intermetallics offer a compromise between metallic and ceramic properties.

Smart intermetallics (TiAl, NiTi, Cu-based and Fe-based intermetallics) found large number of applications in biomedical devices, sensors, etc. Increase in commercial usage of intermetallics is inhibited by their poor ductility and toughness at room temperature what causes difficulties in manufacturing and generates high cost of processing.

Metal Ceramic Composites with novel mechanical, electric, thermal and magnetic functionalities are recognized to hold the promise of revolutionizing the several technological fields including healthcare. A great variety of metal ceramic composites with designed micro- and nanostructure, including particle reinforced and fiber reinforced materials, as well as nanostructured and laminate composites, will enable the design and the fabrication of new multifunctional and structural components.

5. Composite materials

The uses of composites for biomaterials have included three broad areas:

• functionally graded composites,

• polymer-ceramic composites (with and without fiber reinforcements),

• biomimetic composites or composites with biological macromolecules [7].

The main feature of a functionally graded composite is the almost continuously graded composition of the composite that results in two different properties at the two ends of the composite. Powder metallurgy methods have been used to make HAP/titanium functionally graded composites offering the biocompatible HAP on the tissue side and titanium for mechanical property.

Polymer-ceramic composites have superior properties than either ceramics or polymers for use as total hip replacement materials.

The fibers used for toughening polymeric materials for use in THR also need to be biocompatible. Carbon fibers due to their good biocompatibility property have been used to reinforce ultra high molecular weight polyethylene, polypropylene, polybutylene terephthalate, etc. Multilayered laminated composites of carbon fibers and epoxy, carbon fiber and glass fiber epoxy composite are used. The application of polymer fibers as a reinforcement phase in total hip replacement components is limited due to the inadequate strength and stiffness of the fibers.

6. Carbon base materials

Diamond-like carbon (DLC) and carbon nitride (CN) are excellent candidates for use as biocompatible coatings on biomedical implants, which are due to not only their excellent properties but also their chemical composition containing only carbon, hydrogen and nitrogen, which are biologically compatible. DLC with its desirable properties such as high hardness, low coefficient of friction, chemical inertness, high electrical resistivity, high optical transparency, impermeability, etc., offers the potential as a coating for biomedical implants.

The use of hard DLC and CN coatings has a number of applications including: (a) hard carbon films for surgical instruments; (b) implanted fittings such as infusion devices and connecting parts; (c) semi-permanent components such as heart valves, replacement joints and ophthalmics. There is preliminary evidence that DLC coatings can operate as low-friction bearing surfaces and is a growing interest in the application of DLC on orthopedic and other implants [8].

Toxic elements such as Cu, Ag, V, embedded in the DLC will, when exposed to a biological media, can be released and cause toxic reactions. This allows the preparation of surfaces with a tunable antibacterial effect. DLC has proven its outstanding tribological properties in many technical applications due to the transformation of DLC into graphite (a solid lubricant) and the build up of a transfer layer on the counterpart.

Additionally, DLC is an excellent base coating to be alloyed with different elements. The amorphous nature of DLC opens the possibility to introduce certain amounts of additional elements, such as Si, F, N, O, W, V, Co, Mo, Ti and their combinations, into the film and still maintain the amorphous phase of the coating. By this technique, different film properties such as tribological properties, electrical conductivity, surface energy and biological reactions of cells in contact with the surface can be continuously adapted to a desired value [9].

Carbon-based biomaterials are not new. Pyrolytic carbon has been used for several decades in biomedical implants and coatings, particularly in the manufacture of heart valve prostheses. Pyrolytic carbons were initially developed for the aerospace and nuclear industries. Most are highly anisotropic, but isotropic coatings have also been developed using special chemical vapor deposition (CVD) processes. A more recent development in biomedical carbons is diamond-like carbon (DLC). This dense metastable form of amorphous carbon has several properties which make it desirable for biomedical applications. Most notable are its high hardness, low coefficient of friction, chemical inertness and good corrosion and wear resistance.

Carbon nanotubes (CNT) are unique, one-dimensional macromolecules. Single-walled carbon nanotubes are constructed of a single sheet of graphite (diameter 0.4–2 nm), while multi-walled carbon nanotubes consist of multiple concentric graphite cylinders of increasing diameter (2–100 nm). Both CNT types can be used as nano-fillers in existing polymeric materials. They can be used to create electrically conductive polymers and tissue engineering constructs with the capacity to provide controlled electrical stimulation.

One of the major problems encountered by researchers in the investigation of CNT toxicity and biocompatibility is the tendency of CNT to aggregate in large bundles and ropes. The manipulation of large numbers of individual CNT is a difficult task because high molecular weights and strong intertubular forces (both van der Waals and electrostatic). Sonication is a commonly used method for separating CNT aggregates in solution.

There is still much work to be done in establishing the toxicity and biocompatibility of CNT. Are carbon nanotubes safe? However, before such materials can be successfully incorporated into biomedical implants, drug/vaccine delivery vehicles or biosensors, there is a need to establish their biocompatibility. Other carbon-based biomaterials have demonstrated excellent long-term biocompatibility and biological performance in medical device applications. Clearly, these initial results urge caution when handling CNT, and the introduction of safety measures in manufacturing facilities and laboratories should be seriously considered [10].

7. Nanostructured materials

Nanostructured materials refer to certain materials with delicate structures of "small" sizes, falling in the 1–100 nm range, and specific properties and functions related to the "size effect". It has been established that nanotechnology offers a unique approach to overcome shortcomings of many conventional materials. Nanostructured materials offer much improved performances than their larger particle sized counterparts due to their large surface to volume ratio and unusual chemical/electronic synergistic effects. Nanoscale ceramics can exhibit significant ductility before failure contributed by the grain-boundary phase, nanostructured ceramics can be sintered at a lower temperature thereby problems associated with high temperature sintering processes are also eliminated. It is possible to enhance both mechanical and biological performance of materials by controlling characteristic features of powders such as particle size and shape, particle distribution and agglomeration.

In recent times, the arena of nanotechnology has been extensively studied by various researchers to overcome the existing limitations of hydroxyapatite, as well as to fabricate nanostructured scaffolds to mimic structural and dimensional details of natural bone. Natural bone is a composite material made up of collagen fiber matrix stiffened by hydroxyapatite (HAP) ($Ca_{10}(PO_4)_6(OH)_2$) crystals that account for 69% of the weight of the bone [6, 11, 12].

The main constituents of bone are collagen (20 wt.%), calcium phosphate (69 wt.%), and water (9 wt.%). The bone mineral consists of tiny hydroxyapatite crystals in the nano-regime. Calcium phosphate in the form of crystallized hydroxyapatite and/or amorphous calcium phosphate provide stiffness to the bone. The hydroxyapatite crystals, present in the form of plates or needles, are about 40–60 nm long, 20 nm wide, and 1.5–5 nm thick. They are deposited parallel to the collagen fibers (the diameter of the collagen microfibers varies from 100 to 2000 nm), such that the larger dimension of crystals is along the long axis of the fiber. It is found that nanocrystalline hydroxyapatite powders improve sinterability and densification due to greater surface area, which could improve the fracture toughness and other mechanical properties. Nano-hydroxyapatite is also expected to have better bioactivity than coarser crystals [13].

Physical methods, such as molecular coating (or adsorption), surface entrapment, and physical treating with plasma, ozone, or UV have emerged as leading strategies for surface modifications of nanostructured materials. Through physical modifications active chemical groups can be introduced onto the surfaces of nanostructured materials, leading to the functionalization and activation of the surfaces of materials.

In spite of the provided research, poor mechanical properties of the nano-sized implant materials limit their further applications and restricts clinical use of nano-HA as load-bearing implants, and limit their applications to small, unloaded and lightly-loaded implants, powders, coatings, composites, and porous scaffolds for tissue engineering.

8. Mechanical properties

Fatigue fracture and wear have been identified as some of the major problems associated with implant failure. The selection of biomaterials for wear resistance unfortunately cannot rely only on conventional thinking of using hard ceramics because of their low coefficient of friction and high modulus of elasticity. This is because ceramics are generally prone to brittle fracture [14].

The fatigue tests used to evaluate biomaterials can be categorised as follows: - stress/life (S/N) approach; - fracture mechanics approach; - fatigue-wear approach using simulated multi-axial loading.

The advantage of S/N approach is that it represents both initiation and propagation of cracks in the aggressive environment. In the fracture mechanics approach, the fatigue-crack propagation of the biomaterials are studied by long cracks (>3 mm) using compact-tension specimens or small cracks (1–250 μm) using micro indentation methods in a servo-hydraulic machine. This approach is good for studying brittle implant materials like ceramics. The fatigue strengths of metallic implant alloys such as stainless steel, cobalt chrome and titanium, and their relationship to their microstructures, surface and corrosion properties very often is investigated.

Fretting fatigue often occurs at interfaces such as between the metal and the cement in the case of a hip prosthesis. This can result in a sharp reduction in fatigue strength.

Improvement of wear performance has been made from various approaches ranging from ion implantation, cushion bearing to elastohydrodynamic lubrication. The poor tribological properties of titanium alloys as compared to cobalt chromium alloys has prompted the use of surface

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treatments such as plasma vapour deposition coating of TiN and TiC, thermal treatments (nitriding, surface hardening), and ion implantation (N+).

During the last years functionally graded materials (FGM) have been developed from single specimens to industrially oriented applications (for example, metal – ceramics biomaterials).

A functionally graded material (FGM) is a material "with engineered gradients of composition, structure and/or specific properties aiming to become superior over the homogenous materials composed of the same or similar constituents". An FGM was just recently generally described as "a new class of materials" or "a new material". However, an FGM is only a material which has gradients of composition, structure and related properties. It does not become "a new material", if metal or ceramic phase is distributed within the structure in an ordered, functional way.

The Bio-FGM offer enormous possibilities for substitution or repair of lost tissue function. The performance of such materials is validated through a number of physical, chemical, and biological tests. Theory-based understanding of the functioning of biological materials would offer enormous possibilities for technological progress in tissue engineering.

9. Applications of coatings on biomaterials

Current surgical implants such as artificial hip and knee joints undergo degradation after 10–15 years of use. The hip bones are subjected to cyclic loading as high as 10^6 cycles in 1 year. Plasma coating technologies have proven to be effective in improving the performance of artificial joints. Plasma coating can enhance the fatigue strength, the corrosion and wear resistance as well as the load-bearing capacity [15]. Single plasma coating process is seen often in metals resulting improved wear resistance and surface hardness. The duplex coating method can improve further of the tribological properties and load-bearing capacity of materials beyond metals. This method combines plasma coating with other coating technologies, such as PVD and CVD. A duplex plasma surface-engineering process can be achieved by plasma nitriding the low alloy steel first so as to produce a thick, strong substrate and then depositing a thin, hard and wear resistant TiN coating on the nitrided substrate by ion plating. In orthopaedic technology development, biomedical coatings are often used on total joint replacement components. These coatings usually comprise a group of novel (glass) ceramics. Calcium-phosphate-based material ($Ca_{10}(PO_4)_6(OH)_2$) coatings can be applied by a wide range of surface deposition techniques, such as plasma spraying, high-velocity arc or oxy-fuel spraying (HVOF), pulsed laser ablation, ion-beam sputtering, radio frequency magnetron sputtering, sol-gel and conventional ceramic processes that involve pressing and sintering. Plasma spraying is an efficient method of depositing HA coating onto the surface of the implant.

Arc spraying is a thermal spray deposition process in which the materials to be deposited are introduced into the plasma. Arc spray coatings are normally denser and stronger than their equivalent combustion spray coatings. Typical general applications are thermal barriers, wear resistance, corrosion resistance, high dielectric strength, hard dense coating, decorative arts, etc. Arc sprayed coatings are used widely to fight both high and low temperature corrosion. The adhesion of the coatings depends upon the interactions between individual lamellae and between lamellae and substrate. The bond strength of a coating is affected by the extent of both physical and chemical interactions between the coating and the substrate material and on the microstructure of the interfacial region. The thickness of a coating can be controlled between 40 and 400 μm. Thermally sprayed coatings are layers made of individual powder splats oriented parallel to the substrate surface (Fig. 1). These splats produce high level of anisotropy for the coating. There are many parameters chosen in control of the thermal spray technique, e.g. powder particle size and morphology, plasma gas mixture, working distance, substrate cooling, etc. [16].

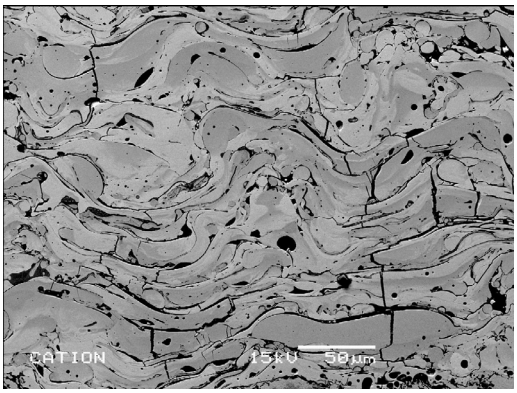

Fig. 1. The SEM photograph of microsection of sprayed coating

Liquid phase deposition (LPD) method is a useful method to create thin oxide films from aqueous solutions under ambient conditions. Deposition of ceramic layers on polymers is a technological challenge because of polymer sensitivity to chemicals and high temperature processing.

The low-cost and convenience of LPD coatings and their lack of line-of-site limitations strongly recommend their being considered as a general strategy. Moreover, the relatively mild conditions for ceramic film formation using LPD methodology makes them prime candidates for application on polymer substrates. Liquid phase deposition of TiO_2 films can be made on different substrates. From aqueous solution, under mild conditions of temperature ($\leq$ 55 °C) can be produced thin (0.1-1.0 μm), adherent TiO_2 films (Fig. 2) [17].

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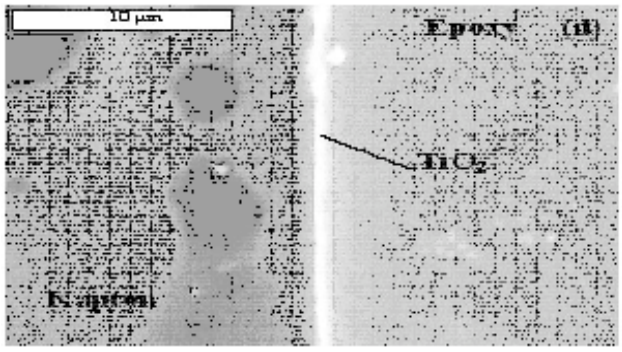

Fig. 2. Cross-sectional SEM images of samples coated with TiO_2 (substrate – Kapton, coating time – 7 hours, thickness – 416 nm)

Transitional metal boride coatings are attracting increasing interest, due to the fact that they combine high hardness with good wear and corrosion resistance. Chromium boride coatings deposited by the pulsed magnetron sputtering enable the deposition of crystalline films with the CrB_2 structure and a strong (001) texture. These films appeared to be crystalline and fully dense with no discernible structural features or defects (Fig. 3). The hardness of the stoichiometric pulsed magnetron sputtered CrB_2 films was found to be of the order of 39 GPa [18].

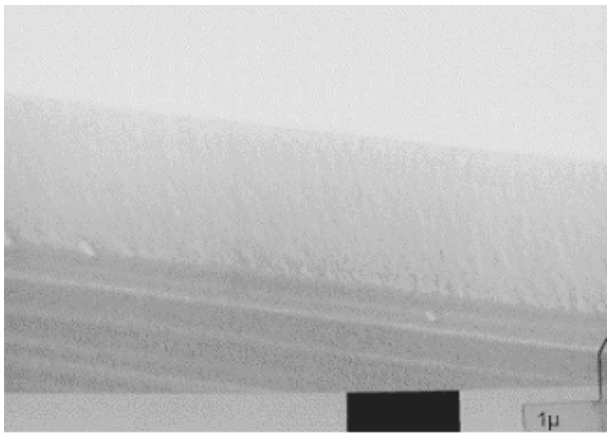

Fig. 3. SEM micrograph of the fracture section of a chromium boride coating deposited onto a silicon wafer substrate by magnetron sputtering

10. Technology platforms and possible research and production cooperation in Lithuania

The space for interdisciplinary research in biomedicine is huge and economically is very attractive. This field of science and production has top priority in main European research programmes (FP-6, FP-7, etc.). More than any other field of contemporary technology, biomaterials science brings together researchers from diverse backgrounds who must communicate properly.

Possible research areas of *biomaterials* and *biomimetic* materials:

- multimaterials (hybrid) systems: metals-plastic, ceramics-metals, composites, Al-steel, metal-rubber, plastic-TPEs (thermoplastic elastomer), plastic-metal-TPEs;
- nanomaterials for use in medical applications and micro/nano-systems;
- biomaterials for prosthesis (metal-metal, metal-polyethilene (PE), ceramic-ceramic, ceramic-PE with or without coatings);
- biomimetic materials (biosensors, biocompatible properties, for implant applications, corrosion control…) and bionics (prosthesis...);
- bioactivity, biocompatibility;
- fast, flexible, economic production of biocompatible materials and coatings including legalization procedures.

Interdisciplinary approach to biomedicine materials research is very promising and horizontal cooperation of different national technology platforms is essential to all players [19]. Such national technology platforms are: National Technology Platform "*Nanotechnologies for Medical Applications"*, National Technology Platform "*Technology Platform for Advanced Engineering Materials and Technologies"*, National Technology Platform "*Manufuture-Lithuania"*.

Partners which can cooperate vary from SME to large institutions. The main possible partners are:

- research institutions:

institutes of Chemistry, Semiconductor physics, Energy, Biochemistry, Biotechnologies, Physics, Lithuanian Association of Materials Research, Applied Research Institute for Prospective Technologies (microelectronics, electronics and sensors – technological development and applications for health care sector);

- Higher Education Institutions: Vilnius University, Vilnius Gediminas Technical University, Kaunas University of Technology, Vytautas Magnus University, colleges…;
- industrial partners (for example, *Intersurgical* has been supplying a wide range of quality respiratory products to hospitals all over the world: aerosol masks (adult, pediatric, aerosol therapy, breatching systems, etc.);
- science and technology parks.

11. Conclusions

New biomaterials and their manufacturing methods have been developed to machine these new biomaterials, paving a way to produce medical devices with better properties.

Monolithic materials have long been used and there is considerable experimental data supporting their continued usage. Such data with respect to polymer composite, nanoscale biomaterials is relatively small.

Many non-metallic biomaterials have demonstrated excellent long-term biocompatibility and biological performance in medical device applications. Before such materials can be successfully incorporated into biomedical implants, or biosensors, there is a need to estimate their biocompatibility.

Modern coating technologies can improve corrosion and wear resistance as well as load-bearing strength of artificial components or joints.

For faster movement ahead must be combined efforts of different actors – researchers, technology developers and producers. The base for such collaboration can be cooperation of National or European Technology Platforms.

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